Government of **Western Australia**
Department of **Water**

Assessing the influence of acid sulfate soils on water quality in south-western Australian catchments and estuaries

A technical report for the project: Tackling acid sulfate soils on the Western Australian coast

Looking after all our water needs

Water*Science*
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Looking after all our water needs

By K Kilminster, S Norton and F Miller

Department of Water

Water Science Technical Series

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Contents

Appendices

Figures

Tables

Summary

Acid sulfate soil (ASS) is the common name given to soil and sediment that contain iron sulfides (e.g. pyrite). Sulfides are formed by bacterial sulfate-reduction, a process requiring anaerobic conditions, sulfate and degradable organic matter. Oxidised or disturbed ASS release acidity and mobilise metals. Metals and acidity released into the aquatic environment may negatively affect the ecosystem by causing adverse impacts on organisms. This study analysed water collected from catchments and estuaries in south-western Australia for abiotic signals of acidic drainage. This was part of the project *Tackling acid sulfate soils on the Western Australian coast*, funded by the Australian and Western Australian governments through the National Action Plan for Salinity and Water Quality and Natural Heritage Trust initiatives.

As part of this project we developed a new indicator (the sulfur isotope indicator) to identify water affected by acidic drainage from disturbed ASS. With this new indicator we sampled estuaries, rivers, streams and drains in south-western Australia. Drainage from ASS was found to be impacting both fresh water and estuarine water in the region. The impact observed was more subtle when compared with the large quantities of acid produced behind floodgates reported for many ASS-affected sites in Australia's eastern states. Forty-one sites in the current study were identified as hotspot sites, with either unusually high aluminium and/or iron concentrations (within the range expected from reported ASS-affected waterways) or with signals of acidic drainage identified by the sulfur isotope indicator.

The sulfur isotope indicator categorises samples into iso-groups, using measurements of sulfate and chloride concentrations and sulfur stable isotope ratio. This indicator appears to provide a useful screening tool for assessing the influence of acidic drainage. Water samples identified as affected by ASS had deteriorated water quality; median concentrations of many metals (Al, Co, Cr, Cu, Fe, Mn, Ni, V, Zn) and phosphorus were higher in ASS-affected samples (iso-group 3) than in other samples not influenced by ASS. The methodology is more sensitive for identifying acidic drainage compared with other indicators previously used in ASS management. Iso-group categorisation also showed that sulfate-reduction was the dominant process for two-thirds of samples, most of which were associated with extra sources of sulfur. It is likely the supply of extra sulfate to these waterways results in enhanced monosulfidic black ooze production, however further work is required to confirm this.

Reported blackwater events (with resuspended metastable monosulfides) on Australia's east coast have been catastrophic – with hundreds to thousands of fish and prawns reported killed as a result of just one event. Further investigation is required to assess the risk of blackwater events in Western Australia.

Water quality guidelines were frequently exceeded, particularly for nutrients and some metals (Al, Fe and less often Co). It is probable that various sources contributed to the metals observed in waterways and estuaries in south-western Australia, including urban, agricultural and industrial influences, as well as disturbed ASS sources. In 70% of freshwater samples aluminium concentrations exceeded the ANZECC & ARMCANZ (2000) guideline for 95%

freshwater species protection. It is not known if aluminium is naturally high in the region, or if this presents a serious environmental problem.

Signals of chronic acidic drainage were observed in this project, most likely resulting in chronic long-term effects on aquatic ecosystems. These effects may ultimately modify the community structure of species within the aquatic ecosystem, with subsequent effects on the trophic food web.

The priorities for further research were identified as:

1. further investigation of hotspot sites identified in this study, including development of management and/or remediation plans for these sites
2. additional work to refine the sulfur isotope indicator for assessing ASS influence in waterways
3. further work at sites identified as probably having enhanced sulfate-reduction to assess the risk associated with blackwater events at these locations
4. ecotoxicology specifically targeted at Western Australian native species to understand whether aluminium concentrations in south-western Australian waterways are presenting a widespread ecological problem.

1 Introduction

1.1 Background to project

The project *Tackling acid sulfate soils on the Western Australian coast* was funded by the Australian and Western Australian governments through the Natural Heritage Trust and the National Action Plan for Salinity and Water Quality. Project funding was administered through the State Natural Resource Management Office with the Department of Water as the lead agency for the project.

This study of water quality within south-western Australian estuaries and catchments was carried out as a surveillance of abiotic indicators to assess the influence of acid sulfate soils on the region's coastal waterways.

1.2 Acid sulfate soil

Acid sulfate soil (ASS) is the common name given to soil and sediment that contains iron sulfides (e.g. pyrite). These are a natural feature of many lowland environments and if left undisturbed under anoxic conditions, they are stable sulfur stores. Sulfides are formed by bacterial sulfate-reduction, a process requiring anaerobic conditions, sulfate and degradable organic matter (Cook et al. 2000). Modern-day ASS formation occurred in the Holocene period after the last major sea-level rise, more than 10 000 years ago (Dent 1986).

When pyrite is disturbed the anoxic sediments are oxidised, producing acidity. This anthropogenically generated acidity may be due to disturbance of sulfide-containing soils during dredging, building or dewatering activities – which may include extraction of groundwater for potable water supplies or forestry practices that result in a lowering of the watertable. The oxidation of iron sulfide produces acid through a number of chemical and biochemical pathways (Langmuir 1997). The overall oxidation reaction of pyrite is described below. Iron hydroxide ($Fe(OH)_3$) is formed when the reaction goes to completion, and in solution iron hydroxide will precipitate as an inert reddish-brown iron-floc.

Equation 1 $FeS_2 + {}^{15}/_{4}O_2 + {}^{7}/_{2}H_2O \rightarrow Fe(OH)_3 + 4H^+ + 2SO_4^{2-}$

Often the oxidation of pyrite does not reach completion under typical environmental conditions. In the Australian coastal environment, incomplete oxidation products such as goethite, ferrihydrite, jarosite and schwertmannite have been identified (Sullivan & Bush 2004). Alunite, an aluminium analogue of jarosite, has also been identified in Western Australian soils (Miller et al. 2010).

1.3 Environmental effects of ASS

Oxidised ASS may have negative impacts on land as well as water resources.

- Vegetation scalds may indicate acidity in the topsoil, inhibiting growth of plants and crops.

- ASS may severely damage infrastructure with acid dissolution of concrete and accelerated corrosion of iron, steel and certain aluminium alloys.
- Water quality may deteriorate as a result of oxidised ASS runoff, with possible effects on aquatic life.
- Acidic discharge has been implicated in fish kills (Brown et al. 1983; Hart et al. 1987). Damage to fish gills and skin from acid exposure increases the susceptibility of fish to fungal infections such as ‘red spot’ (Sammut et al. 1996; Kiryu et al. 2003).

1.4 Metal mobilisation and toxicity

Soils containing sulfides can also contain significant quantities of metals. Metals commonly associated with ASS are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) (Nordmyr 2008) and iron (Fe), of course, is also prominent since pyrite contains Fe (Cook et al. 2000; Green et al. 2006). Peat soils in Western Australia have also been shown to contain arsenic (As) (Appleyard et al. 2006; Miller et al. 2010). Most metals are more water-soluble in acidic conditions, resulting in leaching of metals as acidic water passes through the soil. Oxidation of metal sulfides may liberate metals associated with sulfides (most commonly FeS_2, although low concentrations of other metal sulfides are typically present). Metals leached from sulfidic soils can greatly contribute to metal concentrations in waterbodies (Sundström et al. 2002) and subsequently may negatively affect the ecosystem by causing adverse impacts on organisms; for example, death, changes in abundance, morphology or appearance, bioaccumulation of metals and/or invasion of tolerant species (Phillips & Rainbow 1994).

1.5 Assessing the influence of ASS on water quality

This project sampled natural waters (estuarine and fresh) for abiotic signals of acidic drainage from ASS. Approximately 60 physical and chemical variables were analysed in each water sample. Little information exists for many of these variables in natural waters; thus the project also aimed to provide baseline data by investigating relatively undisturbed as well as disturbed sites. Approximately 150 sites across five freshwater catchment areas (Swan Canning, Peel Harvey, Leschenault, Scott Coastal Plain and the south coast) and approximately 90 sites within 13 estuaries in south-western Australia were investigated. Estuarine sites were typically strongly brackish (>20 psu) to hypersaline (>40 psu) in the summer months, while freshwater flows during winter resulted in some slightly brackish water samples. Catchment samples were fresh to slightly brackish, with most samples <0.5 psu.

2 Potential indicators of acidic drainage

Potential indicators of acidic drainage explored in this project included the chloride:sulfate ratio, sulfur stable isotope ratio, total acidity and metal concentrations (Fe, Al particularly). These potential indicators often need to be considered collectively as many interactions are possible and may confound interpretation.

Chloride:sulfate ratios

Seawater is comprised of many ions: the major ions include chloride (Cl^-), sodium (Na^+), magnesium (Mg^+), sulfate (SO_4^{2-}), calcium (Ca^{2+}) and potassium (K^+). In undiluted seawater, the concentration of chloride is approximately 19 400 mg L^{-1} and sulfate is approximately 2700 mg L^{-1}, producing a ratio between the two ions of 7.2:1 (for Cl^-:SO_4^{2-}). Chloride is considered a conservative ion, so the ratio will be conserved with no other source of sulfate present in a natural water sample (other than seawater). With other inputs of sulfur (e.g. acidic drainage, fertiliser or greywater) this ratio will be reduced. Since sulfate is released by the oxidation of pyrite (Equation 1), low chloride:sulfate ratios (<4 or <3) have previously been used to indicate drainage from disturbed ASS (Sammut et al. 1996; Hinwood et al. 2006; NSW Department of Primary Industries 2008). Note: geochemists will often report the reverse ratio (e.g. SO_4^{2-}:Cl^-).

Total acidity

Measuring acidity by pH alone does not account for all sources of acidity in natural water. Measures of pH quantify the concentration of hydrogen ions (H^+) in solution on a logarithmic scale, and only measure accurately the acidity from fully dissociated acids (i.e. strong acids). Alternatively, the measure of total acidity is a titration-based measurement that provides information on the total amount of base needed to completely neutralise the solution. Total acidity reflects all acidity-generating components in the water and includes H^+, acidity from hydrolysing metals and acidity from weak acids that do not fully dissociate (e.g. formic, acetic acid and those carboxylic groups associated with humic acid).

Metal concentrations (iron and aluminium)

High concentrations of metals are usually associated with acidic drainage, as the solubility of metals increases with decreasing pH. Aluminium and iron are commonly associated with ASS (Cook et al. 2000): soil-leaching studies have shown that these elements are leached in orders-of-magnitude higher concentrations than other metals present within the soil (Miller et al. 2010). The use of metal concentrations in water as an indicator of acidic drainage is complicated by other influences, such as urban and industrial sources of metals and changes in metal solubility related to mixing with buffered estuarine waters. Metals such as Fe and Al can also contribute acidity depending on the form (chemical species) which is present in the waterway; for example, hydrolysis of iron (II) to iron hydroxide produces H^+ (i.e. acid) and this acidity is sometimes referred to as ‘stored acidity’ (Sullivan & Bush 2004).

Sulfur stable isotope ratio

Measuring $\delta^{34}S$ value of sulfate in water provides information on the source of the sulfate. Sulfur occurs naturally in four stable isotope forms, of which ^{32}S and ^{34}S are most abundant (95% and 4.2% respectively). Differences in the relative abundance of ^{34}S are determined relative to a standard and $\delta^{34}S$ is expressed on the per mil scale (‰) (Clarke & Fritz 1997). Sulfur-34 abundance varies between sulfur compounds due to physical processes and biological cycling such as fractionation by sulfate-reducing bacteria (Kaplan & Rafter 1957; Clarke & Fritz 1997). Reduction of sulfate by sulfate-reducing bacteria results in isotopically light $\delta^{34}S$ (i.e. relatively more ^{32}S). The $\delta^{34}S$ value of seawater is highly positive (~20 to 21 ‰) compared with that of sulfide deposits such as pyrite, which are highly negative (-18 to -52 ‰) (Coomer & Robinson 1976; Jowett et al. 1991).

The potential to use sulfur isotope analysis as an indicator of acidic drainage and sulfate-reduction processes within natural waters is investigated in this project. This is a novel and innovative approach to assessing acidic drainage from disturbed ASS.

3 Methods

3.1 Sampling locations

More than 300 surface water samples were collected from estuaries and catchment waterways (main rivers, tributaries and drains) in south-western Australia. The sampling locations included freshwater, brackish and saline systems, but only rarely lakes or wetlands. The regions sampled were:

- Swan-Canning estuary (16 sites) and Swan-Canning catchment (30 sites) (Figure 1)
- Peel-Harvey estuary (30 sites, including shallow sites at the margin of the estuary where fauna was also sampled) and Peel-Harvey catchment (31 sites) (Figure 2)
- Leschenault Estuary (10 sites) and Leschenault catchment (28 sites) (Figure 3),
- Vasse-Wonnerup estuary (seven sites) (Figure 4)
- Hardy Inlet (12 sites) and Scott Coastal Plain catchment (28 sites) (Figure 5)
- Broke, Walpole Nornalup and Irwin inlets (10 sites) (Figure 6)
- Wilson Inlet, Princess Royal Harbour and Oyster Harbour (nine sites) and Albany catchment (30 sites) (Figure 7).

Typically, estuarine sites were sampled twice. These are nominally called ‘summer’ and ‘winter’, and notated throughout the text with –s or –w after the site name (e.g. ELL-s). For the summer sampling period, actual dates range from January to March; for the winter sampling period, May to September (with most samples taken in June to August). Freshwater catchment sites were sampled only once (spring 2007). Details of site locations and sampling dates can be found in Appendix A.

3.2 Sampling method and analysis

Samples were collected using a grab pole sampler from a depth of 0–0.5 m. A subsample was filtered on-site through a 0.45 µm filter. At each site, in situ measurements of dissolved oxygen (DO), pH, conductivity, salinity and oxidation-reduction potential (freshwater samples only and converted to Eh for reporting) were obtained with a multi-parameter probe (either Hydrolab Quanta or Hydrolab minisonde 5). The collected water samples from each site were analysed to determine nutrients – total nitrogen (TN), nitrate and nitrite (NOx), ammonium (NH_4^+), dissolved organic nitrogen (DON), total phosphorus (TP), filterable reactive phosphorus (FRP), total acidity, total alkalinity, dissolved organic carbon (DOC), sulfur stable isotope ($\delta^{34}S$), colour (freshwater samples only) and a suite of total and filtered (or soluble) metals. Metals analysed generally included aluminium (Al), arsenic (As), calcium (Ca) cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), vanadium (V), and zinc (Zn). Total metal suite (i.e. metals determined from an unfiltered sample) was not analysed for the summer estuary snapshot. Analysis detail is described in full in Appendix B.

Procedural blanks (de-ionised water samples prepared in the field) and field replicate samples were collected throughout the sampling events. Quality control evaluation was also carried out on laboratory-reported blanks, duplicates and spike recoveries. Data from quality assurance and quality control are reported in Appendix C.

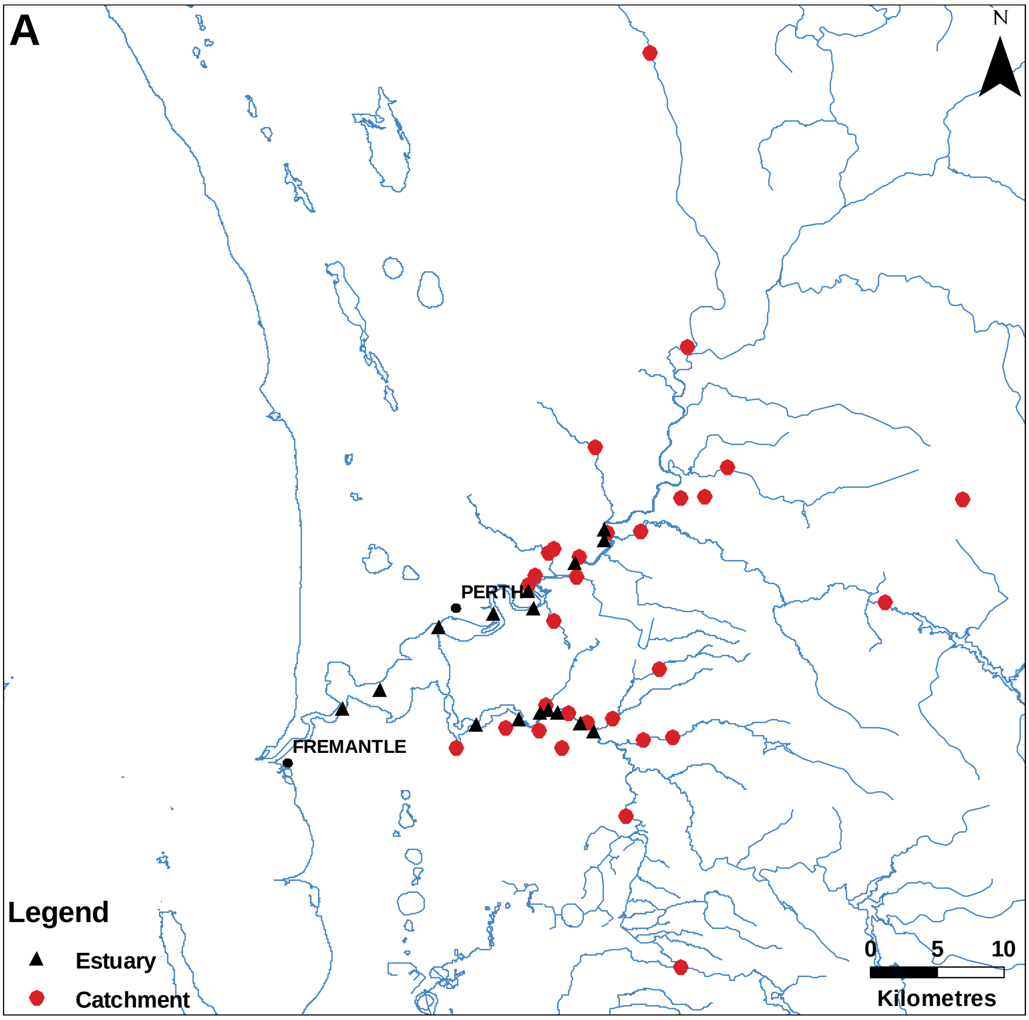

Figure 1 *Surface water sampling sites for the Swan-Canning region. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

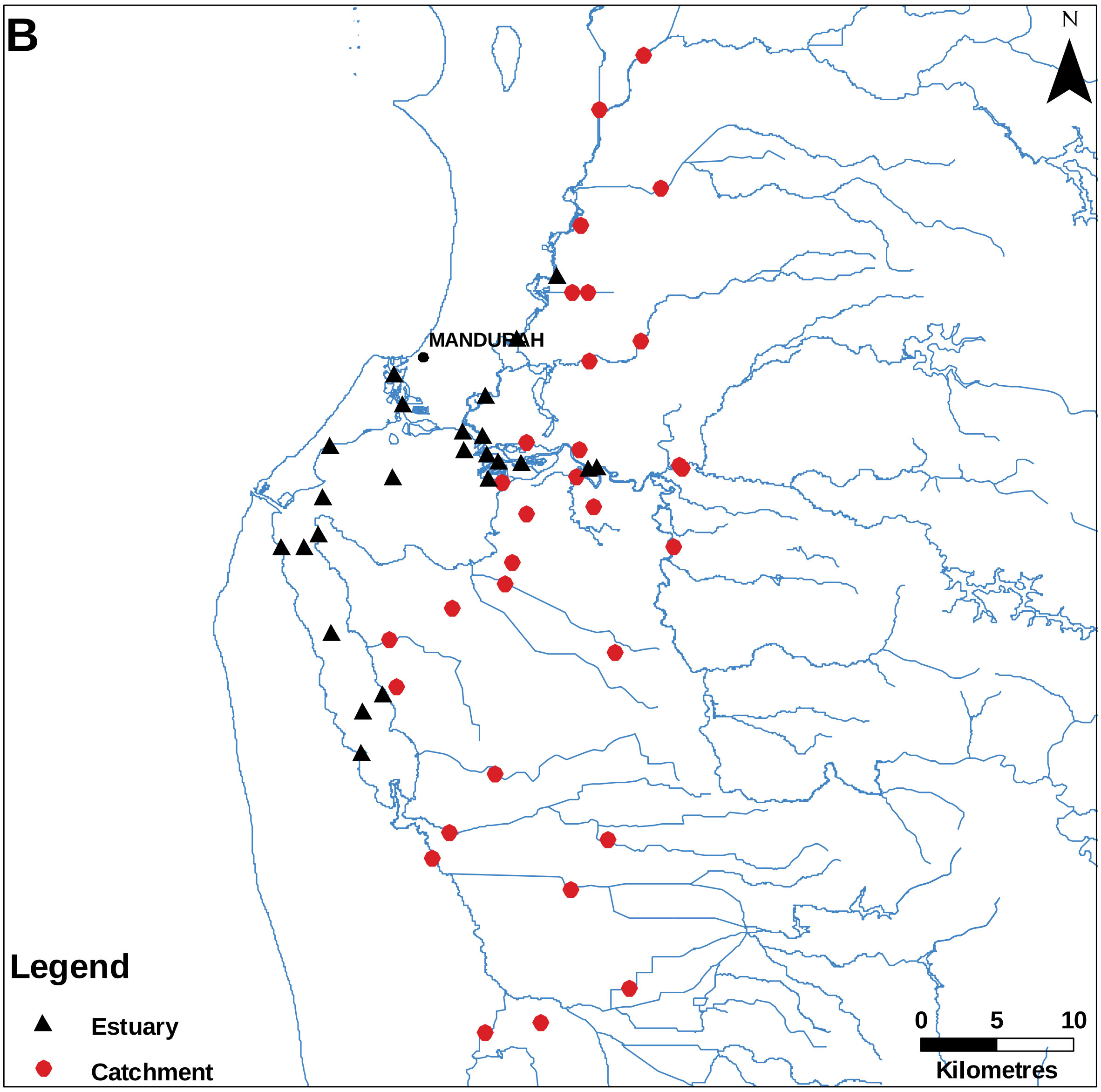

Figure 2 *Surface water sampling sites for the Peel-Harvey region. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

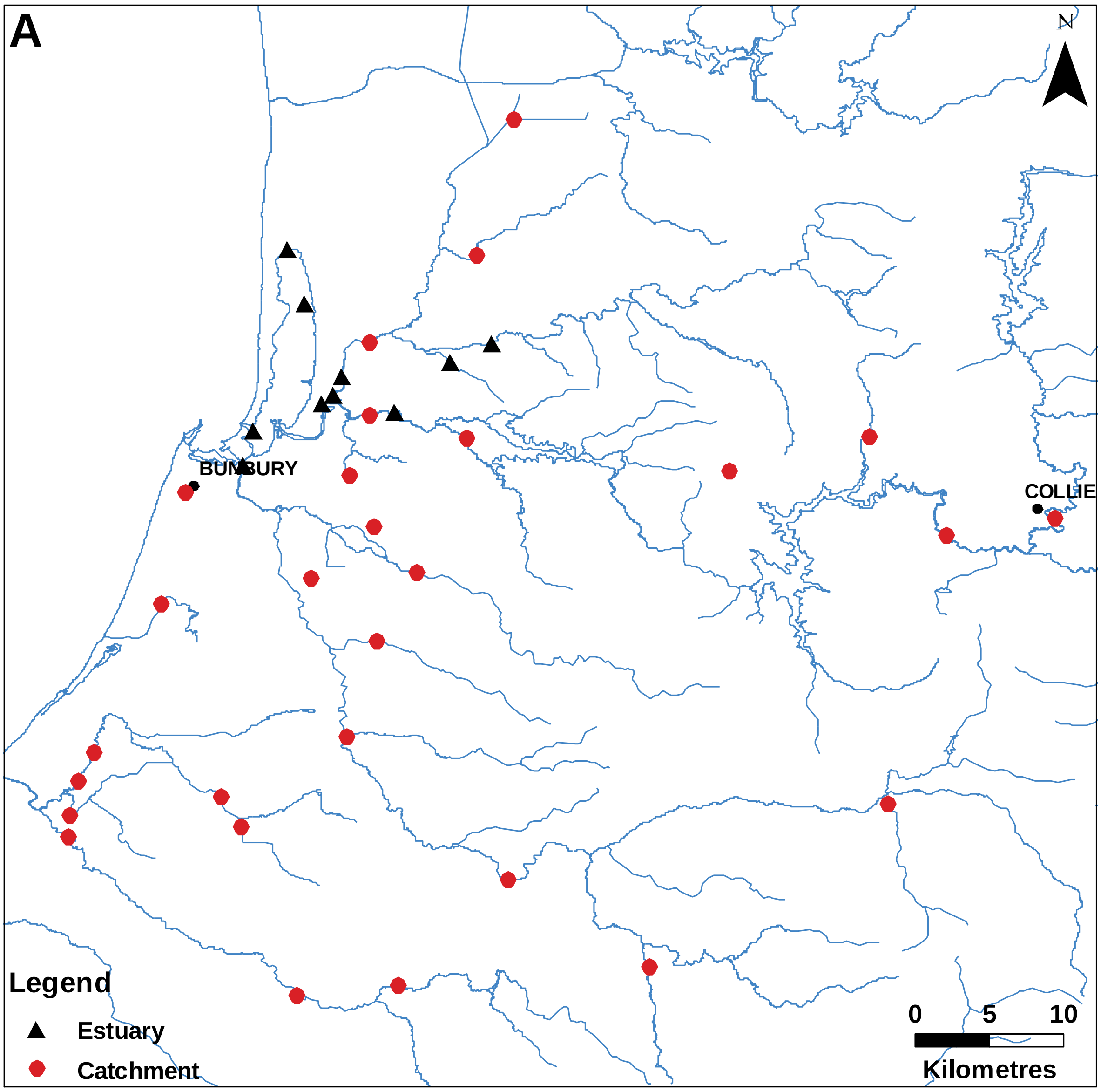

Figure 3 *Surface water sampling sites for the Leschenault region. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

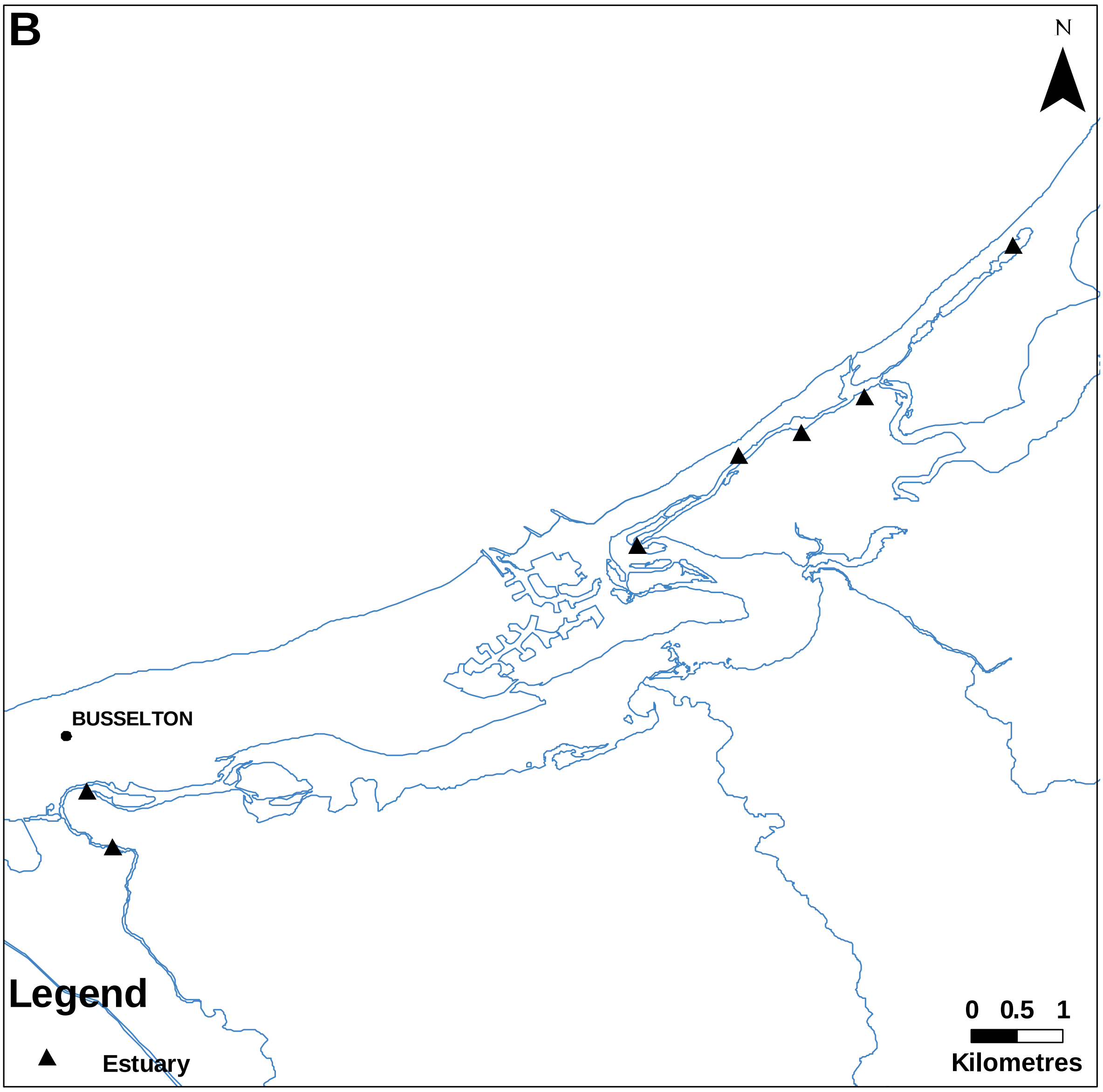

Figure 4 *Surface water sampling sites for the Vasse-Wonnerup estuary (black triangles indicate sampling sites).*

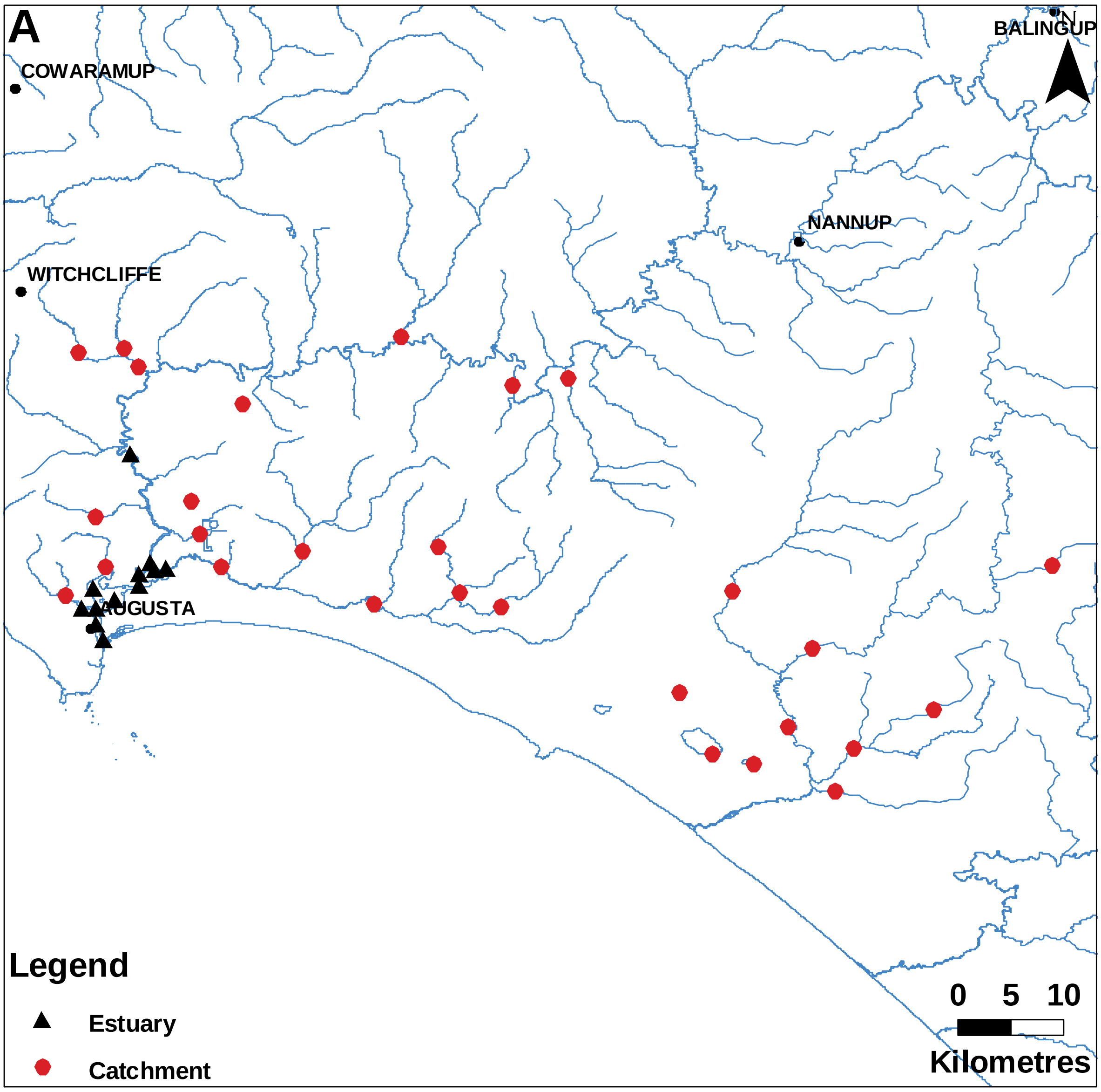

Figure 5 *Surface water sampling sites for the Hardy Inlet and Scott Coastal Plain. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

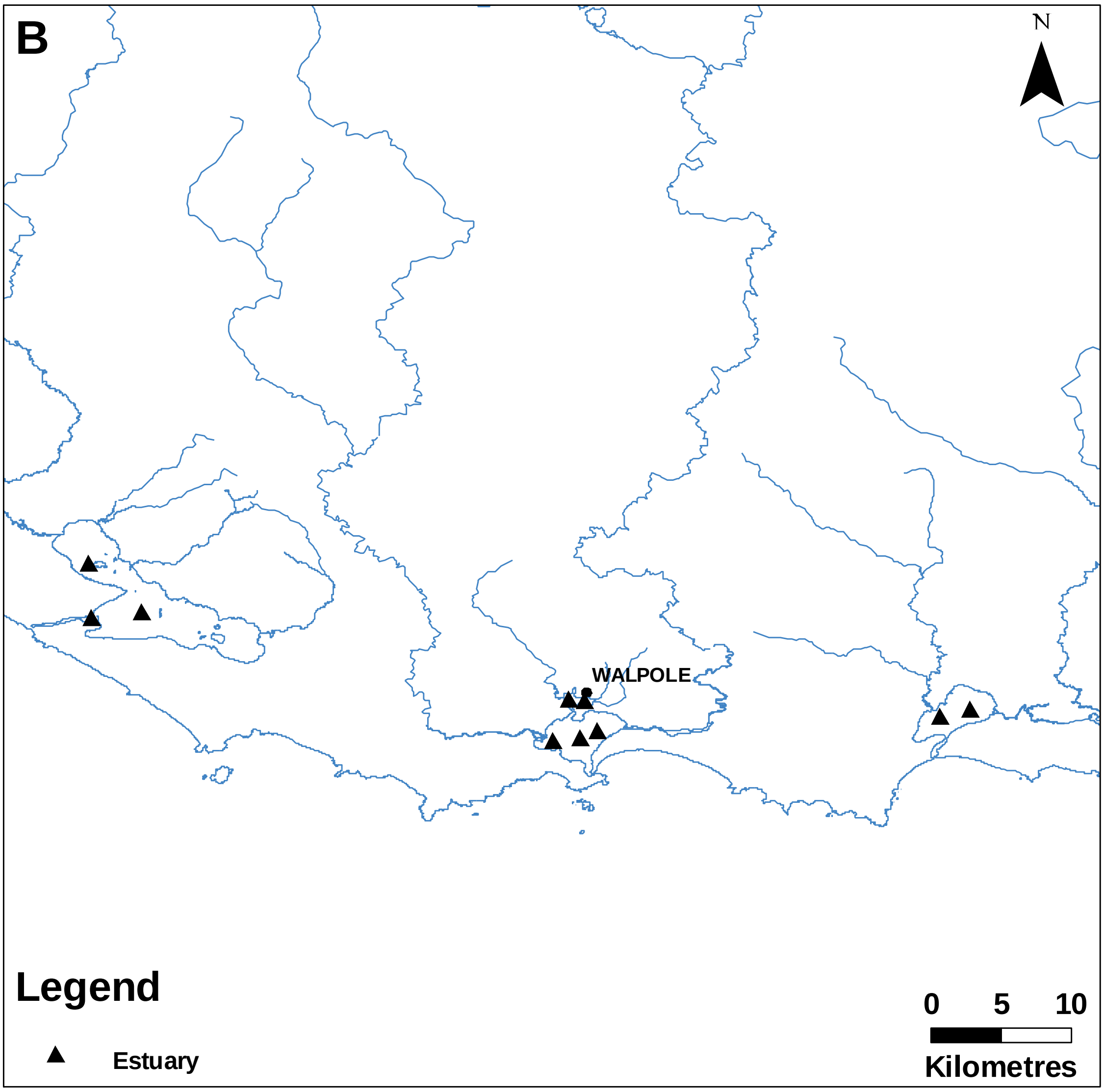

Figure 6 *Surface water sampling sites for Broke, Walpole Nornalup and Irwin inlets. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

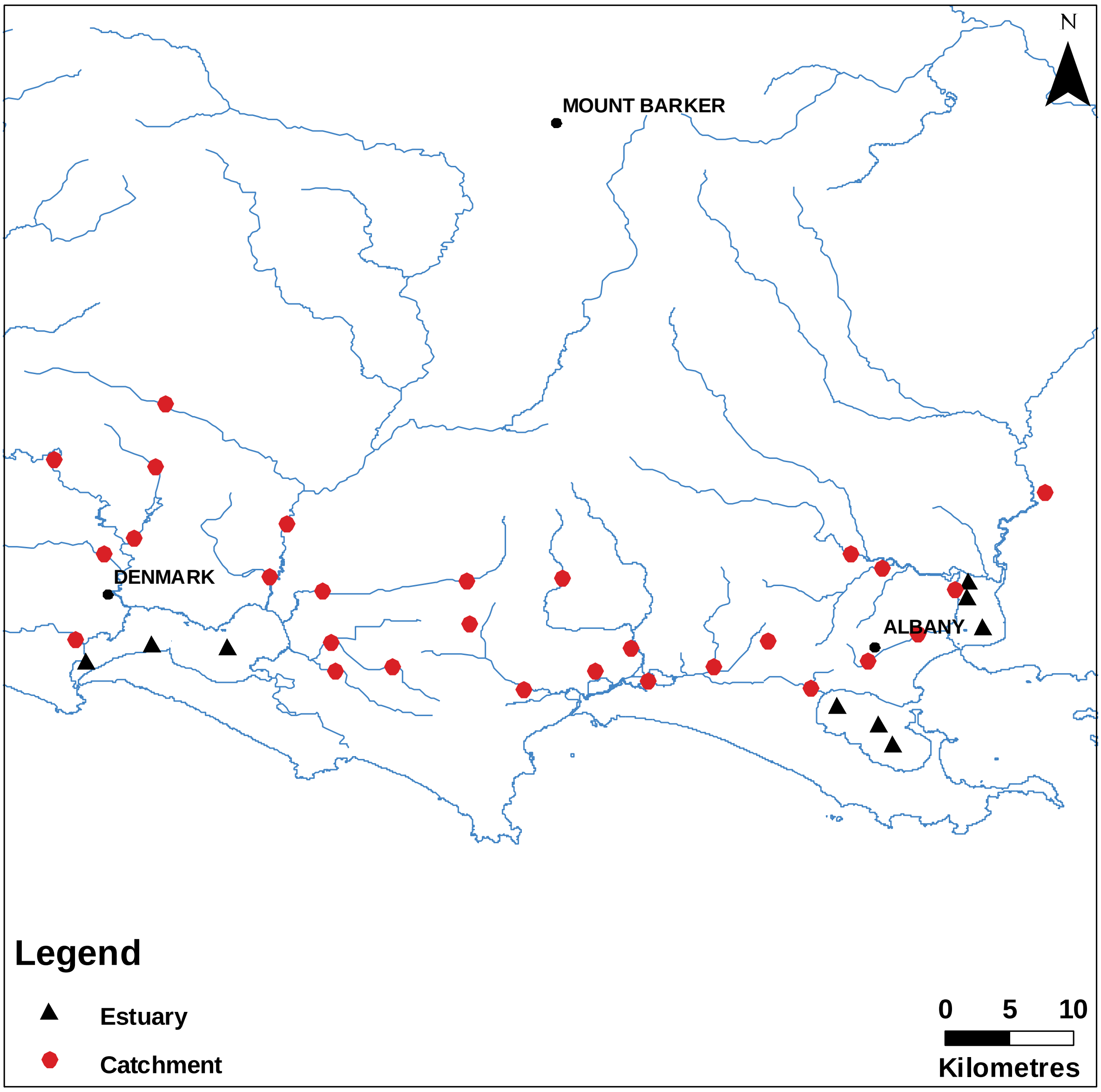

Figure 7 *Surface water sampling sites for Wilson Inlet, Princess Royal Harbour, Oyster Harbour, and south coast catchment. Red dots indicate catchment sampling sites and black triangles indicate estuary sampling sites.*

3.3 Data storage

Data for this project are housed within the Department of Water's Water Information Network (WIN) database. Data reported here are associated with the following project codes: WA-R-WAACIDEST, SG-C-ACIDCATSC, KP-C-WAACIDCATP, SW-C-ACIDCATL, SW-C-ACIDCATSCP, SC-A-ACIDCATA.

3.4 Data analysis

Data were transformed and normalised before statistical analysis. The following programs were used for data manipulation, graphical representation and statistical analysis: Excel 2003, PRIMER v6 with PERMANOVA+, Sigmaplot version 10 (Systat Software Inc) and Statistica version 8 (StatSoft Inc). Where necessary, resemblance matrixes were calculated using Euclidian-distance on transformed and normalised data. Statistical routines used are stated in the text; however, further detail on PRIMER and PERMANOVA+ routines can be found in Clarke and Warwick (2001) and Anderson et al. (2008).

4 Results: regional variation

4.1 Potential ASS indicators by region

The variables outlined in Section 2 as potential indicators of ASS were examined for their variation across different regions. Firstly estuarine and catchment data, pooled from all geographical regions, were compared. A multidimensional scaling (MDS) plot for the variable subset of potential ASS indicators – total acidity, aluminium (soluble), iron (soluble), pH and chloride:sulfate ratio – showed clear differences between estuaries and catchments (Figure 8).

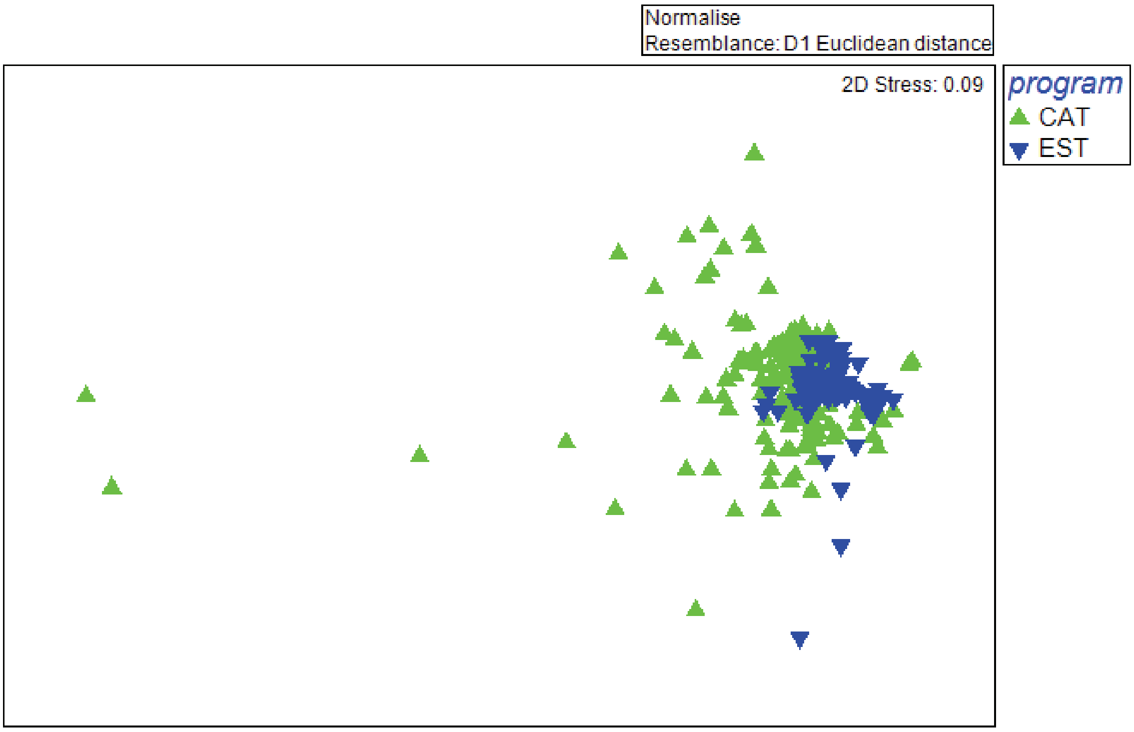

Figure 8 *Multidimensional scaling (MDS) plot for potential acid sulfate soil indicators in water, grouped by whether the sample was from estuaries (blue triangle) or catchments (green triangle).*

Salinity is likely to have a major effect on many of these potential ASS indicators; for example, saline water in estuaries buffers pH, and consequently metals that might be soluble in acidic conditions will precipitate at more neutral pH. To account for this, electrical conductivity was used as a co-variate in a permutational multivariate analysis of variance (PERMANOVA) to analyse differences in the variable subset of potential ASS indicators between catchments and estuaries. Catchment and estuarine data were found to be significantly different (pseudo-F=0.5, p>0.0001). The different distributions of these potential indicators are shown as boxplots in Figure 9. These boxplots are a non-parametric way to display the whole sample distribution, without assumptions about data distribution. Much higher concentrations of Fe and Al were observed in catchment samples than in estuarine samples (Figure 9). In addition, catchment samples showed much higher variability of Al, Fe and $Cl^-:SO_4^{2-}$ than estuarine samples.

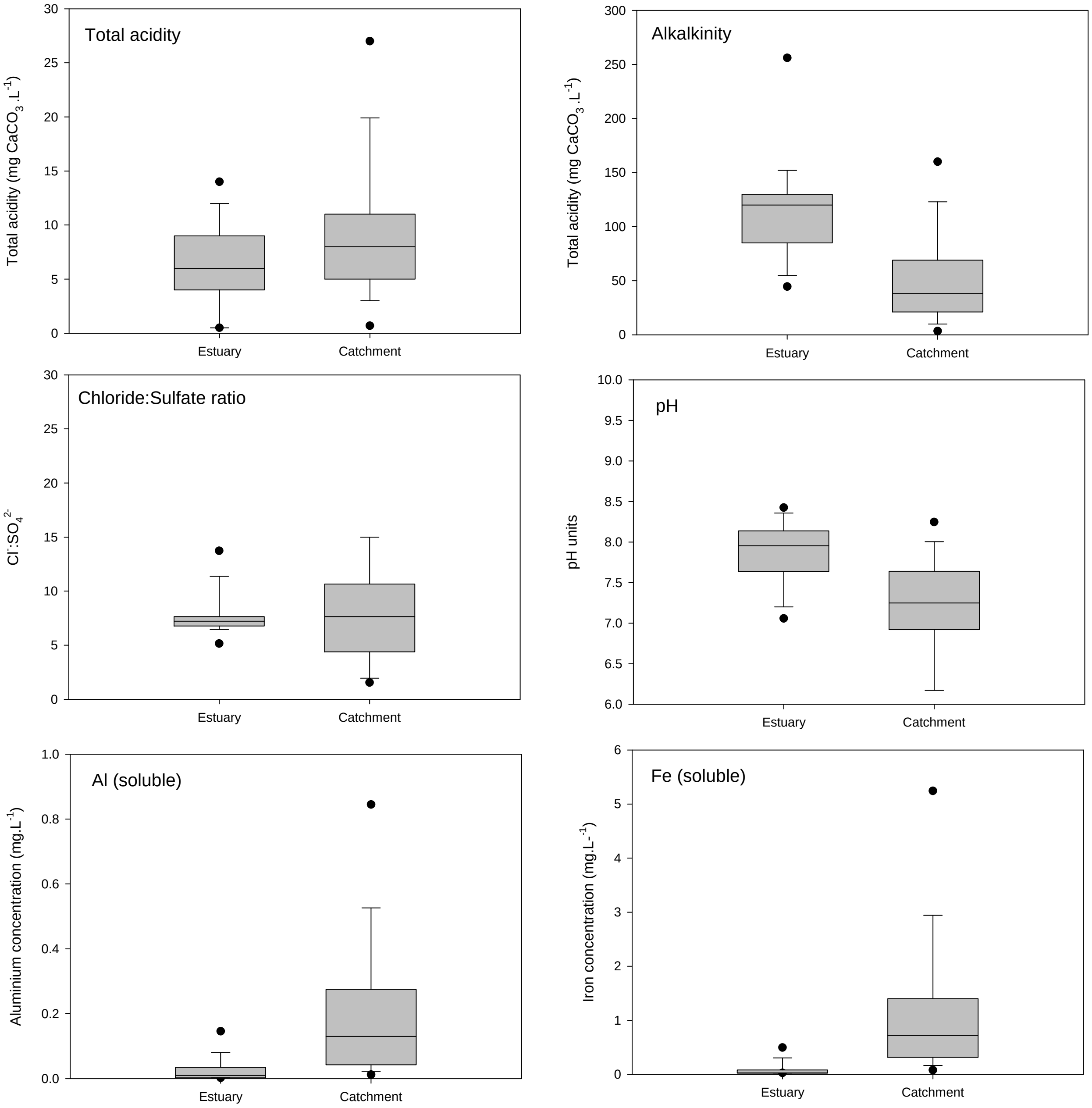

Figure 9 *Boxplots of estuarine and catchment water quality for potential acid sulfate soil indicators – total acidity, alkalinity, chloride:sulfate ratio, pH, Al (soluble) and Fe (soluble), (line = median, edges of box 25th and 75th, whiskers 10th and 90th, and dots 5th and 90th percentile).*

The data were then explored for differences between estuaries (e.g. Swan-Canning *vs* Hardy) and between catchments (e.g. Peel Harvey *vs* Leschenault). The median and range of total acidity, total alkalinity, pH, Eh, concentrations of sulfate and chloride, $Cl^-:SO_4^{2-}$ and the $\delta^{34}S$ are shown in Table 1 for estuarine data and Table 2 for catchment (freshwater) data. Univariate analysis of variance (ANOVA) showed that estuary regions were significantly different ($F>7$, $p<0.00001$) for all variables in Table 1 except $\delta^{34}S$. Univariate ANOVA showed that catchment regions were also significantly different ($F>3.5$, $p<0.01$) for all variables in Table 2 except $\delta^{34}S$. Major differences between estuaries with these parameters are most likely to reflect differences in location (e.g. the Swan-Canning estuary has more up-river sites than Oyster Harbour) and the relative influence of salinity (which may vary with season). The regional differences observed highlight the importance of using electrical conductivity (or salinity) as a co-variate in multivariate analysis of this dataset.

A large range in values was observed for most variables, and in most geographical regions (Table 1 and Table 2). Lower extremes of pH were observed in catchments (lowest-value pH 2.8) than in estuaries (lowest-value pH 6.5), and higher median values of alkalinity were measured in estuaries compared with catchments, demonstrating the higher buffering capacity of estuarine water. Furthermore, higher extremes of total acidity were also seen in catchments (maximum 290 mg $CaCO_3$ L^{-1}), compared with estuaries (maximum 18 mg $CaCO_3$ L^{-1}).

Sites were classified as either ‘acidic’ or ‘reducing’ based solely on the $Cl^-:SO_4^{2-}$ ratio determined for each site. This indicator is a ratio of two chemical analyses, so the combined error associated with each measurement in the ratio was considered when categorising sites as either acidic or reducing (Table 3). Acidic sites were those with the $Cl^-:SO_4^{2-}$ ratio <4 (indicating excess sulfate), and reducing sites were those with a ratio greater than expected for seawater (indicating missing sulfur). Estuarine sites were generally similar to seawater (~7.2 ± error). Only one estuarine site (within the Peel-Harvey estuary) was classified as acidic. The Hardy Inlet had many reducing sites (83%) followed by the Leschenault, Peel-Harvey and Vasse-Wonnerup estuaries (~20%). Within catchment sites, the Swan Canning had the greatest number of acidic sites (70%). Acidic sites were also common in the south coast and Scott Coastal Plain catchments (13% and 11% respectively). Reducing sites in the catchment areas were most often found in the Scott Coastal Plain (25%) and the Peel Harvey (16%).

Table 1 *Summary data (median and range) for water quality in estuaries across south-western Australia for some potential indicators of acidic drainage. <LOR = less than limit of reporting; * indicates bimodal distribution.*

Variable (unit)		**Swan Canning**	**Peel Harvey**	**Leschenault**	**Vasse Wonnerup**	**Hardy**	**South coast estuaries**
Total acidity	median	10	4	6	8	4.5	6
(mg $CaCO_3$ L^{-1})	range	4–18	<1–14	<1–18	<1–16	3–5	2–11
	%<LOR	0%	33%	0%	21%	0%	0%
Alkalinity	median	130	120	58	140	53	120
(mg $CaCO_3$ L^{-1})	range	66–20	59–170	22–330	42–180	45–63	44–140
	%<LOR	0%	0%	0%	0%	0%	0%
pH	median	7.7	8.0	7.7	8.0	7.6	8.1
(pH units)	range	7.0–8.1	6.5–9.3	6.7–8.2	7.3–8.7	7.2–8.6	7.7–8.5
	%<LOR	0%	0%	0%	0%	0%	0%
Chloride	median	14000	18000	1030 *	11600	1650	19000
(mg L^{-1})	range	170–19000	1700–43000	100–30000	160–2400	140–2200	13000–22000
	%<LOR	0%	0%	0%	0%	0%	0%
Sulfate	median	2000	2600	112 *	1750	120	2650
(mg L^{-1})	range	33–2800,	110–5,900	15–4600	10–3200	29–230	1700–3100
	%<LOR	0%	0%	0%	0%	0%	0%
$Cl^-:SO_4^{2-}$	median	7.1	7.2	7.0	6.8	12.0	7.4
(ratio)	range	4.9–9.1	0.7–15.5	4.1–16.5	5.0–47	4.8–14.5	6.5–8.2
$\delta^{34}S$	median	20.3	20.7	20.4	20.8	22.5	20.5
(per mil, ‰)	range	9.8–22.2	-7.0–23.6	3.4–27.9	10.1–22.8	20.5–23.4	18.6–22.8

Table 2 *Summary data (median and range) for water quality in catchments across south-western Australia for some potential indicators of acidic drainage. <LOR = less than limit of reporting.*

Variable (unit)		**Swan Canning**	**Peel Harvey**	**Leschenault**	**Scott Coastal Plain**	**South coast**
Total acidity	median	4.5	9	6	10	11
(mg $CaCO_3$ L^{-1})	range	<1–31	<1–57	1–27	6–62	4–290
	%<LOR	13%	6%	0%	0%	0%
Alkalinity	median	65	56	41	18	23.0
(mg $CaCO_3$ L^{-1})	range	17–250	3–180	12-240	<1–200	<1–260
	%<LOR	0%	0%	0%	4%	10%
pH	median	7.4	7.1	7.16	6.8	7.2
(pH units)	range	6.2 –9.3	4.8–9.5	6.1–7.7	4.1–7.6	2.8–8.1
	%<LOR	0%	0%	0%	0%	0%
Redox (Eh)	median	311	343	345	347	366
(mV)	range	243–386	179–419	262–389	213– 583	249–700
Chloride	median	140	190	105	130	220
(mg L^{-1})	range	80–450	60–9000	50–480	50–1500	60–2300
	%<LOR	0%	0%	0%	0%	0%
Sulfate	median	62	25	15	12	30
(mg L^{-1})	range	15–340	<5–1100	6–43	<5–290	<5–630
	%<LOR	0%	10%	0%	14%	3%
$Cl^-:SO_4^{2-}$	median	3.4	8.2	6.9	10.3	8.0
(ratio)	range	0.7–15	3.2–88	3.3–23	0.9–96	0.6–24
$\delta^{34}S$	median	17.3	22.0	20.8	22.5	19.7
(per mil, ‰)	range	11.7–25.1	7.9-31.4	16.2–26.2	-6.6–27.8	3.2–27.7

Table 3 *Number of sites (or samples) classified as either 'acidic' ($Cl^-:SO_4^{2-}$ <4) or 'reducing' ($Cl^-:SO_4^{2-}$ >7.2) using only the $Cl^-:SO_4^{2-}$ ratio for both estuarine and catchment regions.*

Region	n	Acidic sites (extra sulfate)	Reducing sites (missing sulfate)
Estuaries			
Swan-Canning estuary	32	0	3
Peel-Harvey estuary	51	1	10
Leschenault Estuary	20	0	4
Vasse-Wonnerup estuary	14	0	3
Hardy Inlet	12	0	10
South coast estuaries	28	0	1
Catchments			
Swan Canning	30	21	1
Peel Harvey	37	1	6
Leschenault	28	2	3
Scott Coastal Plain	28	3	7
South coast	31	4	2

4.2 Electrical conductivity by region

Electrical conductivity measured in the field was converted to temperature compensated conductivity (i.e. EC at 25°C) for reporting. Figure 10 shows the distribution of conductivity measured in samples from estuarine areas and samples from the catchment (i.e. rivers, streams, drains). There is some overlap in the conductivity measured between these two groups. Catchment samples with measured electrical conductivity suggest either saltwater intrusion into lowland rivers or highly contaminated sites. Conversely, samples within estuarine reaches showing low conductivity reflect the influence of fresh water in the upper estuary (usually a sample collected in winter). Median conductivities and ranges are shown for each sampled region in Table 1 and Table 2.

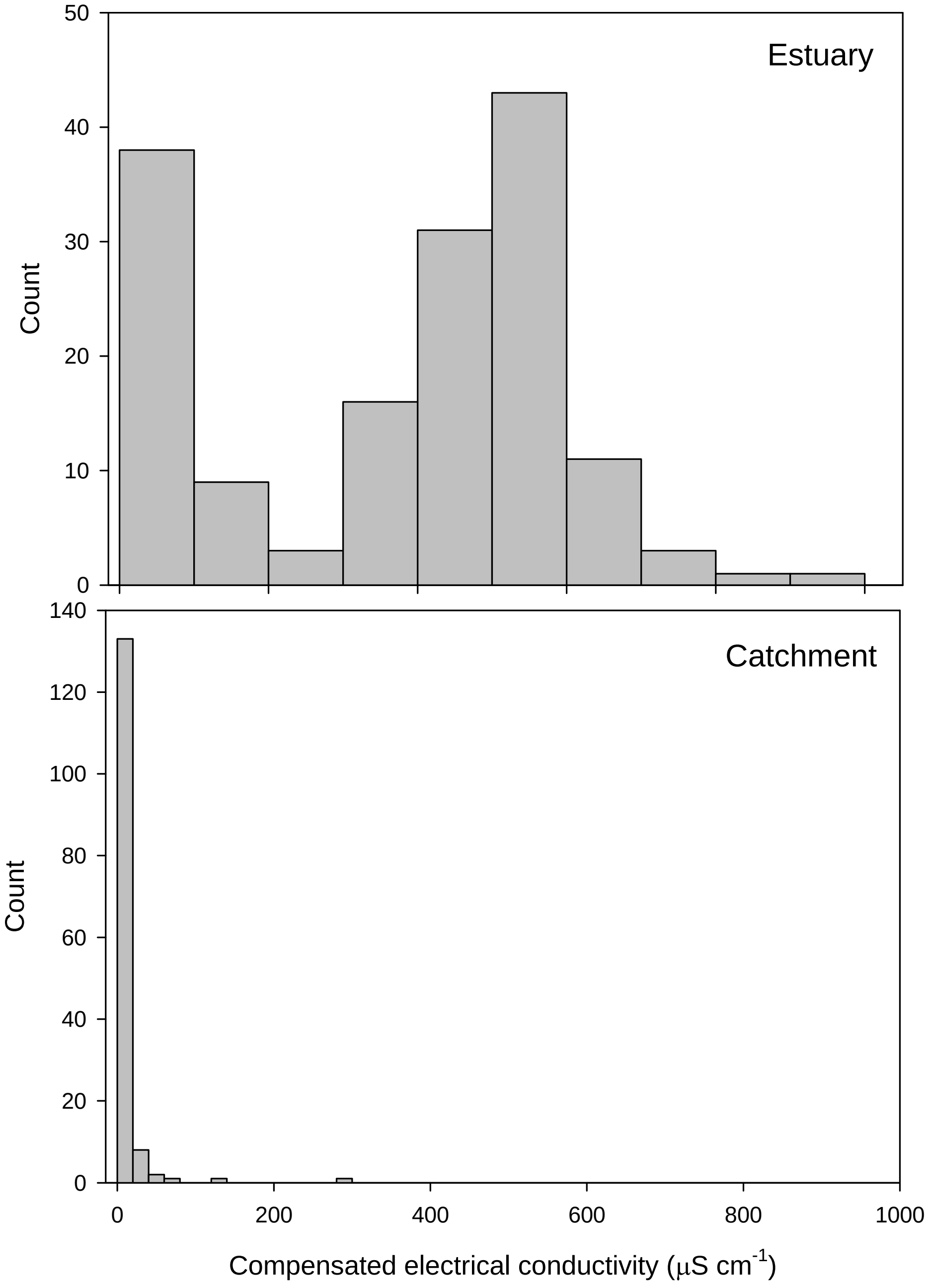

Figure 10 *Histograms of compensated conductivity for samples classified as estuarine and those classified as catchment (freshwater). Samples were designated as either estuarine or catchment prior to sampling.*

5 Results: seasonal differences

Seasonal differences within the data were explored for estuarine samples only (catchment samples were obtained once as a snapshot). PERMANOVA was used to test for differences among groups of variables with electrical conductivity as a co-variate. Including electrical conductivity as a co-variate removes the effect of salinity from the statistical analysis for season. PERMANOVA for the acidity subset of variables (included pH, total acidity, alkalinity and $Cl^-:SO_4^{2-}$) was significant (pseudo-F=3.7, p<0.01). PERMANOVA for the soluble metals subset of variables (included Al, As, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, V, Zn) was significant for season (pseudo-F=5.4, p<0.01). Total metals were only analysed in the second sampling period, so seasonal trends could not be determined.

Soluble Fe, Al and Mn were all higher in winter than in the summer water samples across all south-west estuaries (Figure 11). Soluble Cu, Ni and Zn did not show a seasonal trend, however there was variation across estuary region in these elements, with the highest concentrations of Cu and Zn found in the Swan-Canning estuary (Figure 12).

PERMANOVA for the nutrient subset of variables (included TN, NOx, NH_4^+, DON, TP, FRP) was not significant for season (pseudo-F=0.4, p=0.7). The lack of a significant difference for season is most likely due to high geographical regional variation; that is, differences in nutrient concentrations between sites overwhelmed any overall seasonal variation present.

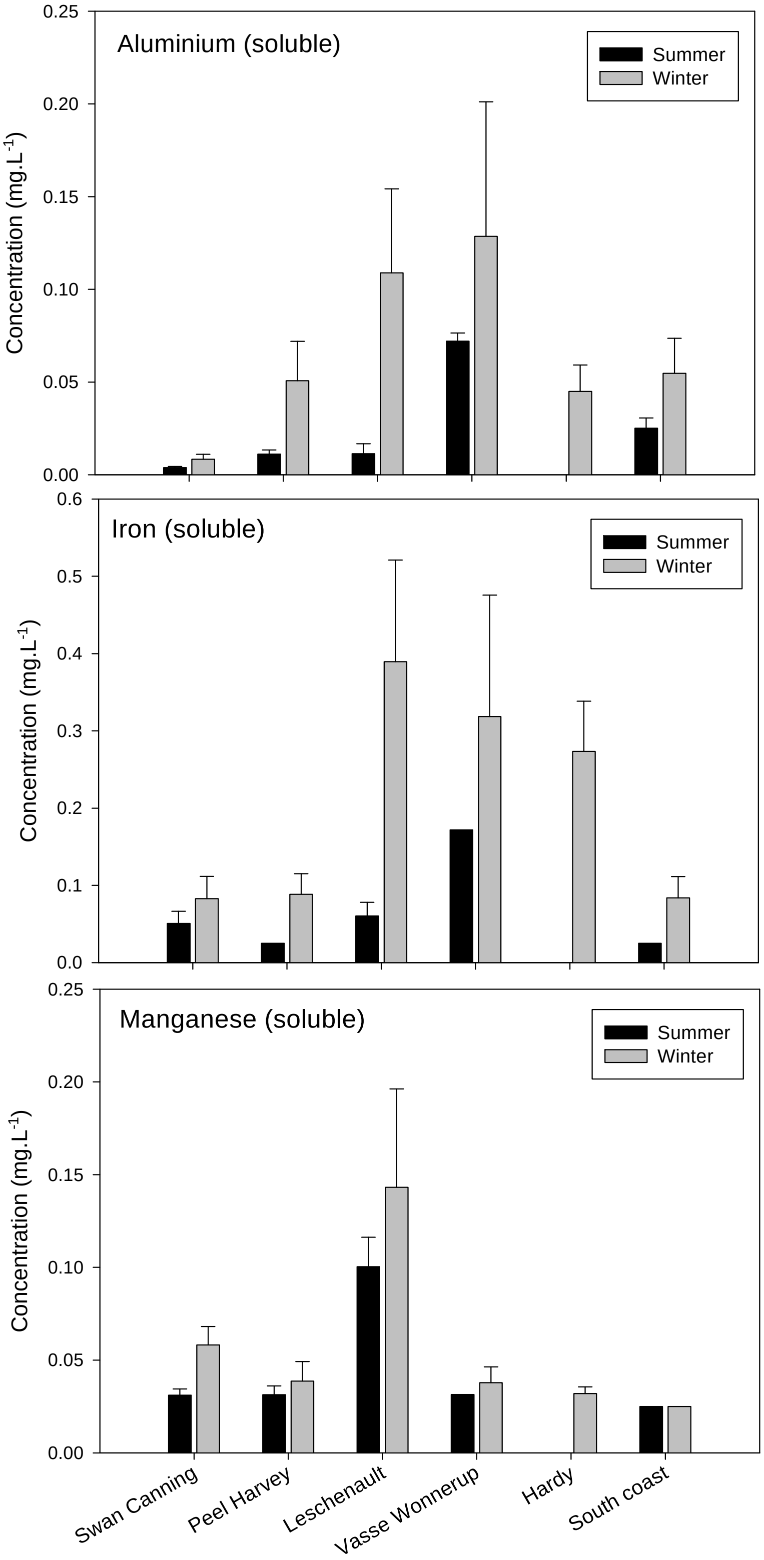

Figure 11 *Average soluble aluminium, iron, and manganese concentrations in summer and winter sampling events across south-western Australian estuaries (mean + st. err.).*

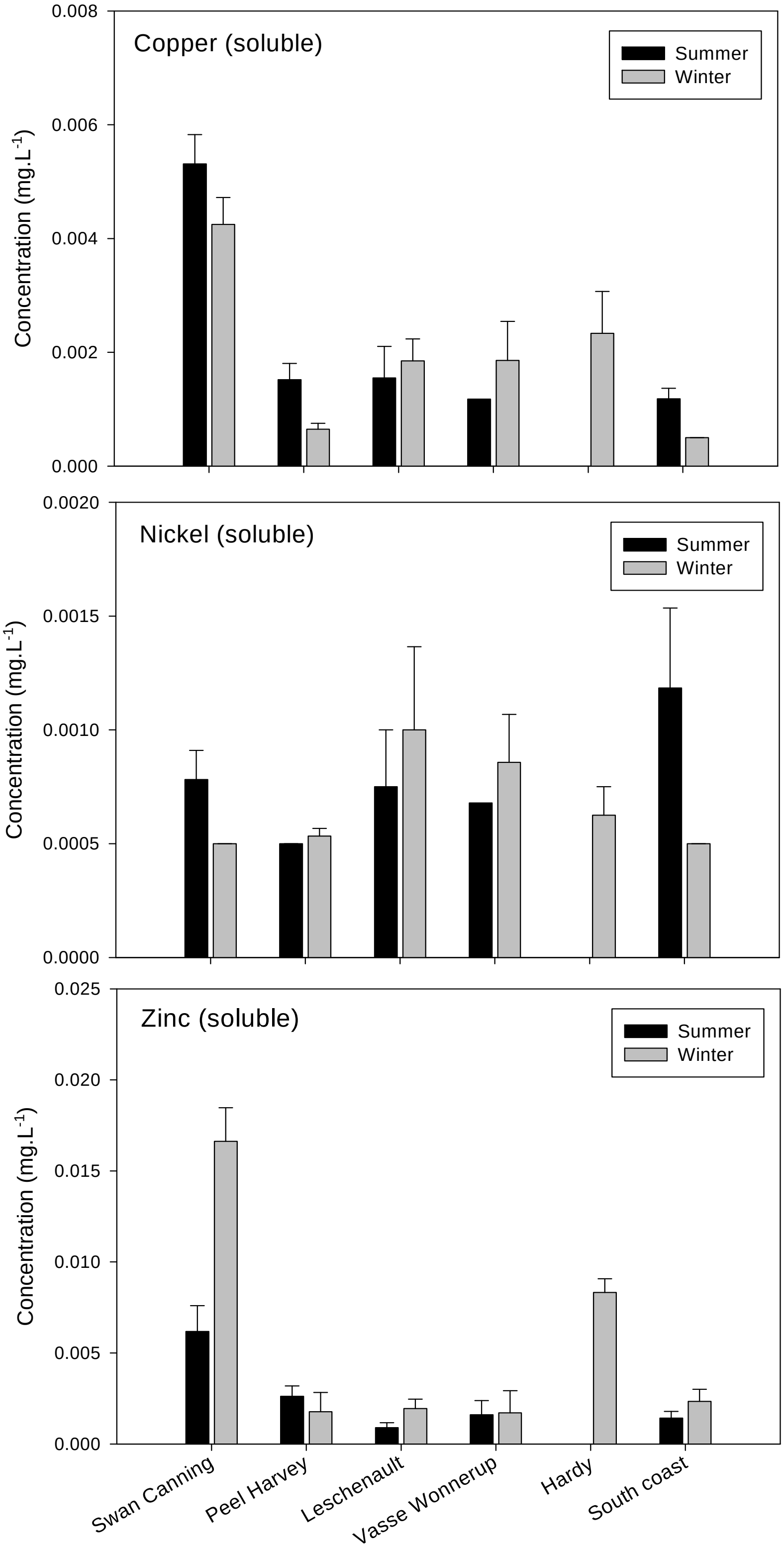

Figure 12 *Average soluble copper, nickel, and zinc concentrations in summer and winter sampling events across south-western Australian estuaries (mean + st. err.).*

6 Results: data relationships

6.1 Correlations of variables

Estuarine and catchment data were combined to compare the relationships of soluble metals with total metals. There were strong positive relationships between soluble and total concentrations for Al, Co, Mn and Mo (R>0.99). Additionally, major ions Mg and Ca showed very strong correlations between soluble and total measurements (R>0.999). Soluble and total concentrations for As, Cr, Cu, Fe, Ni, Pb, V and Zn were not strongly correlated. Dissolved organic carbon was strongly correlated with colour (R=0.93), dissolved organic nitrogen (R=0.86), total phosphorus (R=0.75) and filterable reactive phosphorus (R=0.83).

6.2 Distribution of variables

Not all variables determined in this study have appropriate guideline values against which their concentrations can be compared. In the absence of such guidelines, the distribution of each variable was considered in terms of the percentile range to provide cut-off values for high and low (extreme) values within the dataset (Figure 13). As a lower limit, the 10th percentile value was chosen, representing the value at which 10% of samples were less than the value. Similarly, the 90th percentile value indicates the value at which 10% of samples were higher. The percentile ranges were calculated separately for estuarine and catchment data (Table 4). As expected, acidity was lower and, correspondingly, alkalinity was higher in the estuaries than the catchments; while dissolved organic carbon was higher in the catchments than the estuaries. Median values for Al in both estuaries and catchments were above recommended guideline values. Interestingly, for the estuarine data the 90th percentile value for soluble Fe was 0.3 mg L^{-1}, and for total Fe it was 1.1 mg L^{-1} - values very similar to the recent guidelines proposed for Fe in British Columbia, Canada (Phippen et al. 2008) of 0.35 mg L^{-1} for soluble iron and 1.0 mg L^{-1} for total iron. Higher concentrations of Fe were observed in the catchment samples with medians of 0.72 and 1.35 mg L^{-1} for soluble and total Fe respectively.

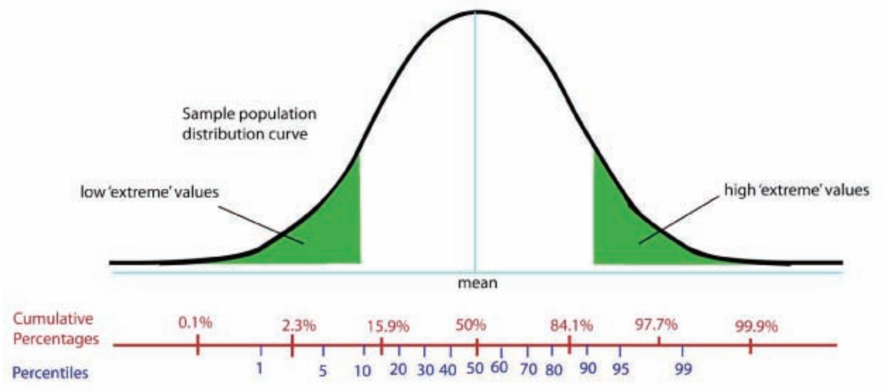

Figure 13 *Diagram showing high and low extreme values from the distribution of the dataset for each variable at 10th and 90th percentiles.*

Table 4 *Summary data for estuarine and catchment water quality showing 10th and 90th percentile values and median for the range of variables analysed. Values preceded by the < symbol did not exceed limit of reporting.*

	Estuaries				**Catchments**			
Variables (units)	**10th percentile**	**90th percentile**	**median**	**n**	**10th percentile**	**90th percentile**	**median**	**n**
Total acidity (mg $CaCO_3$ L^{-1})	<1.0	12	6.0	167	3.0	19	8.0	146
Alkalinity (mg $CaCO_3$ L^{-1})	55	150	120	167	10	120	38	146
pH (pH units)	7.20	8.35	7.95	156	6.11	7.79	7.17	146
Dissolved organic carbon (mg L^{-1})	2.0	24	7.0	167	4.0	72	18	146
Colour (TCU)	n.d.	n.d.	n.d.	n.d.	20	790	110	137
Redox (Eh) (mV)	n.d.	n.d.	n.d.	n.d.	280	401	341	131
Aluminium (sol) (mg L^{-1})	<0.005	0.10	0.10	167	0.024	0.51	0.13	145
Aluminium (tot) (mg L^{-1})	0.022	0.31	0.084	93	0.059	0.93	0.27	146
Arsenic (sol) (mg L^{-1})	<0.001	0.001	0.001	164	<0.001	0.002	<0.001	145
Arsenic (tot) (mg L^{-1})	<0.001	0.008	0.001	85	<0.001	0.002	<0.001	146
Copper (sol) (mg L^{-1})	<0.001	0.001	0.001	164	<0.001	0.002	<0.001	145
Copper (tot) (mg L^{-1})	<0.001	0.007	0.001	85	<0.001	0.003	<0.001	146
Iron (sol) (mg L^{-1})	<0.05	0.3	<0.05	167	0.17	2.9	0.72	145
Iron (tot) (mg L^{-1})	<0.050	1.1	0.28	93	0.36	4.9	1.35	146

Manganese (sol) (mg L^{-1})	<0.050	0.098	<0.050	164	0.008	0.13	0.030	145
Manganese (tot) (mg L^{-1})	0.007	0.16	0.028	85	0.011	0.14	0.038	146
Nickel (sol) (mg L^{-1})	<0.001	0.001	0.001	152	<0.001	0.002	<0.001	145
Nickel (tot) (mg L^{-1})	<0.001	0.002	0.001	73	<0.001	0.003	<0.001	146
Zinc (sol) (mg L^{-1})	<0.001	0.012	0.001	167	<0.001	0.014	0.002	145
Zinc (tot) (mg L^{-1})	<0.001	0.019	0.002	91	<0.001	0.015	0.002	146

7 Results: guideline comparison

The estuarine and catchment water quality data were compared with appropriate guideline values. Physical and nutrient guidelines for aquatic ecosystem stress are ecosystem-specific (e.g. estuarine, lowland rivers etc.), hence guidelines were chosen according to the ecosystem sampled. There are no specific guidelines available for metals in estuaries so, as recommended by ANZECC & ARMCANZ (2000), the lowest-available guideline value was chosen for comparative purposes from either the freshwater or marine guideline values. The freshwater samples (catchment snapshots) were compared with ANZECC & ARMCANZ (2000) trigger values for metals for 95% freshwater species protection. In all cases, the guideline or trigger concentration used for comparison is clearly stated.

7.1 Estuarine water quality: physical guidelines

The pH and dissolved oxygen measured in south-western Australian estuaries were compared with the ANZECC & ARMCANZ (2000) trigger values for estuarine ecosystem stress (Table 5). Where a pH guideline value was triggered, in most cases the sample was below the lower limit of 7.5. The exception to this was the Vasse Wonnerup, where almost a third of sites were above the upper-limit trigger value of 8.5. The pH guideline value was not exceeded for any of the south coast estuaries.

Dissolved oxygen was generally depleted rather than enhanced in the estuarine water samples. The Swan-Canning and Leschenault estuaries showed the lowest oxygen concentrations with 69% and 81% of samples (respectively) having oxygen concentrations below 90% oxygen saturation. High concentrations of dissolved oxygen (i.e. greater than 110% oxygen saturation) generally indicate eutrophic systems where oxygen has been enhanced by primary production (e.g. algal blooms). Instances where samples exceeded the upper-limit trigger value for dissolved oxygen occurred in samples from the Vasse-Wonnerup (26%) and Peel-Harvey (16%) estuaries, as well as Hardy Inlet (8%).

Table 5 *Comparison of estuarine water quality data for pH and dissolved oxygen data against guideline values by area. Guideline values are ANZECC & ARMCANZ (2000) trigger values for estuarine ecosystem stress (pH, DO%).*

Variable (units)	Trigger value	Samples exceeding trigger values
Swan Canning		
pH (pH units)	≤7.5 & ≥8.5	Samples exceeding guideline: 34% below[W]; 0% above range.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 69% below; 0% above range.
Peel Harvey		
pH (pH units)	≤7.5 & ≥8.5	Samples exceeding guideline: 14% below and 6% above range.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 39% below and 16% above range.
Leschenault		
pH (pH units)	≤7.5 & ≥8.5	Samples exceeding guideline: 31% below[S] and 0% above range.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 81% below and 0% above range.
Vasse Wonnerup		
pH (pH units)	≤7.5 & ≥8.5	Samples exceeding guideline: 14% below and 29% above range.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 57% below and 29% above range.
Hardy		
pH (pH units)	≤7.5 & ≥8.5	Samples exceeding guideline: 50% below and 8% above range.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 50% below and 8% above range.
South coast (includes Oyster and Princess Royal harbours, Wilson, Broke, Walpole Nornalup and Irwin inlets)		
pH (pH units)	≤7.5 & ≥8.5	Guideline range not exceeded.
DO (% saturation)	≤90 & ≥110%	Samples exceeding guideline: 3% below and 0% above range.

[W] indicates the majority of samples which exceeded guidelines were collected in winter

[S] indicates the majority of samples which exceeded guidelines were collected in summer.

7.2 Estuarine water quality: nutrient guidelines

The nutrient concentrations measured in south-western Australian estuaries were compared with the ANZECC & ARMCANZ (2000) trigger values of physical and chemical stressors using the estuaries ecosystem classification (Figure 14). Nutrient concentrations exceeded guideline values (TN, NOx, NH_4^+, TP, FRP) in the majority of samples for most estuaries. The south coast estuaries (including Oyster and Princess Royal harbours and Wilson, Broke, Walpole Nornalup and Irwin inlets) were the least disturbed in terms of nutrient concentrations, with only a low percentage of sites exceeding nitrogen and phosphorus guideline values. However, filterable reactive phosphorus (FRP) was elevated in the south coast estuaries with 76% of samples exceeding the guideline. In the Swan-Canning, Peel-Harvey and Leschenault estuaries, TP and FRP exceeded the guidelines more often than nitrogen (total nitrogen (TN), nitrate + nitrite (NOx) and ammonium (NH_4^+)). The Hardy Inlet exceeded both TN and NOx guideline values for all samples. The number of times the trigger value was exceeded for the oxidised form of soluble nitrogen (NOx) was lower than that of the reduced form (NH_4^+) in all estuaries except for the Hardy.

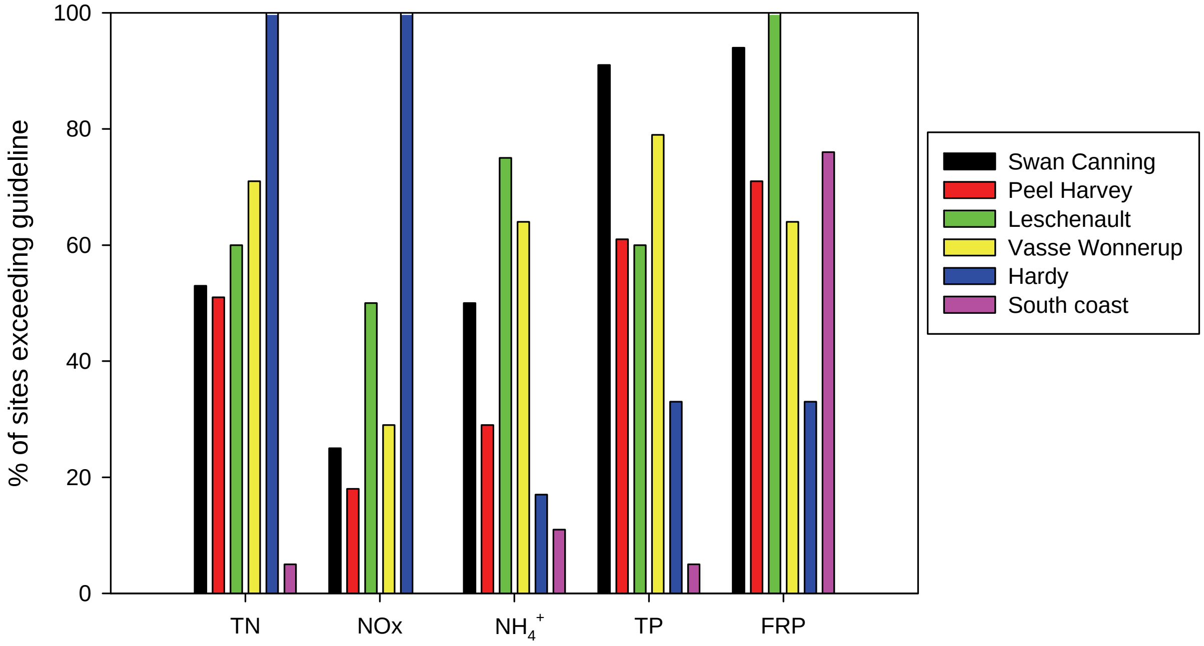

Figure 14 *Percentage of sites exceeding ANZECC & ARMCANZ (2000) guideline values for pH, total nitrogen (TN), nitrate + nitrite (NOx), ammonium (NH_4^+), total phosphorus (TP) and filterable reactive phosphorus (FRP) for south-western Australian estuaries.*

7.3 Estuarine water quality: metal guidelines

No specific guidelines for metals in estuaries are available; hence we used the lowest guideline value from either the freshwater or marine guideline values - as recommended by ANZECC & ARMCANZ (2000). The rationale behind this recommendation is that estuaries may contain biota from both fresh and marine systems and thus the lowest value should be adopted to ensure adequate species protection. In most cases the freshwater guideline gave the most conservative value at the 95% protection level, except for Cu and Hg where the marine values were used (because these were more sensitive). Trigger values were adjusted using the hardness algorithm for Cd, Cr, Cu, Ni, Pb, and Zn to derive hardness modified trigger values (HMTVs). The comparison of data with HMTVs was carried out for both total and soluble metal fractions, however biological concern is greater for cases where the soluble fraction exceeds guidelines (as this is more likely to be available to organisms).

A large number of estuarine sites exceeded the non-hardness adjusted trigger value for copper and zinc; however, when adjusted for the high hardness in estuarine waters, these measurements no longer exceeded guideline values. Aluminium and iron were the metals that most frequently exceeded the trigger values for the soluble fraction (Figure 15). The percentage of sites exceeding the trigger values for each estuary is shown in Appendix C. The aluminium guideline was exceeded for the total fraction in 47% to 93% of samples (per estuary) compared with that for the soluble fraction (less than 35%). Trigger values were not (or only rarely) exceeded for mercury, manganese, molybdenum, nickel, lead, selenium, zinc and vanadium. Total arsenic exceeded guideline values in the Peel Harvey, but the soluble concentration was lower than the guideline values in all cases. Total metals were not sampled in the first (summer) sampling period, and this sometimes led to reporting of a higher percentage of samples exceeding trigger values for soluble rather than total metals.

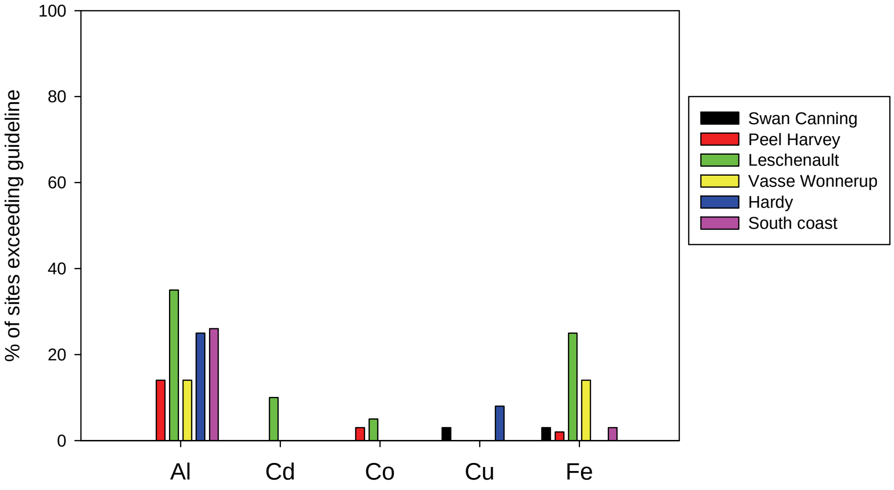

Figure 15 *Percentage of sites exceeding trigger values (hardness modified where possible) for soluble aluminium (Al), cadmium (Cd), cobalt (Co) copper (Cu) and iron (Fe) for south-western Australian estuaries.*

7.4 Catchment water quality: physical guidelines

The pH and dissolved oxygen measured in south-western catchment areas (main rivers, tributaries and drains) were compared with the ANZECC & ARMCANZ (2000) trigger values for lowland river ecosystem stress (Table 6). Both the low and high guideline values were exceeded for pH, with approximately 30% of samples in the Swan Coastal Plain and south coast catchments lower than pH 6.5. Dissolved oxygen was more often depleted (i.e. <80% saturation) than enhanced (>120% saturation) in the catchment water quality across all catchments (Table 6). The Peel Harvey and the Scott Coastal Plain catchments had the greatest number of samples exceeding the low guideline value with 45% and 39% of samples, respectively, below 80% oxygen saturation.

7.5 Catchment water quality: nutrient guidelines

The nutrient concentrations measured in south-western catchments were compared with the ANZECC & ARMCANZ (2000) trigger values for lowland river ecosystem stress (Figure 16). Nutrient concentrations were consistently higher than guideline values for a significant proportion of samples across all catchments. The Peel Harvey samples exceeded total nitrogen (TN) and total phosphorus (TP) guidelines in approximately 70% of samples. The nitrate and nitrite (NOx) guideline was exceeded in approximately 75% of sites in the Swan Canning, whereas for the Peel Harvey only 3% of sites exceeded the NOx guideline value, but a higher proportion of the latter sites exceeded the ammonium (NH_4^+) guideline value.

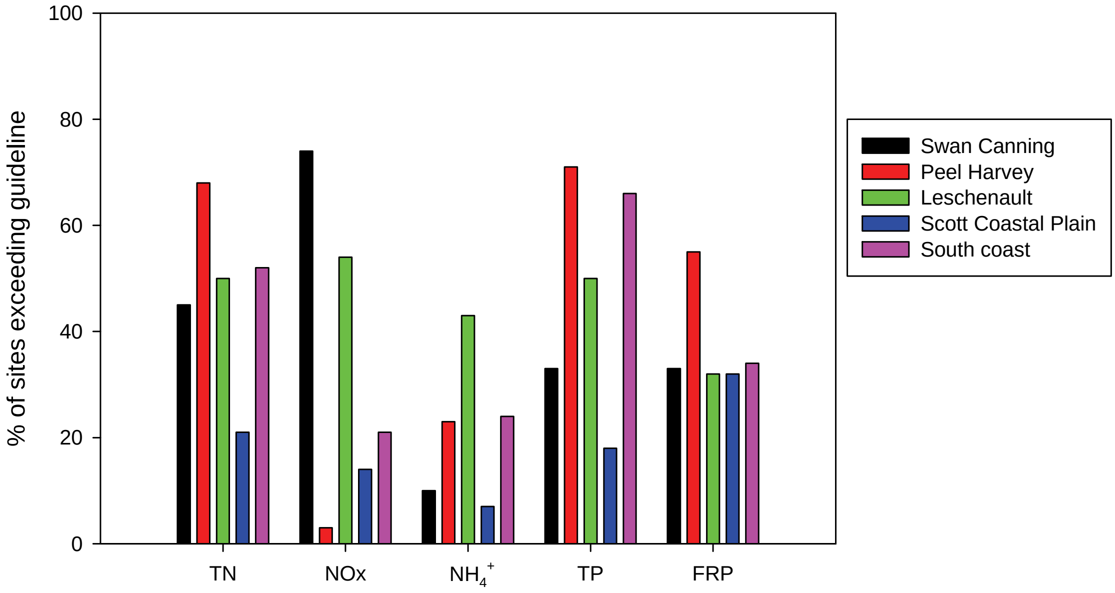

Figure 16 *Percentage of sites exceeding guideline values for total nitrogen (TN), nitrate + nitrite (NOx), ammonium (NH_4^+), total phosphorus (TP) and filterable reactive phosphorus (FRP) for south-western Australian catchments.*

Table 6 *Comparison of catchment (fresh water) water quality data for pH and dissolved oxygen data with ANZECC & ARMCANZ (2000) trigger values for lowland river ecosystem stress (pH, DO%).*

Variable (units)	Trigger level	Samples exceeding trigger values
Swan Canning		
pH (pH units)	≤6.5 & ≥8.0	Samples exceeding guideline: 7% below and 17% above range.
DO (% saturation)	≤80 & ≥120%	Samples exceeding guideline: 20% below and 40% above range.
Peel Harvey		
pH (pH units)	≤6.5 & ≥8.0	Samples exceeding guideline: 13% below and 10% above range.
DO (% saturation)	≤80 & ≥120%	Samples exceeding guideline: 45% below and 10% above range.
Leschenault		
pH (pH units)	≤6.5 & ≥8.0	Samples exceeding guideline: 7% below and 0% above range.
DO (% saturation)	≤80 & ≥120%	Samples exceeding guideline: 29% below and 7% above range.
Scott Coastal Plain		
pH (pH units)	≤6.5 & ≥8.0	Samples exceeding guideline: 32% below and 0% above range.
DO (% saturation)	≤80 & ≥120%	Samples exceeding guideline: 39% below and 4% above range.
South coast		
pH (pH units)	≤6.5 & ≥8.0	Samples exceeding guideline: 31% below and 7% above range.
DO (% saturation)	≤80 & ≥120%	Samples exceeding guideline: 24% below and 17% above range.

^{w} *indicates the majority of exceedences occurred in winter*

^{S} *indicates the majority of exceedences occurred in summer*

7.6 Catchment water quality: metal guidelines

Samples analysed to determine metals and metalloids were compared with ANZECC & ARMCANZ (2000) trigger values for 95% freshwater species protection (high reliability) unless otherwise stated. Trigger values were adjusted using the hardness algorithm for Cd, Cr, Cu, Ni, Pb and Zn to produce hardness modified trigger values (HMTVs). Al, Fe, Cu, Co, Zn and Cr in catchment samples were the metals that most frequently exceeded trigger values (Figure 17). The percentage of sites exceeding the trigger values for each catchment can be found in Appendix D.

The Al trigger value was exceeded in most samples across all catchments, with a slightly higher proportion of samples exceeding the trigger value for the total (77–100%) compared with the soluble fraction (45–89%). As, Cd, Hg, Ni, Pb, Se and Mo trigger values were not exceeded in any sample. N and V trigger values were exceeded occasionally. Fe commonly exceeded trigger values throughout all catchments. The south coast catchment samples exceeded the Fe guideline values most often (83% total and 72% soluble).

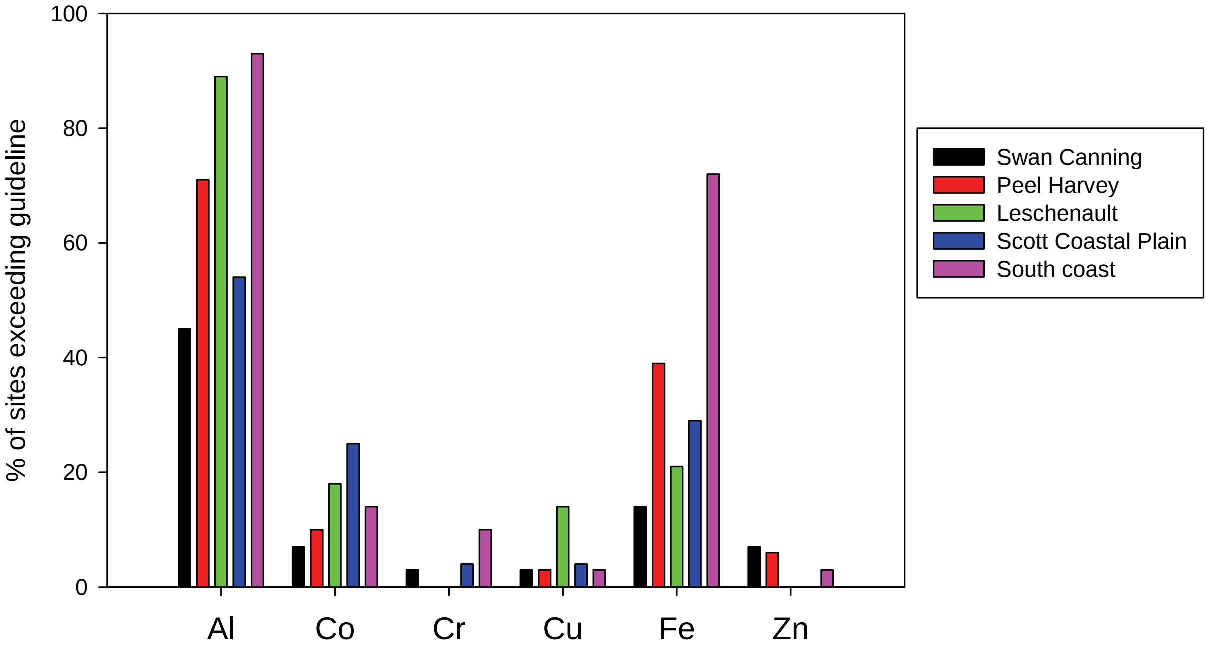

Figure 17 *Percentage of sites exceeding trigger values (hardness modified where possible) for soluble aluminium (Al), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and zinc (Zn) for south-western Australian catchments.*

8 Results: analysis of sulfur stable isotopes

8.1 Background

Identifying sources of sulfur in natural waters is important for managing aquatic ecosystems potentially affected by ASS. Pyritic soils once oxidised may discharge high concentrations of metals, acid and sulfate to surrounding waterbodies. Sulfate in waterways may also be derived from seawater, rainfall, fertiliser and greywater. Analysing the isotopic composition of the sulfur ($\delta^{34}S$) in sulfate may distinguish between these sources and provide a screening tool for waterway management to identify water resources affected by disturbed ASS.

Sulfur occurs naturally as four stable isotopes, of which ^{32}S and ^{34}S are most abundant (95% and 4.2% respectively). Differences in the relative abundance of ^{34}S are determined relative to a standard and expressed on the per mil scale; that is, parts per thousand (‰), for $\delta^{34}S$ (Clarke & Fritz 1997). Sulfur-34 abundance varies between sulfur compounds due to physical processes and biological cycling such as fractionation by sulfate-reducing bacteria (Kaplan & Rafter 1957; Clarke & Fritz 1997), which results in isotopically light $\delta^{34}S$ for the sulfides (i.e. relatively more ^{32}S). Sulfur isotope ratios measured in brackish and more saline estuarine systems are likely to be mostly a mixture of sulfur from seawater sulfate and sulfate derived from oxidation of pyrite or other reduced sources. The sulfur in seawater has highly positive $\delta^{34}S$ values (~21 ‰) (isotopically enriched), whereas sulfur from reduced sources has negative $\delta^{34}S$ values (-18 to -52 ‰) (isotopically depleted). Other natural and anthropogenic sources of sulfur may also contribute to the measured isotopic ratio, including geothermal waters rich in sulfur, mineralised organically bound sulfur in soil, leached sulfate minerals and sulfate found in fertilisers and urban areas, as well as detergents, many of which contain sodium sulfate as a filler agent. Additionally, the degradation of sulfur-containing compounds in surfactants (e.g. sulfonates) may also contribute further sulfate to waterways. The average $\delta^{34}S$ often varies between different sources of sulfur and this property may be exploited to distinguish contributing sulfur sources in natural waters (Figure 18).

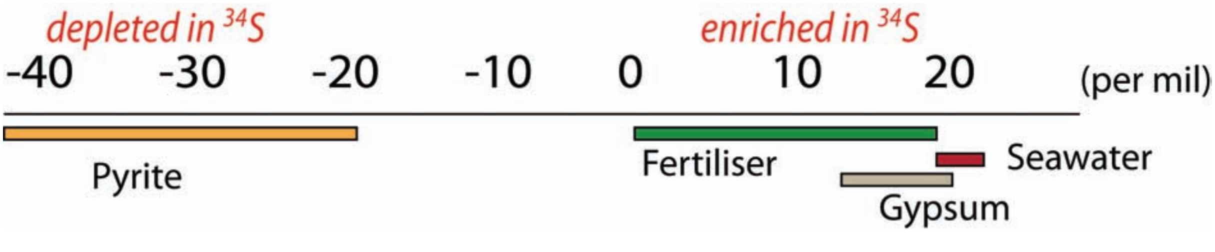

Figure 18 *Approximate distribution of $\delta^{34}S$ values measured in pyrite, fertiliser, gypsum and seawater.*

8.2 Study design and methods

Approximately 300 surface water samples were collected from estuaries and catchment waterways (main rivers, tributaries and drains) in south-western Australia, with locations including freshwater, brackish and saline systems. The Hardy Inlet, Swan-Canning, Peel-Harvey, Leschenault and Vasse-Wonnerup estuaries were sampled, along with the Broke, Walpole Nornalup, Irwin and Wilson inlets and the Princess Royal and Oyster harbours. Catchments were sampled in the Swan-Canning, Peel-Harvey, Leschenault, Vasse-Wonnerup, Scott Coastal Plain and south coast (near Albany) regions.

Filtered water (0.45 μm) for $\delta^{34}S$ isotope analysis was collected in HDPE bottles with 10% nitric acid added as a preservative in the field and transported to Monash University for analysis. Before analysis, samples were further acidified and concentrated by evaporation. Sulfate in the sample was precipitated as barium sulfate ($BaSO_4$) by the addition of barium chloride in excess. The dried $BaSO_4$ was analysed by continuous flow isotope ratio mass spectrometry. $\delta^{34}S$ values are expressed in per mil (‰) notation on the Canyon Diablo Troilite (CDT) standard scale; standardisation of $\delta^{34}S$ values used NBS-127 and IAEA-SO5 standards. Precision (1σ) based on replicate analyses was ±0.2 ‰. Metals, nutrients, major ions and acidity measurements were also determined for these water samples, as described in Appendix B.

The sulfur isotope value was used to determine whether water quality was influenced by other sources of sulfate (acidic drainage, fertiliser or greywater) or dominated by sulfate-reduction processes. Samples were assigned to groups based on the criteria described in Table 7, with these so-called iso-groups categorising samples according to similar influences.

An isotopic mass-balance approach was used to categorise water samples into iso-groups. For more information about this approach see Kilminster and Cartwright (2011).

- Chloride was used as a conservative tracer to calculate the abundance of sulfur in the surface water derived from seawater (the chloride:sulfate ratio in seawater is approximately 7.2 (Clarke & Fritz 1997))
- Where sulfate was present in the water in excess of what could be derived from seawater, a mass-balance calculation was performed to determine what isotope ratio of the extra sulfate would be required to produce the measured $\delta^{34}S$ for the sample.
- A threshold for the calculated $\delta^{34}S$ for excess sulfur was determined by the lowest isotopic value of fertilisers (0 ‰) from a subset of those commercially available in Western Australia (see Appendix G).
- The two groupings most likely to be representative of acidic drainage (i.e. sulfur from pyrite oxidation) are iso-groups 3 and 5.

8.3 Iso-group proposed meaning and distribution

The proposed six iso-groups can be further grouped based on whether the sites are likely to be natural or disturbed in terms of external sulfur inputs. If disturbed, they can then be further divided into those likely to be receiving acidic drainage, and those dominated by sulfate-reduction.

Table 7 *Categorisation criteria for iso-groups based on measured δ^{34}S value, presence of extra sulfate, and the calculated isotopic value expected for the extra sulfate.*

Iso-group	Measured δ^{34}S	Extra sulfate?	Calculated δ^{34}S for excess S	Proposed meaning
1	20-21 ‰	No	n/a	Sulfur pristine
2	>21 ‰	Sulfate missing	n/a	Sulfate-reducing dominant (with only seawater sulfate as a sulfate source)
3	<19.5 ‰	Yes	<0	Sulfate inputs from oxidised acid sulfate soils (acidic drainage)
4a	>21 ‰	Yes	>20.4	Sulfate-reducing dominant and extra source of sulfur
4b	<19.5 ‰	Sulfate missing	n/a	Sulfate-reducing dominant and non-seawater sulfate
5	<19.5 ‰	Yes	0–20.0	Extra source of sulfate but is a mixed signal (could be a combination of sulfate from oxidised pyrite and/or fertiliser/greywater)

Natural sites: Iso-group 1 samples were considered pristine in terms of sulfur sources; that is, only showed signals related to seawater. Iso-group 2 samples were considered sulfate-reducing dominant, but without an extra source of sulfur (only sulfate from seawater) these were likely to be unperturbed systems.

Acidic and probably acidic sites: Samples falling into iso-group 3 were proposed as showing a clear signal of acidic drainage from disturbed ASS. These samples have extra sulfate (on average 9% extra sulfate relative to that expected from seawater) and the calculated δ^{34}S of the extra sulfate is highly negative (i.e. indicating a reduced sulfur source like pyrite). Iso-group 5 often showed significantly more extra sulfate than iso-group 3 (on average 50% extra), but the δ^{34}S of the extra sulfate suggested the sulfur could be derived from multiple sources (e.g. fertiliser, greywater or acidic drainage).

Disturbed, sulfate-reducing: Iso-group 4a and 4b samples have extra sources of sulfur (relative to seawater) contributing to the measured parameters, but sulfate-reduction dominates in both cases. Samples in these groups come from sites that may pose risk of blackwater events (monosulfidic materials deoxygenating the water column following heavy rainfall).

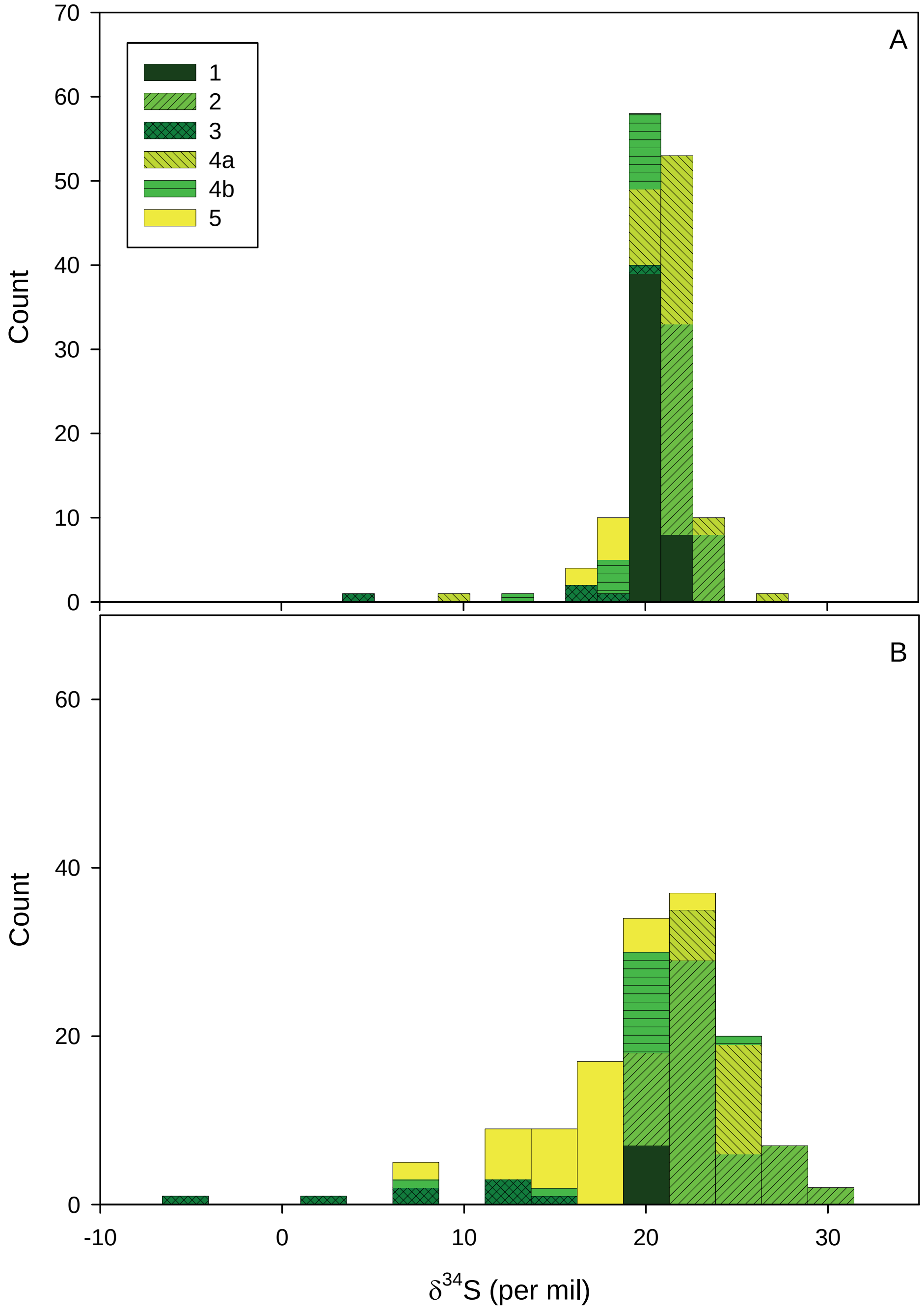

Figure 19 *Histogram plots showing distribution of the stable sulfur isotope ratio measured in A) estuarine surface water and B) catchment surface water. Iso-group category is represented by column colour and shading.*

Histogram plots showing distribution of the stable sulfur isotope ratio measured in both estuarine and catchment water, combined with the frequency at which each iso-group occurs, are shown in Figure 19. These iso-group classifications suggest that sulfate-reducing sites (iso-groups 2, 4a and 4b) dominate most estuaries. The Swan-Canning catchment is dominated by iso-group 5 sites, suggesting multiple sources of external sulfur are contributing to the water quality measured in this catchment. The distribution of sites belonging to each iso-group according to region are shown in Table 8 and Table 9.

Table 8 *Distribution of estuarine sites within iso-group categories across regions.*

Iso-group	Swan Canning	Peel Harvey	Leschenault	Vasse Wonnerup	Hardy	south coast
1	6	17	3	3	0	8
2	2	13	3	1	10	2
3	1	2	3	0	0	0
4a	7	10	6	5	2	7
4b	4	4	2	2	0	4
5	8	3	3	2	0	9

Table 9 *Distribution of catchment (fresh water) sites within iso-group categories across regions.*

Iso-group	Swan Canning	Peel Harvey	Leschenault	Scott Coastal Plain	south coast
1	0	0	3	2	0
2	4	15	6	17	12
3	1	1	1	1	4
4a	3	4	8	2	2
4b	0	2	5	2	6
5	22	5	4	3	5

8.4 Relevance of iso-groups

From an environmental management viewpoint, the most significant concern in relation to drainage from ASS is the input of acidic metal-rich water. This may deleteriously affect biota and ecosystem function (rather than the input of extra sulfate). Therefore, if the screening tool is to be useful to management, we would also require it to inform us about metal distribution in the water, and these ideas are explored within this section.

Data analysis of the multivariate dataset collected was undertaken to see if the iso-group classification was meaningful with respect to the other variables analysed. Analysis was performed with PERMANOVA in the PRIMER v6 and PERMANOVA + software package. Data was transformed (log (x+1)), normalised and euclidian-distance resemblance matrices determined. PERMANOVA analyses were run on subsets of variables with electrical conductivity as a co-variate and iso-group as a fixed factor. It was important to consider electrical conductivity (or salinity) as a co-variate because the solubility of metals and pH is strongly affected by the salinity of the water, and analysis showed the co-variate was significant ($p<0.0001$) for all analyses run. Three variable subsets were considered: acidity, soluble metals, and total metals (Table 10). Within the acidity subset, variables considered to be describing some aspect of the acidity were included; for example, total acidity, alkalinity, pH and filtered iron and aluminium. Analysis of the data by PERMANOVA for the acidity subset was not significant for iso-group category, however both metal subsets showed significant differences between iso-group categories ($p<0.05$ and $p<0.005$ for filtered and unfiltered metals respectively).

When Fe and Al concentrations within water samples were considered individually, there was a relationship with the iso-groups. In estuarine samples, for both filtered Al and filtered Fe, iso-group 3 had a greater concentration than the other iso-groups (Figure 20). Iso-group 3 had an average of 0.12 mgL^{-1} filtered Al compared with <0.05 mgL^{-1} for the other groups. Similarly, filtered Fe was 0.49 mgL^{-1} for iso-group 3 and <0.15 mgL^{-1} for the other groups. For unfiltered Al, iso-group 3 and 5 were also higher on average (0.41 and 0.28 mgL^{-1} respectively) than the other iso-groups (<0.18 mgL^{-1}). Unfiltered Fe was also higher for iso-group 3 and 5 (1.0 and 0.91 mgL^{-1} respectively) than the other iso-groups (<0.54 mgL^{-1}). These variations are indicative only – due to small sample sizes in some of the iso-groups statistical significance was not met. Similarly, in the catchment samples iso-groups 3 and 5 had a higher average concentration of Al than the other iso-groups (Figure 21). For filtered Al, iso-groups 3 and 5 had an average concentration of 0.55 and 1.7 mgL^{-1} respectively compared with <0.26 mgL^{-1} for the other iso-groups. For unfiltered Al, iso-groups 3 and 5 had an average concentration of 0.74 and 2.1 mgL^{-1} respectively compared with <0.45 mgL^{-1} for the other iso-groups. There did not seem to be a strong pattern for iron concentrations in catchment samples across iso-group categories (Figure 21).

Median concentrations of many metals (Al, Co, Cr, Cu, Fe, Mn, Ni, V, Zn) and phosphorus were higher in ASS-affected samples (iso-group 3) than in other samples not influenced by ASS (Kilminster & Cartwright 2011). Additionally, total phosphorus and filterable reactive phosphorus had higher median concentrations (0.14 mgL^{-1} and 0.057 mgL^{-1} respectively) for iso-group 3 samples compared with the median concentrations for the other iso-groups combined (0.038 mgL^{-1} and 0.01 mgL^{-1} for TP and FRP).

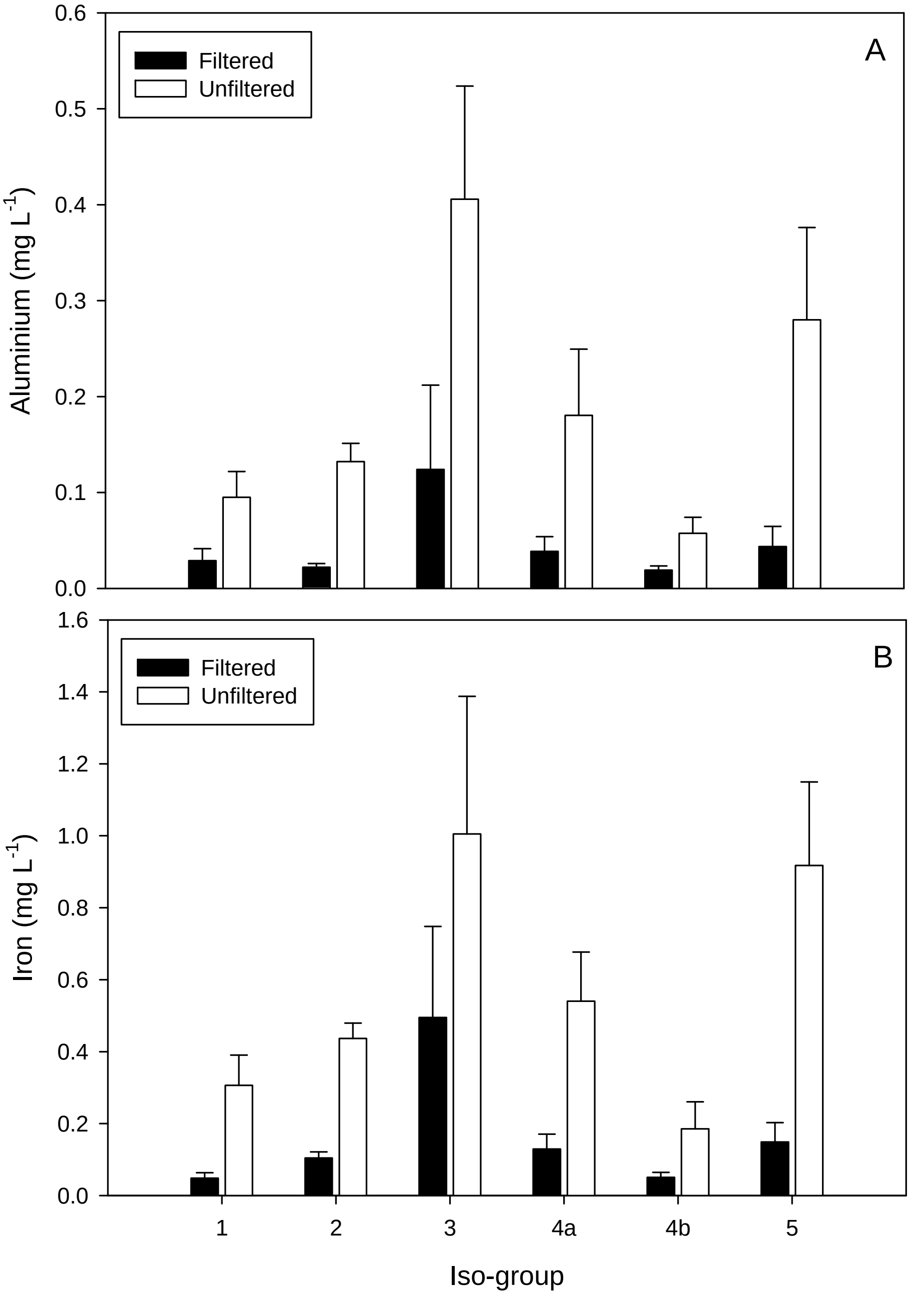

Figure 20 *Concentrations of A) aluminium, and B) iron within estuarine surface water samples, where black columns represent the filtered (soluble) metal fraction and white columns represent the unfiltered (or total) metal fraction (mean + st. err.).*

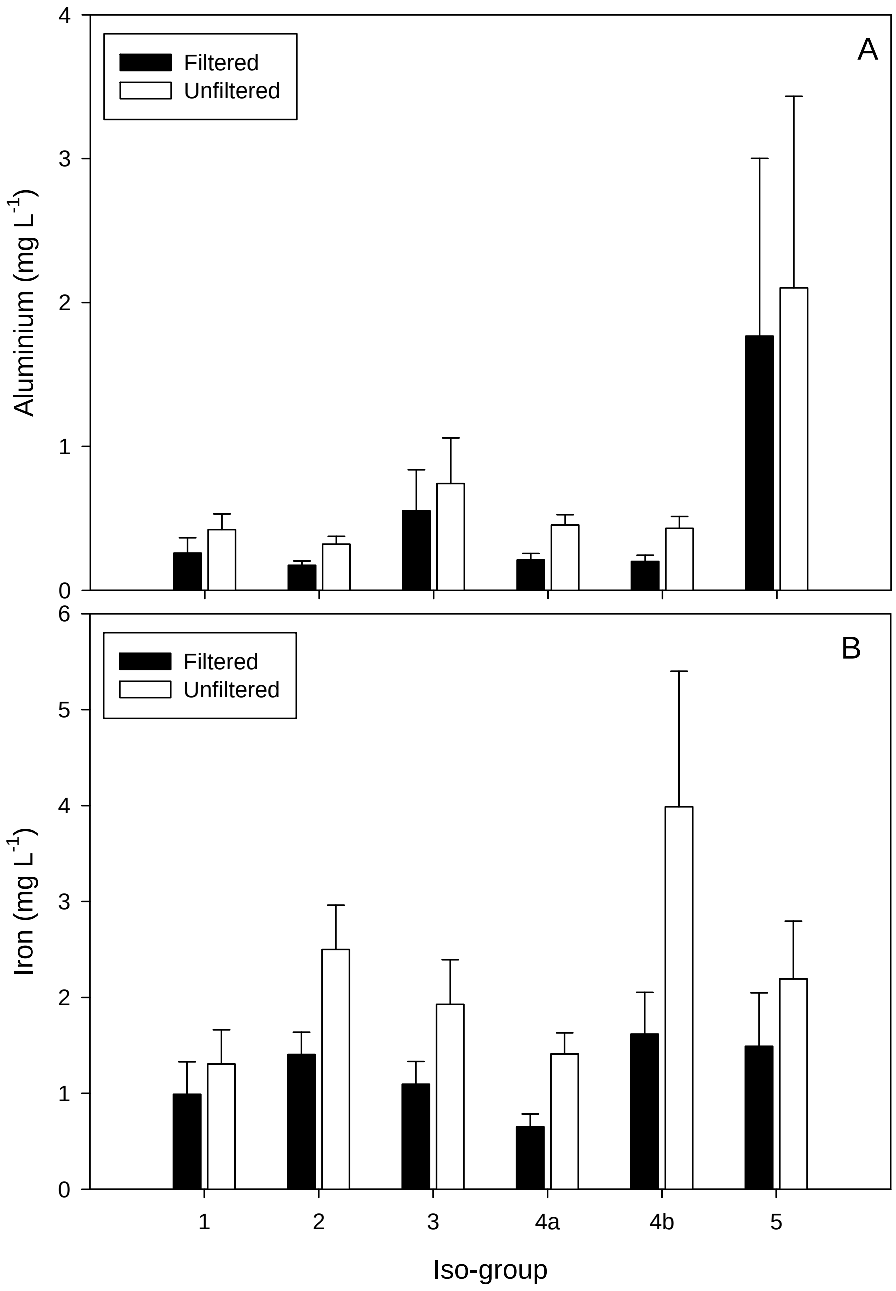

Figure 21 *Concentrations of A) aluminium, and B) iron within catchment surface water samples, where black columns represent the filtered (soluble) metal fraction and white columns represent the unfiltered (or total) metal fraction (mean ± st. err.).*

Table 10 *Results of PERMANOVA analyses of data for variable subset with iso-group as a fixed factor and conductivity as a co-variate.*

Data Subset	**Variables**	**Pseudo-F**	***p* value**
Acidity	total acidity, alkalinity, pH, Fe (filt) and Al (filt)	1.62	0.10
Filtered metals	filtered Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn	1.72	<0.05
Total metals	unfiltered Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn	2.00	<0.005

8.5 Conclusion regarding iso-groups

The categorisation of samples into iso-groups appears to provide a useful signal as to whether acidic drainage is influencing a waterbody. This methodology is more sensitive for identifying acidic drainage than other indicators such as the chloride:sulfate ratio or total acidity. These other indicators of acidic drainage are less suited to identifying the influence of ASS drainage in an estuary since the concentrations of sulfate from seawater are likely to override the input from acidic drainage and any acidity is likely to be neutralised by the seawater. This difference in sensitivity is seen in the plot of chloride:sulfate ratio *vs* iso-group for estuaries and catchments (Figure 22) where only the ratio for iso-group 5 (for catchments) is sufficiently low (i.e. <4) to suggest the influence of acidic drainage.

The iso-group categorisation also identified sites where sulfate-reduction was probably stimulated by a supply of excess sulfur (iso-group 4a and 4b). Approximately 59% of sites sampled appear dominated by sulfate-reduction (i.e. iso-groups 2, 4a and 4b), with half of these likely to have enhanced sulfate-reduction resulting from an anthropogenic source of additional sulfur (i.e. iso-group 4a and 4b). Possible sources of extra sulfur are acidic drainage as well as urban and agricultural sources such as fertiliser and greywater. It is also possible that sulfate-reduction may be enhanced through organic-matter enrichment associated with eutrophication in areas where sulfate is not limiting.

The process of sulfate-reduction efficiently removes metals from the water column, binding them into the sediment. However when this process is accelerated, the reduced sulfur is only bound in an easily oxidisable form, commonly called monosulfidic black ooze (MBO). MBO is a gelatinous black muck that accumulates on the sediment surface and is readily re-oxidised, stripping oxygen from the water column and remobilising the metals that were previously bound (Burton et al. 2006). MBO formation in drains and streams can cause major environmental problems as heavy rainfall mobilises the MBO - deoxygenating the water and resulting in blackwater events. Reported blackwater events on Australia's east coast have been catastrophic with hundreds to thousands of fish and prawns reported killed as a result of just one event (Sammut et al. 1995; Russell & Helmke 2002; ASSAY 2008). Further investigation is required to assess the risk of blackwater events in Western Australian waterways.

Iso-group 3 is most likely influenced by acidic drainage. For catchments, the iso-group 3 samples often exceeded Al, Fe, Co and Cr and nutrient guidelines (Appendix D and E). Iso-group 5 samples are potentially influenced by acidic drainage, but the isotopic signature is mixed, suggesting that sources other than oxidised pyrite are potentially influencing the signal. Catchment samples from iso-group 5 frequently exceeded Al, Fe, Cr, Cu, Co, Zn and nutrient guidelines (Appendix D and E).

The iso-groups do not indicate the intensity of the acidic drainage influence. Also they do not accurately predict the occurrence of metals in a water sample. It seems plausible that this is due in part to the many other potential sources of metals from urban, agricultural and industrial land uses that may influence waterways.

The Western Australian coastal environment is particularly suited to the use of sulfur stable isotopes as an indicator of disturbed ASS. The landscape is geologically old, with no volcanic or geothermal inputs of sulfur. Additionally, unlike many other regions (especially those in the northern hemisphere) acid rain has little influence, while rainwater in Western Australia has δ^{34}S values very similar to seawater sulfate (18.2–20.0 ‰). Gypsum from Western Australia also reflects a seawater sulfur source (Bowen & Benison 2009). Australian fertiliser δ^{34}S values were previously reported to be between +6.4 and +8.5 ‰ (Mizota & Sasaki 1996), however the current study showed a greater range was present in commercially available fertilisers (-0.1 to +18.7 ‰). Regardless, there remains a large separation of the δ^{34}S values of sulfate from oxidised pyrite, seawater, precipitation and fertiliser, which has been used in the current screening tool for ASS-affected waterways. There is scope for this tool to be employed in other environments world-wide, however the δ^{34}S values of sulfur sources would need to be locally determined, and the iso-groups' threshold values adjusted accordingly.

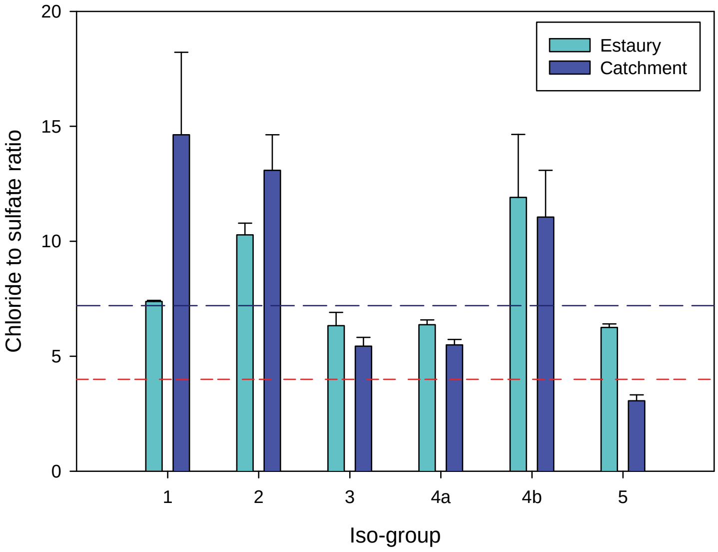

Figure 22 *Chloride:sulfate ratio (mass) of estuarine and catchment water quality categorised by iso-group (mean + standard error). The blue long dashed line indicates the ratio (7.2) observed in seawater, and the red short dashed line indicates a value below which the influence of acid sulfate soil drainage is suggested.*

9 Results: hotspot sites

A few sites within the dataset appeared to be significantly different to the rest of the dataset, and thus were considered hotspot sites. The water quality and appearance of these sites are discussed below. Sites showing extremely high values of aluminium and iron (>90th percentile values) are also highlighted.

9.1 Rich Road drain, near Capel

Site 6100095 (also known as BY01 or Minninup drain) is a drain that flows southward through low-lying agricultural land near Capel and the coast (Figure 23). Acidic water was identified in this drain, and water was sampled for chemical analysis on six occasions between 12 August and 25 September 2007. The drain had dried up by December 2007.

Figure 23 *Northern view of Rich Road drain in September 2007.*

Water quality was consistently poor. Al concentrations ranged from 2–4.5 mg L^{-1} for soluble, and 2.1–4.7 mg L^{-1} for total. Both ranges exceeded the 90th percentile values of 0.51 and 0.93 mg L^{-1} observed for all catchment samples for soluble and total Al respectively (Table 4). Iron concentrations were also extremely elevated, ranging from 130–230 mg L^{-1} and 140–240 mg L^{-1} for soluble and total Fe respectively. The 90th percentile value for the catchment water quality was 2.9 mg L^{-1} for soluble iron, and 4.9 mg L^{-1} for total iron (Table 4). In addition

Fe precipitate (floc) was observed to be highly abundant in surficial sediments present in the bottom of the drain (Figure 24). Mn concentrations were also high in the drain, with a range of 3–4.1 mg L^{-1} for soluble, and 3.2–4.5 mg L^{-1} for total; again much higher than the 90th percentile value for catchment data of 0.13 and 0.14 mg L^{-1} for soluble and total Mn respectively (Table 4).

Low pH (2.7–3) and extremely high total acidity measurements (410–850 mg $CaCO_3.L^{-1}$) also characterised the water from the site. Sulfur isotope values measured in September 2007 were slightly lower than seawater (average ~18.2 ‰), and excess sulfur was present (97% more sulfur than would be expected from seawater mixing alone). For the September sampling, the site was classified as iso-group 5, and this indicates the extra sulfate is likely to have originated from a mixture of sources (e.g. fertiliser and acidic drainage).

Figure 24 *Surficial sediments within the drain (site 6100095) showing the presence of iron floc.*

9.2 Swan-Canning region

The Swan-Canning catchment had a large proportion of sites assigned to iso-group 5, suggesting potential impacts from acidic drainage with large quantities of extra sulfate. One of these, site BWMDBPI (a drain discharging to the Canning Estuary) (Figure 25) appeared impacted by disturbed ASS with 90% extra sulfate, relatively high total acidity (31 mg $CaCO_3.L^{-1}$) and high total Fe (11 mg L^{-1}) and total Al (3.1 mg L^{-1}). Only one site within the Swan-Canning region, SRBDS, showed a clear acidic drainage signal (i.e. iso-group 3), with 26% extra sulfate (Figure 26).

Figure 25 Location of BWMDBPI site in Swan-Canning catchment, adjacent to the Canning River.

Figure 26 Location of site SRBDS classified as iso-group 3 within the Swan-Canning region.

9.3 Peel-Harvey region

Most sites in the Peel-Harvey region were influenced by sulfate-reduction processes (mainly iso-groups 2 and 4a). Fe and Al were high at many sites within the Peel-Harvey catchment when compared with the 90th percentile values. Sites MR05005, MR05010, MR01010 and PATRDTRIB had concentrations of Fe (either soluble or total) higher than the 90th percentile value. Al concentrations (both total and soluble) were higher than the 90th percentile value for catchment samples MPH003, 613053, HR02005 and PHS7. Soluble Al was high at

SR04014 and 614120 and total Al was high at MR01010 and PATRDTRIB. See Figure 27 for the locations of these sites.

The MPH003 catchment sample showed a clear acidic drainage signal. This site is located on a drain that discharges directly into the Peel-Harvey estuary (Figure 28). The site was classified as iso-group 3 with 32% additional sulfate than would be expected from seawater alone. High total acidity (28 mg $CaCO_3.L^{-1}$) and high soluble and total aluminium were also measured at this site. Estuarine sites PHRS4-s and MPH015-w also exhibited a clear acidic drainage influence (iso-group 3) (Figure 29).

9.4 Leschenault region

Several sites in the Leschenault catchment displayed elevated Fe and Al. Sites exceeding the 90th percentile boundary level for soluble Al were ACID02 and LESCH04, and for total Al were GBC02 and ACID13 (Figure 30). Site ACID17 had extremely elevated Fe, both soluble and total, with measurements of 9.9 mg L^{-1} for soluble Fe and 21 mg L^{-1} for total Fe (both higher than the 90th percentile level of 2.9 mg L^{-1} for soluble Fe and 4.9 mg L^{-1} for total Fe (Table 4). The ACID17 sample site is located on the Collie River (Figure 31) downstream from a site discharging contaminated groundwater from an abandoned coal mine (Webb 2009).

Three estuarine sites (6121173-w, 6121162-w and 6121161-w) and one catchment site (LESCH05) were categorised as iso-group 3 (Figure 32), indicating they have received acidic drainage waters. Of these sites, the acidic drainage influence appeared strongest for site 6121173 (also known as Parkfield drain) with 43% extra sulfate than what would be expected from seawater alone. Site 6111043 had the next-greatest influence of acidic drainage with 16% extra sulfate present.

Figure 27 *Catchment site locations in the Peel-Harvey region exhibiting extremely high concentrations of aluminium and/or iron in the water samples.*

Figure 28 *Photograph showing sampling at site MPH003, where the drain enters Peel-Harvey estuary.*

Figure 29 *Location of sites in the Peel-Harvey region with clear acidic drainage influence (iso-group 3).*

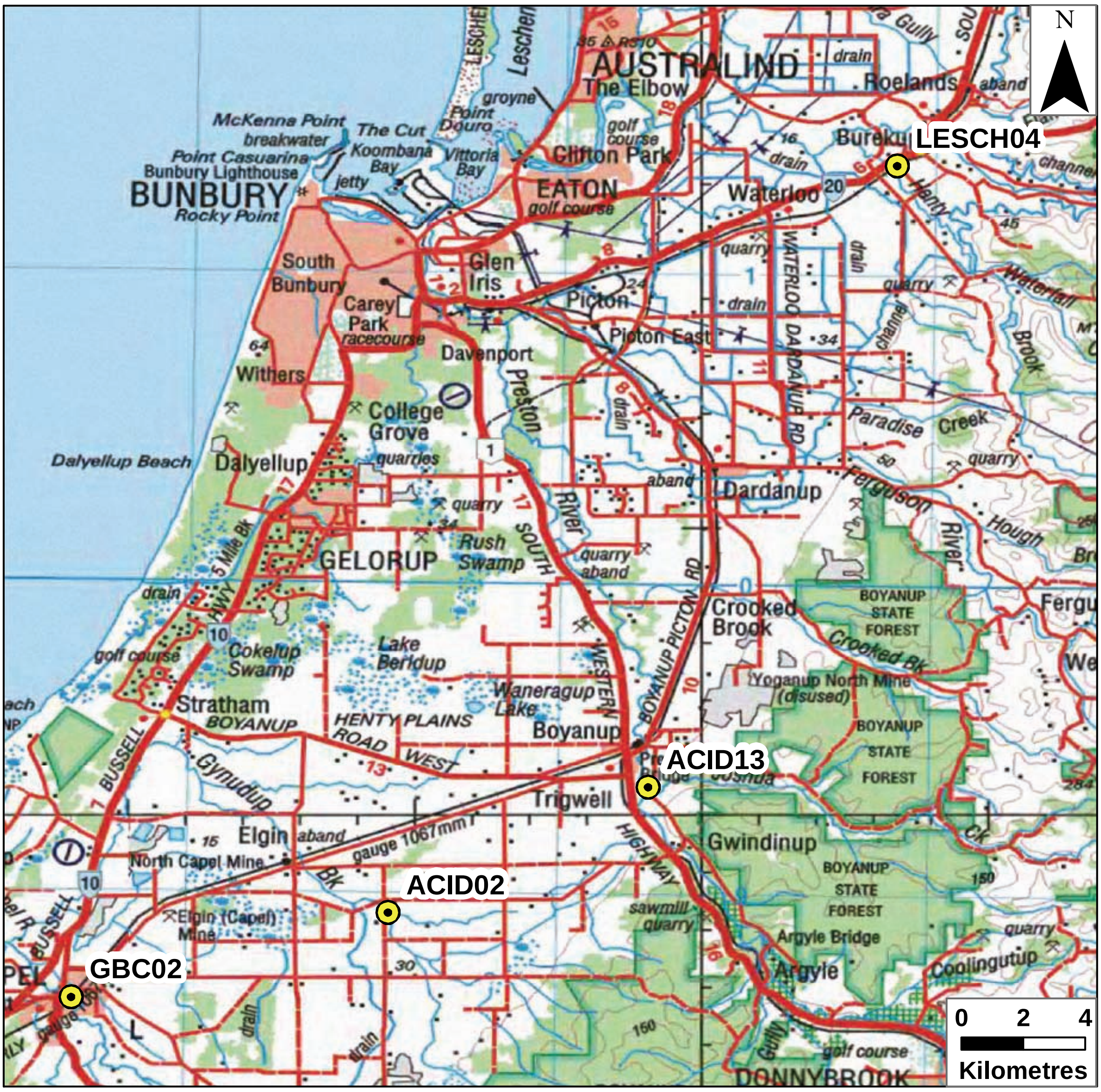

Figure 30 *Location of sites in the Leschenault catchment displaying elevated aluminium concentrations in water samples.*

Figure 31 *Location of site ACID17 along the Collie River, downstream from an abandoned coal mine.*

Figure 32 Location of iso-group 3 sites within the Leschenault region.

9.5 Scott Coastal Plain

Several sites in the Scott Coastal Plain catchment showed elevated Fe and Al. Site 6091758 exceeded the 90th percentile value for Al with extremely high concentrations of 4.8 mg L^{-1} and 5.9 mg L^{-1} for soluble and total Al respectively. Sites 6091222, 6091223 and 6091596 exceeded the 90th percentile boundary value for Fe with concentrations of 3.8–4.2 mg L^{-1} for soluble Fe and 5.3–8.8 mg L^{-1} for total Fe. See Figure 33 for the locations of these sites with high concentrations of Fe or Al. One site showed clear signals of acidic drainage (i.e. iso-group 3), which was 6091755, with 26% extra sulfate (Figure 34).

9.6 South coast region

A number of sites in the south coast catchment displayed elevated Al and Fe. Site WOOD1 (Figure 35) had the most extreme Al concentrations (46 mg L^{-1} and 50 mg L^{-1}) compared with the 90th percentile values of 0.51 and 0.93 mg L^{-1} for soluble and total Al. Site TILP012 (also known as Elleker Grassmere drain) also had extremely elevated Al (11 mg L^{-1} and 12 mg L^{-1} for soluble and total Al). Sites TILP001 and TILP047 also exceeded the 90th percentile value for total Al. Elevated Fe was found at sites INFLOW, LEAY, MANCK, SUN, TILP012, TILP047 and WOOD1. Fe was highest at TILP012, with 19 mg L^{-1} soluble Fe, and 21 mg L^{-1} total Fe. Site locations can be seen in Figure 36 and Figure 37. Total acidity was particularly high for WOOD1 and TILP012 with measurements of 290 mg $CaCO_3$ L^{-1} and 160 mg $CaCO_3$ L^{-1} respectively. WOOD1 and TILP012 were the only two sites with pH <4 (2.98 and 2.84 respectively).

Four sites within the south coast region had a clear acidic drainage signal (iso-group 3) (Figure 38), and three of these are adjacent to estuarine environments. Sites LOWKG, TILP001 and MRD display a similar intensity of signal with 25–45% extra sulfate, while by comparison the extra sulfate signal of MTBARKRD was relatively minor (<1%) at this sampling time.

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Figure 33 *Location of sites on the Scott Coastal Plain with very high concentrations of either aluminium or iron.*

Figure 34 *Location of sites with iso-group 3 on the Scott Coastal Plain.*

Figure 35 *Site WOOD1, drain running along Woodies Road near Lake Powell.*

Figure 36 Location of sites with elevated aluminium and/or iron in water samples within Torbay catchment near Albany.

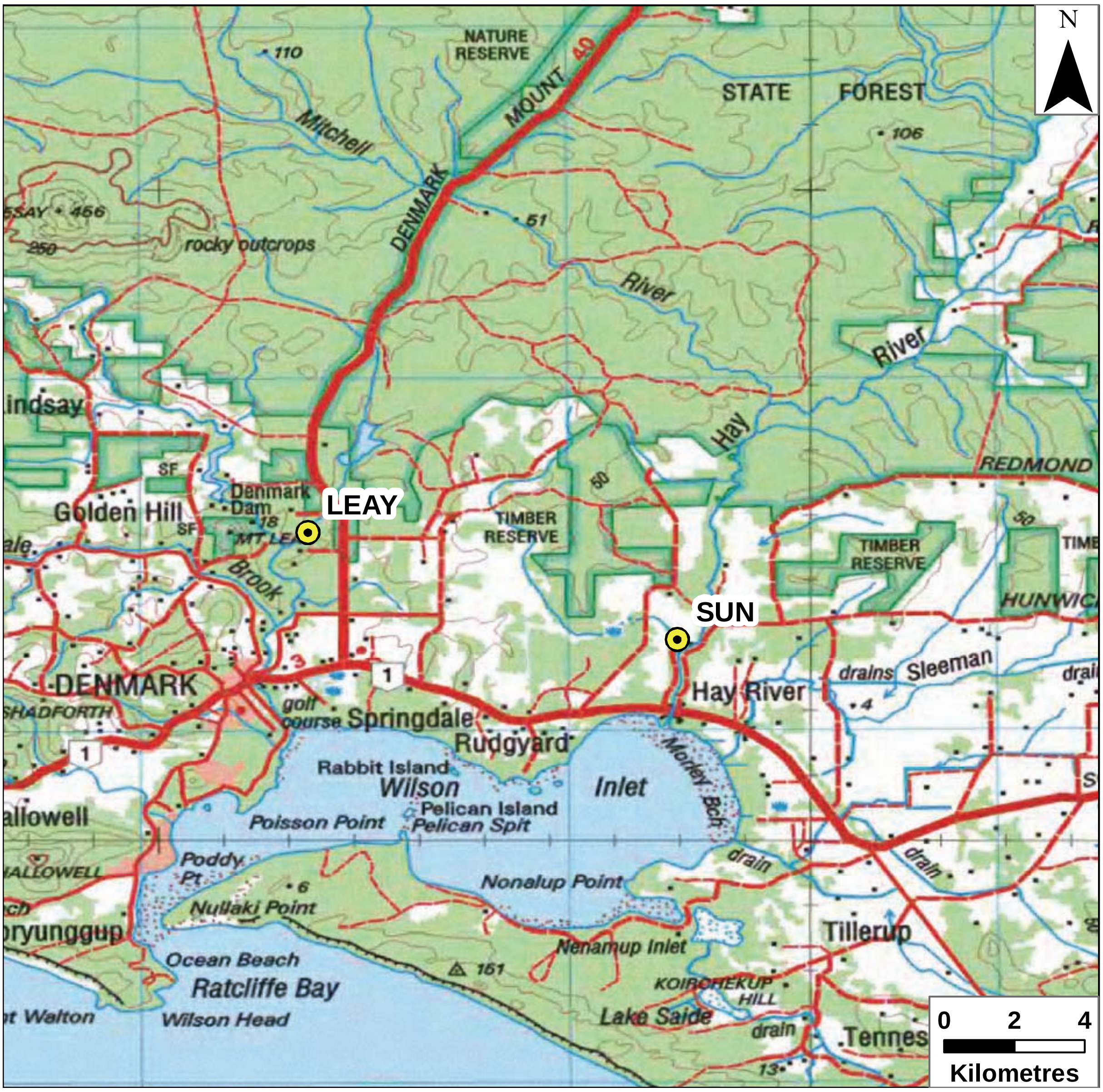

Figure 37 *Location of sites SUN and LEAY near Wilson Inlet with elevated iron concentrations in water samples.*

Figure 38 *Location of sites with iso-group 3 in Albany region, with sites near Oyster and Princess Royal harbours and Wilson Inlet.*

10 General discussion

10.1 Comparison to Australia’s east coast

On Australia’s east coast, deteriorated water quality and impacts on aquatic ecosystems associated with drainage from disturbed ASS have been well documented. Often these events have been rather dramatic. For example, the Richmond River experienced a massive fish kill of thousands of fish and prawns in January 2008, in a blackwater event that saw dissolved oxygen levels of the estuarine water remain below 1 mg L^{-1} for about a week (ASSAY 2008). In another example, heavy rains in 1987 resulted in a 23 km stretch of the Tweed River Estuary acidifying - with possibly more than 1000 tonnes of aluminium being mobilised and the river remaining almost devoid of life for a further 18 months (White et al. 2006). Events at this scale have not been reported in Western Australia. Smaller episodic acidification events have also been reported on the east coast (Sammut et al. 1996; Russell & Helmke 2002).

The range in deteriorated water quality reported to be associated with acidic discharge from disturbed ASS in Australia’s eastern states is shown in Table 11. While this list of locations is not exhaustive, it does provide a contextual comparison for data collected in this study. Typically pH values from ASS-affected drains and streams on the east coast were much lower (pH <4) than observed in the current study, where only two samples out of more than 300 samples were below pH 4. A couple of sites from this Western Australian study had elevated Al concentrations in the range observed for the east coast, (i.e. WOOD1 had soluble iron of 46 mg L^{-1} and TILP012 had soluble iron of 11 mg L^{-1}), however higher extreme values were still reported from the east coast study sites of Firewood Creek, Qld, and Clothiers Creek, NSW. Fe showed a similar trend, with a number of sites displaying elevated Fe within the range reported in the literature (e.g. soluble iron was between 3–19 mg L^{-1} for 14 sites in the current study), but higher extremes were still reported at Firewood Creek, East Trinity and Clothier Creek. Only two sites, PATRDTRIB and 6091223, showed significantly elevated Mn, with values between 2.2–2.6 mg L^{-1} for soluble and total Mn.

In general, very low $Cl^{-}:SO_4^{2-}$ ratios were observed for the study sites in the eastern states. $Cl^{-}:SO_4^{2-}$ ratios lower than 4 were observed in 31 sites in the current study, of which 29 sites were iso-group 5 (suggesting sulfate influence from multiple sources, not only acidic drainage). Interestingly, no iso-group 3 sample had a low sulfate:chloride ratio (<4), suggesting that these clear signals of acidic drainage reflect chronic rather than acute acidic drainage.

10.2 Acidity measurements

Measures of pH quantify the concentration of hydrogen ions (H^{+}) in solution, and only accurately represent the acidity from fully dissociated acids (i.e. strong acids). Acidity in ASS drainage water is not fully described by pH alone. Acidic drainage waters may also contain metal ions that produce H^{+} by hydrolysis and oxidation reactions. The hydrolysis and oxidation of one mole of Fe is estimated to produce two moles of H^{+}; and one mole of Al, three moles of H^{+} (Cook et al. 2000). For south-western Australian waters, few samples had low pH values (only two samples were less than pH 4). Much of the total acidity measured in the water samples is likely to be associated with the hydrolysis of Fe and Al. To estimate the proportion of the contribution to acidity by Fe and Al we assume:

1. that soluble Fe and soluble Al are in the form capable of producing acidity (i.e. Fe^{2+}, Al^{3+}), and
2. that each mole of Fe will produce two moles of H^+ and each mole of Al will produce three moles of H^+.

From analysis of the data in this way we deduce that metal acidity was a significant contributor to the total acidity measured. Soluble Fe and Al concentrations explained 68% and 80% of the total acidity measured for iso-group 3 and iso-group 5 in catchment samples respectively. These assumptions probably over-represent the contribution of metal hydrolysis and oxidation to the measurements of total acidity, however they highlight the importance of metal hydrolysis and oxidation to acidification of waterways further downstream of an ASS disturbance source.

Table 11 *Ranges of water quality values for water reported to be affected by acid sulfate soils within Australia's eastern states*

Location	**pH**	**Iron concentration (mg L^{-1})**	**Aluminium concentration (mg L^{-1})**	**Other metals (mg L^{-1})**	**Other variables**	**Reference**
Magazine Creek, Qld	2.5–4	8–55^{S}	5–50^{S}			(Russell & Helmke 2002)
Firewood Creek, Qld	2.5–4	5–186^{S}	15–75^{S}		Sulfate 1000–2000 mg L^{-1} Nitrate = 0.08 mg L^{-1} Periodic deoxygenation (<20% saturation).	(Russell & Helmke 2002)
Trinity Inlet, Qld	4.5-7.5	0.2–4^{S}	0.05–0.35^{S}			(Russell & Helmke 2002)
Tuckean Swamp, NSW	3–4	0.3–2.4^{S}	1.8–7.3^{S}	Mn: 0.3–0.9^{S} Cu: 0.02–0.2^{S} Zn: 0.03–0.2^{S}	Sulfate: 50–250 mg L^{-1} $Cl^-:SO_4^{2-}$: 0.35–1.2	(Sammut et al. 1996)
Rocky Mouth Creek floodplain, NSW	3.2–3.7	0.7–11.2^{T}	0.8–1.5^{T}	Mn: 0.4-1.0^{T} Zn: 0.02–0.08^{T}	Total acidity: 41–97 $Cl^-:SO_4^{2-}$:0.36–0.7	(Lin et al. 2004)
East Trinity, Qld	<4	3.1–120^{S}	0.51–11^{S}	Zn: 0.19–0.3^{S}		(Cook et al. 2000)
Pimpama, Qld	~1	0.07–33^{S}	2.5–20^{S}	Zn: 0.04–0.22^{S}		(Cook et al. 2000)
Tweed River, NSW	3.2–5	3–8.6^{S}	1.2–6.2^{S}		Sulfate: 155 mg L^{-1} $Cl^-:SO_4^{2-}$: 0.4	(Willett et al. 1993)

Richmond River, NSW	3.5–7.2	0.1–1.3^{S} (0.4–4.4^{T})	1.6–9.7^{S} (0.3–9.2^{T})		$Cl^{-}:SO_4^{2-}$: 0.4 –7.9	(Roach 1997)
McLeods Creek, NSW	3.2–7.9	0–6.7^{T}	0–22^{T}	Mn: 0.05–2.9^{T} Zn: 0–0.4^{T}	Sulfate: 864 mg L^{-1} $Cl^{-}:SO_4^{2-}$: 3.00	(Green et al. 2006)
Clothiers Creek, NSW	2.6–3.4	13.9–123^{T}	48.6–254^{T}	Mn: 1.4–8.3^{T} Zn: 0.52–2.0^{T}	Sulfate: 1900 mg L^{-1} $Cl^{-}:SO_4^{2-}$: 0.02	(Green et al. 2006)

^{S} *soluble metals determined*
^{T} *total metals determined*

10.3 Aluminium and iron toxicity

Aluminium was high at most sites, with almost all sites in the south coast and Leschenault catchments exceeding the ANZECC & ARMCANZ (2000) trigger value for 95% freshwater species protection. Al is known to have deleterious effects on both plants and animals. Adverse biological effects of short-term pulses of Al and acidity have been reported for Atlantic salmon (Kroglund et al. 2008). Al is known to limit crop production by the inhibition of cell elongation and to some extent cell division. Some plants resist these effects by excreting carboxylates (e.g. malate or citrate) through their roots, which results in detoxification of Al by the formation of organic complexes (Jones 1998). Al may also be complexed with organic compounds, which reduces toxicity within humic-rich streams or wetlands. The toxicity of Al is expected to increase at extreme pH levels (<5.5 or >9) and high temperatures, and to reduce if Al forms complexes with fluoride, citrate or humic substances. Toxicity is also reduced in the presence of silicon and with high water hardness (ANZECC & ARMCANZ 2000). Al is a highly abundant element within deeply weathered soils throughout south-western Australia (Division of Soils CSIRO 1983). As such, Al may be naturally mobile within the environment, however anthropogenic activities and ASS disturbance may also contribute considerable quantities of Al. If Western Australian native flora and fauna have evolved in Al-rich environments, it is likely they will be tolerant to high concentrations of Al (i.e. above current guideline values). Without undertaking ecotoxicological testing specific to Western Australian native species, we cannot comprehend how extensively the state's ecosystems are threatened by high Al concentrations.

There is no ANZECC & ARMCANZ guideline for iron. Instead, comparisons of Fe concentrations within this study have been made with new guidelines proposed in British Columbia, Canada (Phippen et al. 2008) of 1 mg L^{-1} for total Fe, and 0.35 mg L^{-1} for soluble Fe. One of the main arguments for including a separate guideline for total Fe was to consider both the direct toxic effects of Fe (usually in its dissolved ferrous form), and the indirect effects on habitat and species displacement that generally relate to total Fe concentrations (often as Fe hydroxide precipitates). Factors such as hardness and humic acid complexation of Fe also influence toxicity. Again, without undertaking ecotoxicological testing of Western Australian native species, the threat posed by high Fe concentrations will remain uncertain.

10.4 Chronic acidic drainage influence

Most sites in south-western Australia exhibiting 'acidification' from ASS appear as a chronic influence on waterways rather than acute expressions. Very low pH values were rarely observed in the dataset. Although a few sites were identified where strong signals of ASS exist (e.g. WOOD1, TILP012), in most cases the volume of water associated with these drains is small relative to the volume of the receiving waterbodies.

The impacts of acidic drainage are most likely to express as chronic long-term effects on aquatic ecosystems. A number of sub-lethal effects on aquatic organisms may occur as a response to acidic drainage. For example, inputs of iron were shown to increase the growth rate of the toxic cyanobacteria *Lynbya majuscula* (Ahern et al. 2006). Also, the decrease of alkalinity by acidic discharges may inhibit growth of crustaceans within estuaries (Sammut et al. 1996). Acidification also appears to favour acid tolerant species, such as mosquitoes (McCullough & Horwitz In Press), larval biting midges (family Ceratopogonidae), water boatmen (family Corixidae) and water fleas (family Macrothricidae) (Sommer & Horwitz 2009). These effects may ultimately modify the community structure of species within the aquatic ecosystem, with subsequent effects on the trophic web.

Determining a sample's iso-group appears to provide a useful categorisation in terms of the sulfur cycle, as well as a useful screening tool to decide whether a site is likely to be receiving acidic drainage. The other advantage of this method is that the 'fingerprint' of acidic drainage still remains, even if the actual acidity has been neutralised. However, further work is required to fully understand the mixed signals, such as for iso-group 5, where multiple sources of external (non-seawater) sulfur are possible. Disentangling multiple sulfur signals seems most important for the Swan-Canning catchment, where more than 70% of sites were grouped into iso-group 5.

10.5 Sulfate-reduction in waterways

The process of sulfate-reduction efficiently removes metals from the water column, binding them into the sediment. However when this process is accelerated, the reduced sulfur is only bound in an easily oxidisable form (metastable monosulfides). Acid volatile sulfur abundance is higher in drains with gentle flow that are affected by ASS leachate (Bush et al. 2004). Monosulfide formation in drains and streams can cause major environmental problems as heavy rainfall mobilises the monosulfide, deoxygenating the water and resulting in blackwater events.

On the basis of the iso-group determination, sulfate-reduction was the dominant process for two-thirds of all samples (i.e. iso-groups 2, 4a and 4b). Of these samples, approximately two-thirds of estuarine samples and half the catchment samples were associated with extra (other than seawater) sources of sulfur (i.e. they were iso-group 4a and 4b). It is likely that the supply of extra sulfate to these waterways results in enhanced monosulfide production, however further work is required to confirm this. In estuaries, with their large natural supply of sulfate from seawater, excess sulfate is unlikely to promote further sulfate-reduction. Instead, high organic matter loading (associated with eutrophication) may enhance monosulfide production. It seems possible that within an estuary such as the Peel Harvey, the effects of eutrophication and disturbance of ASS act synergistically to produce the extremely reducing conditions observed throughout much of this region.

11 Conclusion and recommendations

Disturbance of ASS is likely to be having a chronic (rather than an acute) effect on south-western Australian waterways. Sites likely to be influenced by acidic drainage were found in all investigated regions. Water at catchment sites was more likely to exhibit acidity than the estuarine sites (perhaps due to sulfate dilution). It seems that acidic drainage in south-western Australia more often presents as a trickle, whereas the examples from the eastern states point to large quantities of acid being produced behind floodgates. It is possible that this difference is related to the lower rainfall experienced in Western Australia. Additionally, the sandy nature of ASS in south-western Australia (Degens & Wallace-Bell 2009) suggests that groundwater resources may be more susceptible to acidification than in other areas with clay-dominated soils. In Western Australia the impacts of acidic drainage are most likely to express as chronic long-term effects on ecosystems – potentially affecting aquatic community structure, aquatic trophic web interactions and groundwater quality.

The categorisation of samples into iso-groups, by using sulfur isotopic analysis combined with determinations of sulfate and chloride concentrations, appears to provide a useful screening tool for assessing the influence of acidic drainage. Median concentrations of many metals and phosphorus were higher in ASS-affected samples (iso-group 3) than in other samples not identified as influenced by ASS. This methodology is more sensitive for identifying acidic drainage than other indicators previously used in ASS management. Forty-one out of the 313 sites sampled were identified as hotspot sites by either sulfur isotopic analysis or by unusually high concentrations of Al and Fe, relative to the rest of the baseline dataset. These sites were found in all the geographic regions investigated in this study.

Sulfate-reduction was probably enhanced by the supply of extra sulfate (relative to seawater) in 42% of estuarine sites and 33% of catchment sites. It is likely the supply of extra sulfate to these waterways, combined with decaying organic matter (perhaps as a result of eutrophication), results in enhanced MBO production. While sulfate-reduction has a role to play in improving water quality (through the temporary binding of metals), the environmental risk is high for locations where the monosulfides are susceptible to re-suspension from heavy rainfall and floodwaters. Blackwater events result when sediment containing monosulfides are re-suspended in the water column, causing it to deoxygenate rapidly. Blackwater events on Australia's east coast have been catastrophic, with hundreds to thousands of fish and prawns reported killed (Sammut et al. 1995; Russell & Helmke 2002; ASSAY 2008).

In this study, water samples were frequently reported above ANZECC & ARMCANZ (2000) metal guideline trigger values. It is probable that various sources of metals contributed to the metals observed in waterways and estuaries in south-western Australia, including urban, agricultural and industrial influences as well as disturbed ASS sources. Al was highly prevalent, with approximately 70% of catchment samples exceeding the ANZECC & ARMCANZ (2000) trigger values. It is not known whether Al is naturally high in south-western Australia or whether this finding represents a real environmental issue.

The following recommendations are provided as a result of this work:

Recommendation 1: Further investigation of hotspot sites identified in this study, including development of management and/or remediation plans for these sites.

Recommendation 2: Additional work to refine the sulfur stable isotope as an indicator of ASS influence in waterways.

Recommendation 3: Further work at sites which have been identified as probably having enhanced sulfate-reduction to assess the risk associated with blackwater events at these locations.

Recommendation 4: Ecotoxicology specifically targeted at Western Australian native species is required to understand whether aluminium concentrations in south-western Australian waterways are presenting a widespread ecological problem.

Appendices

Appendix A — Full site details

A1. *Site name and location for estuarine sites with sampling dates for both sampling occasions, nominally called ‘summer’ and ‘winter’.*

Site reference	Easting	Northing	Sampling date (summer)	Sampling date (winter)
ARM (WRC1)	387504	6458161	19/02/2007	18/06/2007
BLA (WRC1)	385081	6456807	19/02/2007	18/06/2007
KIN (WRC1)	401768	6468783	19/02/2007	18/06/2007
MAY (WRC1)	396801	6465716	19/02/2007	18/06/2007
NAR (WRC1)	391215	6463014	19/02/2007	18/06/2007
NIL (WRC1)	394660	6464027	19/02/2007	18/06/2007
RON (WRC1)	399802	6467786	19/02/2007	18/06/2007
STJ (WRC1)	397308	6464439	19/02/2007	18/06/2007
SUC (WRC1)	401585	6470349	19/02/2007	18/06/2007
KEN (WRC1)	398104	6456676	20/02/2007	19/06/2007
BAC (WRC1)	396637	6456525	20/02/2007	19/06/2007
CAS (WRC1)	397591	6456565	20/02/2007	19/06/2007
ELL (WRC1)	401006	6455131	20/02/2007	19/06/2007
NIC (WRC1)	400108	6455732	20/02/2007	19/06/2007
RIV (WRC1)	396239	6455988	20/02/2007	19/06/2007
SAL (WRC1)	393509	6455593	20/02/2007	19/06/2007
PHE58 (WRC1)	374388	6388576	14/03/2007	5/07/2007
PHRM9 (WRC1)	390581	6394024	14/03/2007	5/07/2007
PHRM4 (WRC1)	390106	6393899	14/03/2007	5/07/2007
PHRM2 (WRC1)	386385	6394324	14/03/2007	5/07/2007
PHE04 (WRC1)	383128	6395061	14/03/2007	5/07/2007
PHRS7 (WRC1)	388165	6406598		3/07/2007
PHE01 (WRC1)	375970	6383055	14/03/2007	5/07/2007
PHE07 (WRC1)	379243	6393234	14/03/2007	5/07/2007
PHRS4 (WRC1)	384316	6398669		3/07/2007
PHRS6 (WRC1)	385996	6402376		3/07/2007
PHE31 (WRC1)	377709	6377884	14/03/2007	5/07/2007
PHE02 (WRC1)	375330	6391875	14/03/2007	5/07/2007
MPH061 (WRC1)	375739	6395307	6/03/2007	13/09/2007
MPH071 (WRC1)	379199	6399997	6/03/2007	13/09/2007
MPH083 (WRC1)	379748	6398065	6/03/2007	13/09/2007
MPH006 (WRC1)	373073	6388550	7/03/2007	12/09/2007

Site reference	Easting	Northing	Sampling date (summer)	Sampling date (winter)
MPH019 (WRC1)	377701	6375206	7/03/2007	12/09/2007
MPH025 (WRC1)	375151	6389430	7/03/2007	13/09/2007
MPH015 (WRC1)	378847	6379013	8/03/2007	12/09/2007
MPH044 (WRC1)	383112	6396277	8/03/2007	14/09/2007
MPH091 (WRC1)	384200	6396033	8/03/2007	13/09/2007
MPH040 (WRC1)	384543	6393206	9/03/2007	11/09/2007
MPH155 (WRC1)	384450	6394812	9/03/2007	11/09/2007
MPH158 (WRC1)	385067	6394326	9/03/2007	11/09/2007
MPH001 (WRC1)	385992	6393212		8/06/2007
MPH002 (WRC1)	385517	6392972		8/06/2007
MPH003 (WRC1)	385265	6392982		8/06/2007
6121130 (AWRC)	390301	6319885	15/03/2007	11/07/2007
6121203 (AWRC)	387979	6318601	15/03/2007	11/07/2007
6121162 (AWRC)	381937	6317537	15/03/2007	11/07/2007
6121161 (AWRC)	381473	6316299	15/03/2007	11/07/2007
6111043 (AWRC)	376407	6311508	15/03/2007	11/07/2007
6121173 (AWRC)	378719	6326057	15/03/2007	11/07/2007
6121166 (AWRC)	380821	6315693	15/03/2007	11/07/2007
6121168 (AWRC)	384914	6315194	15/03/2007	11/07/2007
6121206 (AWRC)	379734	6322355	15/03/2007	11/07/2007
6121207 (AWRC)	376978	6313870	15/03/2007	11/07/2007
6101072 (AWRC)	355173	6281116	8/03/2007	26/07/2007
6101067 (AWRC)	353278	6279048	8/03/2007	26/07/2007
6101065 (AWRC)	351800	6277800	8/03/2007	26/07/2007
610019 (AWRC)	352702	6278792	8/03/2007	26/07/2007
6101064 (AWRC)	346823	6275036	8/03/2007	26/07/2007
6101063 (AWRC)	347070	6274433	8/03/2007	26/07/2007
610020 (AWRC)	353845	6279448	8/03/2007	26/07/2007
BRF02 (WRC1)	333481	6218227		15/08/2007
HIF01 (WRC1)	331650	6200534		15/08/2007
HIF02 (WRC1)	331060	6202031		15/08/2007
HIF03 (WRC1)	331083	6203506		15/08/2007
HIF04 (WRC1)	329948	6203551		15/08/2007
HIF05 (WRC1)	330810	6205366		15/08/2007
HIF06 (WRC1)	332512	6204368		15/08/2007
MIF01 (WRC1)	334394	6205820		15/08/2007
MIF02 (WRC1)	334417	6206863		15/08/2007
MIF03 (WRC1)	335631	6207254		15/08/2007
SRF01 (WRC1)	336527	6207379		15/08/2007

BRF01 (WRC1)	335239	6208009		15/08/2007
WAL003 (WRC1)	475534	6128782	24/01/2007	10/07/2007

Site reference	Easting	Northing	Sampling date (summer)	Sampling date (winter)
WAL001 (WRC1)	474613	6128916	24/01/2007	10/07/2007
WAL006 (WRC1)	476299	6126594	24/01/2007	10/07/2007
WI6 (WRC1)	535051	6127398	20/02/2007	24/05/2007
WI30 (WRC1)	530840	6126087	20/02/2007	24/05/2007
WI12 (WRC1)	539902	6127235	20/02/2007	24/05/2007
WAL004 (WRC1)	475299	6126102	24/01/2007	10/07/2007
IRW003 (WRC1)	496447	6127669	24/01/2007	10/07/2007
BRO002 (WRC1)	446374	6138504	23/01/2007	9/07/2007
IRW001 (WRC1)	498180	6128240	24/01/2007	10/07/2007
WAL005 (WRC1)	473701	6125892	24/01/2007	10/07/2007
BRO004 (WRC1)	446568	6134564	23/01/2007	9/07/2007
BRO001 (WRC1)	449537	6134997	23/01/2007	9/07/2007
AOH 5 (WRC1)	587221	6131995	19/02/2007	15/05/2007
AOH 4 (WRC1)	587133	6130708	19/02/2007	15/05/2007
AOH 2 (WRC1)	588118	6128413	19/02/2007	15/05/2007
APRH 3 (WRC1)	581412	6120955	19/02/2007	15/05/2007
APRH 4 (WRC1)	582257	6119330	19/02/2007	15/05/2007
APRH 2 (WRC1)	578731	6122409	19/02/2007	15/05/2007

A2. Site name, region and location of catchment sites with sampling dates of snapshot.

Site reference	Catchment	Easting	Northing	Sampling date
BBDSMP	Swan Canning	400825	6476349	3/10/2007
BCBW	Swan Canning	398979	6453910	3/10/2007
BCRUS	Swan Canning	395344	6455397	3/10/2007
BICKBK 05	Swan Canning	404089	6454565	4/10/2007
BICKBKEDS	Swan Canning	405926	6454778	4/10/2007
BLACMDS	Swan Canning	406298	6472567	3/10/2007
BNCADEN	Swan Canning	399913	6468163	3/10/2007
BSMDO	Swan Canning	398327	6468780	4/10/2007
BWD9	Swan Canning	392250	6453870	4/10/2007
BWMDBI	Swan Canning	397529	6455220	5/10/2007
BWMDBPI	Swan Canning	397917	6468415	3/10/2007
BWMDBR	Swan Canning	397917	6468415	5/10/2007
CAMDOUT	Swan Canning	396734	6466050	5/10/2007

Site reference	Catchment	Easting	Northing	Sampling date
EBBHDS	Swan Canning	404034	6505642	3/10/2007
EBMBUS	Swan Canning	406657	6483773	3/10/2007
HRDSMW	Swan Canning	419366	6464921	4/10/2007
HRES	Swan Canning	403798	6470091	4/10/2007
JBDG	Swan Canning	409267	6474881	3/10/2007
JBSDS	Swan Canning	424179	6472664	4/10/2007
LACDD	Swan Canning	400532	6455895	4/10/2007
LIEP6	Swan Canning	399380	6456586	4/10/2007
MSCWW	Swan Canning	397920	6457129	4/10/2007
PAS01	Swan Canning	399730	6466720	4/10/2007
SBMD4	Swan Canning	398321	6463354	4/10/2007
SCCIS10	Swan Canning	406665	6437717	3/10/2007
SLMBAIGIN	Swan Canning	397140	6466698	5/10/2007
SRBDS	Swan Canning	403042	6448942	3/10/2007
WBHW	Swan Canning	405079	6459867	4/10/2007
WCEBDS	Swan Canning	407821	6472730	3/10/2007
YBRPUS	Swan Canning	402151	6456165	4/10/2007
613014 (AWRC)	Peel Harvey	392689	6359878	23/10/2007
613027 (AWRC)	Peel Harvey	385062	6373803	23/10/2007
613029 (AWRC)	Peel Harvey	385527	6386327	24/10/2007
613031 (AWRC)	Peel Harvey	382559	6369968	23/10/2007
613052 (AWRC)	Peel Harvey	381689	6368298	23/10/2007
613053 (AWRC)	Peel Harvey	384739	6356848	23/10/2007
614030 (AWRC)	Peel Harvey	392770	6421040	24/10/2007
614063 (AWRC)	Peel Harvey	390024	6400950	23/10/2007
614065 (AWRC)	Peel Harvey	394839	6388849	24/10/2007
614094 (AWRC)	Peel Harvey	393880	6412350	24/10/2007
614120 (AWRC)	Peel Harvey	389034	6405484	23/10/2007
614121 (AWRC)	Peel Harvey	390409	6417490	24/10/2007
AMRL3 (WRC1)	Peel Harvey	389389	6409823	24/10/2007
HR01012 (WRC1)	Peel Harvey	389367	6366352	23/10/2007
HR01014 (WRC1)	Peel Harvey	391400	6369611	24/10/2007
HR02005 (WRC1)	Peel Harvey	387802	6357545	24/10/2007
MPH003 (WRC1)	Peel Harvey	385265	6392982	25/10/2007
MR01002 (WRC1)	Peel Harvey	390365	6391448	25/10/2007
MR01010 (WRC1)	Peel Harvey	389410	6393338	25/10/2007
MR01012 (WRC1)	Peel Harvey	389473	6395185	25/10/2007
MR03017 (WRC1)	Peel Harvey	386600	6390933	25/10/2007
MR04014 (WRC1)	Peel Harvey	391675	6381880	25/10/2007

Site reference	Catchment	Easting	Northing	Sampling date
MR04019 (WRC1)	Peel Harvey	385845	6387694	24/10/2007
MR05004 (WRC1)	Peel Harvey	379099	6382535	24/10/2007
MR05005 (WRC1)	Peel Harvey	382615	6384645	25/10/2007
MR05010 (WRC1)	Peel Harvey	379573	6379472	24/10/2007
NYUND (WRC1)	Peel Harvey	386532	6395596	25/10/2007
PATRDTRIB (WRC1)	Peel Harvey	395230	6393976	23/10/2007
PHM3 (WRC1)	Peel Harvey	395086	6394140	25/10/2007
PHS7 (WRC1)	Peel Harvey	389833	6405505	23/10/2007
SR04014 (WRC1)	Peel Harvey	392869	6402343	24/10/2007
ACID01	Leschenault	385534	6276808	26/09/2007
ACID02	Leschenault	375449	6289328	25/09/2007
ACID03	Leschenault	376559	6287298	25/09/2007
ACID04	Leschenault	368268	6292218	26/09/2007
ACID05	Leschenault	384039	6299898	28/09/2007
ACID06	Leschenault	391615	6283971	26/09/2007
ACID07	Leschenault	416039	6307248	27/09/2007
ACID08	Leschenault	411589	6313848	27/09/2007
ACID09	Leschenault	383789	6307548	25/09/2007
ACID10	Leschenault	366938	6287998	25/09/2007
ACID11	Leschenault	389393	6325756	26/09/2007
ACID12	Leschenault	403793	6311435	27/09/2007
ACID13	Leschenault	382420	6293450	25/09/2007
ACID14	Leschenault	399618	6278171	26/09/2007
ACID15	Leschenault	412898	6289225	27/09/2007
ACID16	Leschenault	380309	6304016	25/09/2007
ACID17	Leschenault	422143	6308473	27/09/2007
BRUN6	Leschenault	383436	6319879	26/09/2007
GBC01	Leschenault	367393	6290283	26/09/2007
GBC02	Leschenault	366938	6286498	25/09/2007
GBC03	Leschenault	379829	6276020	26/09/2007
LESCH01	Leschenault	383488	6314995	26/09/2007
LESCH02	Leschenault	382411	6310960	26/09/2007
LESCH03	Leschenault	386256	6304512	26/09/2007
LESCH04	Leschenault	388922	6313550	26/09/2007
LESCH05	Leschenault	391345	6334903	26/09/2007
LESCH06	Leschenault	371940	6302173	27/09/2007
LESCH07	Leschenault	373180	6309674	28/09/2007
608003	Scott Coastal Plain	387489	6200598	20/11/2007
608147	Scott Coastal Plain	390819	6191198	20/11/2007

Site reference	Catchment	Easting	Northing	Sampling date
608171	Scott Coastal Plain	389419	6187018	20/11/2007
609022	Scott Coastal Plain	333976	6226544	21/11/2007
609041	Scott Coastal Plain	363450	6225248	20/11/2007
609060	Scott Coastal Plain	339085	6210670	21/11/2007
6081009	Scott Coastal Plain	406189	6208648	20/11/2007
6081010	Scott Coastal Plain	381055	6205878	20/11/2007
6081026	Scott Coastal Plain	385598	6193126	20/11/2007
6081040	Scott Coastal Plain	379758	6190432	20/11/2007
6081053	Scott Coastal Plain	397051	6194911	20/11/2007
6091008	Scott Coastal Plain	367889	6225989	20/11/2007
6091044	Scott Coastal Plain	328588	6204698	22/11/2007
6091222	Scott Coastal Plain	362853	6204232	21/11/2007
6091223	Scott Coastal Plain	359594	6205436	21/11/2007
6091224	Scott Coastal Plain	347154	6209255	21/11/2007
6091302	Scott Coastal Plain	330774	6212188	22/11/2007
6091305	Scott Coastal Plain	338370	6213872	21/11/2007
6091408	Scott Coastal Plain	354607	6229702	21/11/2007
6091596	Scott Coastal Plain	342220	6223054	21/11/2007
6091735	Scott Coastal Plain	382943	6189560	20/11/2007
6091752	Scott Coastal Plain	340749	6207628	21/11/2007
6091753	Scott Coastal Plain	332824	6228166	21/11/2007
6091754	Scott Coastal Plain	329210	6227737	21/11/2007
6091755	Scott Coastal Plain	352910	6204280	21/11/2007
6091756	Scott Coastal Plain	377028	6196322	22/11/2007
6091757	Scott Coastal Plain	357832	6209811	22/11/2007
6091758	Scott Coastal Plain	331712	6207481	22/11/2007
CHE	South coast	592084	6138740	17/10/2007
DML	South coast	528789	6141697	18/10/2007
FREEBOROUGH	South coast	546653	6125263	16/10/2007
HAY	South coast	543694	6136740	16/10/2007
HENNING	South coast	555135	6132230	16/10/2007
INFLOW	South coast	555270	6128945	16/10/2007
KR	South coast	579700	6134127	17/10/2007
LEAY	South coast	533929	6135647	18/10/2007
LIT	South coast	530128	6127742	18/10/2007
LOWKG	South coast	586272	6131297	17/10/2007
MANCK	South coast	563262	6125233	16/10/2007
MIT	South coast	535925	6146009	18/10/2007
MRD	South coast	564443	6127486	16/10/2007

MTBARKRD	South coast	535289	6141127	18/10/2007
RD	South coast	577005	6123705	17/10/2007
RZ7	South coast	550369	6125548	16/10/2007
SCO	South coast	531765	6134382	18/10/2007
SLE	South coast	545938	6131464	16/10/2007
SUN	South coast	542550	6132572	16/10/2007
Site reference	**Catchment**	**Easting**	**Northing**	**Sampling date**
TILP001	South coast	558735	6123788	16/10/2007
TILP006	South coast	570845	6125482	17/10/2007
TILP008	South coast	574290	6127447	17/10/2007
TILP012	South coast	567877	6123677	17/10/2007
TILP013	South coast	565565	6126997	17/10/2007
TILP047	South coast	561215	6132397	16/10/2007
WCWF	South coast	581660	6133070	17/10/2007
WOOD1	South coast	566613	6124409	17/10/2007
YAK1	South coast	566613	6124409	17/10/2007
YU	South coast	580650	6125797	17/10/2007

Appendix B — Sample collection and chemical analysis details

B1. Details of the sample collection and chemical analysis methods for water samples collected from estuarine and catchment sites.

Parameter	Lab	Method code	Container details		Collection details
			Volume	*Bottle type*	
Total nitrogen (TN)	National Measurement Institute (NMI)	WL 239	250 mL	Plastic	Unfiltered water sample. Sample bottle filled directly from grab sample to shoulder.
Total phosphorus (TP)	National Measurement Institute (NMI)	WL 239			
Filtered reactive phosphorus (FRP)	National Measurement Institute (NMI)	WL 239	250 mL	Plastic	Filtered water sample (0.45 µM nitrocellulose membrane). Rinse bottle three times with filtered water, and fill sample bottle to shoulder.
Nitrate and nitrite (NO_x-N)	National Measurement Institute (NMI)	WL 239			
Ammonium (NH_4-N)	National Measurement Institute (NMI)	WL 239			
Dissolved organic nitrogen (DON)	National Measurement Institute (NMI)	WL 239			
Sulfate	National Measurement Institute (NMI)	WL 119			
Chloride	National Measurement Institute (NMI)	WL 119			
Colour	National Measurement Institute (NMI)				
Total acidity	National Measurement Institute (NMI)	WL 197	1 L	Plastic	Unfiltered water sample. Sample bottle completely filled with unfiltered water directly from grab sample.
Total alkalinity	National Measurement Institute (NMI)	WL 122			
Dissolved organic carbon (DOC)	National Measurement Institute (NMI)	WL 240	100 mL	Dark amber glass	Filtered water sample (0.45 µM PP syringe filter disk). Sample bottle filled to shoulder.
Filtered metal suite (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Na, Mn, Mo, Ni, Pb, Se, V, Zn)	National Measurement Institute (NMI)	WL 125 WL 272 WL 41	125 mL	Plastic Nalgen	Filtered water sample (0.45 µM nitrocellulose membrane) Pre-acidified sample bottle filled to shoulder.

Total metal suite (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Pb, Ni, Se, V, Zn)	National Measurement Institute (NMI)	WL 125 WL 272 WL 41	125 mL	Plastic Nalgen	Pre-acidified sample bottle filled to shoulder with unfiltered sample.
Hardness	National Measurement Institute (NMI)	Calculated from Mg + Ca in metal suite			
Sulfur stable isotope (in precipitated $BaSO_4$)	Monash University (Geosciences)	BaCl added to preacidified water to precipitate $BaSO_4$, which is then combusted to SO_2 gas and measured on IRMS.	250 mL HDPE	Plastic	Field filtered sample with a 0.45 μM nitrocellulose membrane. Filtered water added to pre-acidified (nitric acid) sample bottles and filled to shoulder. Final pH ~ 2.

WL 239 autoanalyser method based on APHA (several methods) – APHA (1998) Standard methods for the examination of water and wastewater 20th Edition
WL 119 ion chromatography
WL 197 titration (APHA 2310B)
WL 122 titration (APHA 2320B)
WL 240 (APHA 5310)
WL 125, 272, 125 AAS and ICPMS methods
IRMS = isotope ratio mass spectroscopy

Appendix C — Quality assurance and quality control

C1. Highest recorded measurement for field blank (procedural blank) samples collected within each sampling catchment.

Analyte (units)	Swan Canning	Peel Harvey	Leschenault	Scott	South coast
Acidity (mg L^{-1} $CaCO_3$)	4	4	<1	3	2
Al (sol) (mg L^{-1})	<0.005	<0.005	<0.005	0.009	<0.005
As (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Ca (sol) (mg L^{-1})	0.024	0.016	0.014	0.014	0.016
Cd (sol) (mg L^{-1})	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cl (sol) (mg L^{-1})	<10	<10	<10	<10	<10
Co (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Colour (TCU)	<1	11	1	<1	<1
Cr (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Cu (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Fe (sol) (mg L^{-1})	<0.005	<0.005	<0.005	<0.005	<0.005
Hg (sol) (mg L^{-1})	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Mg (sol) (mg L^{-1})	0.025	0.009	0.008	<0.005	<0.005
Mn (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Mo (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
DON (mg L^{-1})	0.054	0.031	0.07	<0.025	<0.025
NOx (mg L^{-1})	0.019	<0.01	0.028	<0.01	<0.01
TN (mg L^{-1})	0.078	0.049	0.11	<0.025	<0.025
NH_3 (mg L^{-1})	<0.01	0.014	<0.01	<0.01	0.011
Na (sol) (mg L^{-1})	<0.05	<0.05	<0.05	0.088	<0.05
Ni (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001

TP (mg L^{-1})	<0.005	<0.005	0.006	<0.005	<0.005
FRP (mg L^{-1})	<0.005	<0.005	0.005	<0.005	<0.005
Pb (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
SO_4^{2-} (mg L^{-1})	<5	<5	<5	<5	<5
Se (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
V (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Zn (sol) (mg L^{-1})	0.002	0.004	0.001	0.023	0.002

C2. *Greatest difference between replicate measurements for field replicate samples within each catchment.*

Analyte (units)	Swan Canning	Peel Harvey	Leschenault	Scott	South coast
Acidity (mg L^{-1} $CaCO_3$)	1	1	-	-	-
Al (sol) (mg L^{-1})	0.006	0.07	0.01	0.003	0.04
Al (tot) (mg L^{-1})	0.075	0.07	0.12	0.01	0.03
Alkalinity (mg L^{-1} $CaCO_3$)	5	23	1	-	-
As (sol) (mg L^{-1})	-	-	-	-	-
As (tot) (mg L^{-1})	-	-	-	-	-
DOC (mg L^{-1})	1	11	1	1	2
Ca (sol) (mg L^{-1})	1	2	-	-	0.3
Ca (tot) (mg L^{-1})	1	2	-	-	0.3
Cd (sol) (mg L^{-1})	-	-	-	-	-
Cd (tot) (mg L^{-1})	-	-	-	-	-
Cl (sol) (mg L^{-1})	-	50	-	10	-
Co (sol) (mg L^{-1})	-	-	-	-	-
Co (tot) (mg L^{-1})	-	-	-	-	-

Colour (TCU)	10	3	-	2	20
Cr (sol) (mg L^{-1})	-	-	-	-	-
Cr (tot) (mg L^{-1})	-	-	-	0.001	-
Cu (sol) (mg L^{-1})	-	-	-	-	-
Cu (tot) (mg L^{-1})	-	-	-	-	-
δ^{34}S (‰)	1.9	0.6	3.1	3.1	1.3
Fe (sol) (mg L^{-1})	0.02	0.05	-	0.03	0.1
Fe (tot) (mg L^{-1})	0.2	0.06	0.2	0.01	0.1
Hg (sol) (mg L^{-1})	-	-	-	-	-
Hg (tot) (mg L^{-1})	-	-	-	-	-
Mg (sol) (mg L^{-1})	1	0.8	0.1	-	0.4
Mg (tot) (mg L^{-1})	0.1	3	0.1	-	0.1
Mn (sol) (mg L^{-1})	0.004	0.003	0.001	0.003	0.001
Mn (tot) (mg L^{-1})	0.002	-	-	0.001	0.013
Mo (sol) (mg L^{-1})	-	-	-	-	-
Mo (tot) (mg L^{-1})	-	0.001	-	-	-
DON (mg L^{-1})	0.03	0.08	0.2	0.022	0.03
NOx (mg L^{-1})	0.02	0.074	0.01	0.013	0.05
TN (mg L^{-1})	0.1	0.08	0.1	0.024	0.03
NH_3 (mg L^{-1})	0.005	0.017	0.02	0.011	0.003
Na (sol) (mg L^{-1})	10	6	-	-	2
Ni (sol) (mg L^{-1})	-	-	-	0.001	-
Ni (tot) (mg L^{-1})	-	-	-	-	-
TP (mg L^{-1})	0.005	0.015	-	-	0.009
FRP (mg L^{-1})	-	0.027	-	-	0.006

Pb (sol) (mg L^{-1})	-	-	-	-	-
Pb (sol) (mg L^{-1})	-	-	-	-	-
SO$_4^{2-}$ (mg L^{-1})	1	11	2	2	1
Se (sol) (mg L^{-1})	-	-	-	-	-
Se (tot) (mg L^{-1})	-	-	-	-	-
V (sol) (mg L^{-1})	-	-	-	-	-
V (tot) (mg L^{-1})	-	-	0.001	-	-
Zn (sol) (mg L^{-1})	0.001	0.002	0.002	0.001	0.001
Zn (tot) (mg L^{-1})	0.002	0.003	0.001	-	-

C3. Highest recorded measurement for field blank (procedural blank) samples collected within each estuary.

Analyte (units)	Peel Harvey	Leschenault	Vasse	Hardy	South coast
Acidity (mg L^{-1} CaCO$_3$)	4	-	5	-	-
Al (sol) (mg L^{-1})	0.034	<0.005	0.012	<0.005	<0.005
As (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Ca (sol) (mg L^{-1})	0.4	0.06	0.12	0.015	0.008
Cd (sol) (mg L^{-1})	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cl (sol) (mg L^{-1})	20	<10	<10	<10	-
Co (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Cr (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Cu (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Fe (sol) (mg L^{-1})	<0.05	<0.05	<0.05	<0.05	<0.05
Hg (sol) (mg L^{-1})	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Mg (sol) (mg L^{-1})	1.1	0.038	0.27	0.019	0.009

Mn (sol) (mg L^{-1})	<0.005	<0.005	<0.005	<0.005	0.061
Mo (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
DON (mg L^{-1})	0.037	<0.025	<0.025	<0.025	<0.025
NOx (mg L^{-1})	0.01	<0.01	0.01	<0.01	<0.01
TN (mg L^{-1})	0.067	<0.025	0.063	0.085	0.025
NH_3 (mg L^{-1})	0.013	<0.01	<0.01	<0.01	<0.01
Na (sol) (mg L^{-1})	8.7	0.17	1.9	0.062	0.061
Ni (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
TP (mg L^{-1})	0.008	0.005	<0.05	0.01	<0.005
FRP (mg L^{-1})	<0.005	0.005	<0.005	0.009	<0.005
Pb (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
SO_4^{2-} (mg L^{-1})	<5	<5	<5	<5	<5
Se (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
V (sol) (mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
Zn (sol) (mg L^{-1})	<0.001	<0.001	<0.001	0.007	<0.001

C4. *Greatest difference between replicate measurements for field replicate samples within each estuary.*

Analyte (units)	Swan Canning	Peel Harvey	Leschenault	Vasse	Hardy	South coast
Acidity (mg L^{-1} $CaCO_3$)		1	-	2	1	-
Al (sol) (mg L^{-1})		0.005	0.011	0.007	0.003	0.001
Al (tot) (mg L^{-1})		0.029	0.025	0.025	0.01	0.018
Alkalinity (mg L^{-1} $CaCO_3$)	30	5	10	10	2	10
As (sol) (mg L^{-1})		-	0.001	-	-	-
As (tot) (mg L^{-1})		0.003	-	-	-	-

DOC (mg L^{-1})	1	2	2	4	2	-
Ca (sol) (mg L^{-1})		10	-	10	2	10
Ca (tot) (mg L^{-1})		10	20	-	2	-
Cd (sol) (mg L^{-1})		-	-	-	-	-
Cd (tot) (mg L^{-1})		-	-	-	-	-
Cl (sol) (mg L^{-1})		-	300	200	30	
Co (sol) (mg L^{-1})		-	-	-	-	-
Co (tot) (mg L^{-1})		-	-	-	-	-
Cr (sol) (mg L^{-1})		-	-	-	-	-
Cr (tot) (mg L^{-1})		-	-	-	-	-
Cu (sol) (mg L^{-1})		-	0.002	-	0.005	-
Cu (tot) (mg L^{-1})		-	0.001	-	-	-
δ^{34}S (‰)		2.1	1.1	0.2	0.4	0.5
Fe (sol) (mg L^{-1})		0.08	0.09	-	0.01	-
Fe (tot) (mg L^{-1})		0.09	0.03	-	0.09	-
Hg (sol) (mg L^{-1})		-	-	-	-	-
Hg (tot) (mg L^{-1})		-	-	-	-	-
Mg (sol) (mg L^{-1})		50	20	10	8	10
Mg (tot) (mg L^{-1})		50	40	-	9	10
Mn (sol) (mg L^{-1})		0.001	0.05	0.009	-	-
Mn (tot) (mg L^{-1})		0.001	0.05	-	0.004	-
Mo (sol) (mg L^{-1})		0.001	-	-	-	-
Mo (tot) (mg L^{-1})		0.001	-	-	-	0.001
DON (mg L^{-1})	0.06	0.1	0.1	0.1	0.06	0.01
NOx (mg L^{-1})	-	0.02	0.001	0.019	0.003	-

TN (mg L^{-1})	0.1	0.1	0.6	-	0.06
NH_3 (mg L^{-1})	0.006	0.05	0.09	0.001	-
Na (sol) (mg L^{-1})	330	190	180	40	200
Ni (sol) (mg L^{-1})	-	-	-	-	-
Ni (tot) (mg L^{-1})	-	0.001	-	-	0.01
TP (mg L^{-1})	0.002	-	0.12	0.01	0.006
FRP (mg L^{-1})	0.003	0.03	-	0.003	0.003
Pb (sol) (mg L^{-1})	-	-	-	-	-
Pb (sol) (mg L^{-1})	-	-	-	-	-
SO_4^{2-} (mg L^{-1})	100	100	-	3	
Se (sol) (mg L^{-1})	-	-	-	-	-
Se (tot) (mg L^{-1})	-	-	-	-	-
V (sol) (mg L^{-1})	-	-	-	-	-
V (tot) (mg L^{-1})	-	0.001	-	-	-
Zn (sol) (mg L^{-1})	0.001	-	-	-	-
Zn (tot) (mg L^{-1})	0.009	0.005	-	0.008	0.002

Appendix D — Guidelines trigger values per estuary

D1. *Comparison of Swan-Canning estuary water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 32 (16 for total metals). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)^{A}	Samples above guideline: 50% total; 0% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})^{A}	≥0.0014	Guideline not exceeded.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total and soluble) (mg L^{-1})	≥0.0013^{M}	Samples above guideline: total and soluble Cu 3%.
Iron (total and soluble) (mg L^{-1})^{B}	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 13% total; 3% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0004^{M}	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) ^{A}	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.

Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)
[M] Marine ANZECC & ARMCANZ guideline value.
[S] indicates the guideline triggered mainly in summer.
[W] indicates the guideline triggered mainly in winter.

D2. *Comparison of Peel-Harvey estuary water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 51 (27 for total metals). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	**Trigger level**	**Samples exceeding trigger values**
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 93% total; 14% soluble. *33% are 4x trigger value.*
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Samples above guideline: 30% total; 0% soluble.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 7% total; 3% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total and soluble) (mg L^{-1})	≥0.0013[M]	Guideline not exceeded.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 4% total; 2% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0004[M]	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.

Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)
[M] Marine ANZECC & ARMCANZ guideline value.
[S] indicates guideline triggered mainly in summer.

D3. *Comparison of Leschenault Estuary water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 20 (10 for total metals). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 83% total; 35% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Samples above guideline: 10% total; 5% soluble
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 20% total; 10% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total and soluble) (mg L^{-1})	≥0.0013[M]	Samples above guideline: 20% total[W]; 0% soluble.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 50% total; 25% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0004[M]	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.

Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Samples above guideline: 10% total; 5% soluble.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)
[M] Marine ANZECC & ARMCANZ guideline value.
[W] indicates the guideline triggered mainly in winter.

D4. *Comparison of Vasse-Wonnerup estuary water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 14 (7 for total metals). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 57% total; 14% soluble[W].
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Guideline not exceeded.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total and soluble) (mg L^{-1})	≥0.0013[M]	Guideline not exceeded.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 43% total; 14% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0004[M]	Guideline not exceeded.

Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) ^{A}	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Samples above guideline: 14% total; 0% soluble.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)
[M] Marine ANZECC & ARMCANZ guideline value.
[W] indicates the guideline triggered mainly in winter.

D5. *Comparison of Hardy Inlet water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 12 (only sampled once). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)^{A}	Samples above guideline: 75% total; 25% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})^{A}	≥0.0014	Guideline not exceeded.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total) (mg L^{-1})	≥0.0013^{M}	Samples above guideline: 8% total; 0% soluble.

Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Guideline not exceeded.
Mercury (total and soluble) (mg L^{-1})	≥0.0004[M]	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] *Low reliability ANZECC & ARMCANZ guideline value.*
[B] *Ambient water quality guidelines for iron, Province of British Columbia (2008)*
[M] *Marine ANZECC & ARMCANZ guideline value.*

D6. *Comparison of south coast estuaries' water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV (metals, metalloids) unless otherwise stated. N = 12 (only sampled once). Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	**Trigger level**	**Samples exceeding trigger values**
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 47% total; 26% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Guideline not exceeded.

Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Guideline not exceeded.
Copper (total and soluble) (mg L^{-1})	≥0.0013[M]	Guideline not exceeded.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 0% total; 3% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0004[M]	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] *Low reliability ANZECC & ARMCANZ guideline value.*

[B] *Ambient water quality guidelines for iron, Province of British Columbia (2008)*

[M] *Marine ANZECC & ARMCANZ guideline value.*

Appendix E — Guideline trigger values per catchment

E1. *Comparison of Swan-Canning catchment water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV, unless otherwise stated. N = 30. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	**Trigger level**	**Samples exceeding trigger values**
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)^{A}	Samples above guideline: 77% total; 45% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})^{A}	≥0.0014	Samples above guideline: 7% total; 7% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Samples above guideline: 7% total; 0% soluble.
Copper (total and soluble) (mg L^{-1})	≥0.0014	Samples above guideline: 3% total; 3% soluble.
Iron (total and soluble) (mg L^{-1})^{B}	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 33% total; 14% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0006	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) ^{A}	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Samples above guideline: 3% total; 3% soluble.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble)	≥0.008	Samples above guideline: 7% total; 7%

(mg L^{-1})		soluble.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)

E2. *Comparison of Peel-Harvey catchment water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV, unless otherwise stated. N = 31. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	**Trigger level**	**Samples exceeding trigger values**
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 100% total; 71% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 13% total; 10% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Samples above guideline: 13% total; 0% soluble.
Copper (total and soluble) (mg L^{-1})	≥0.0014	Samples above guideline: 6% total; 3% soluble.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 65% total; 39% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0006	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Samples above guideline: 3% total; 0% soluble.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.

Vanadium (total and soluble) (mg L^{-1})	≥0.006	Samples above guideline: 16% total; 13% soluble.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Samples above guideline: 6% total; 3% soluble.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)

E3. *Comparison of Leschenault catchment water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV, unless otherwise stated. N = 28. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 100% total; 89% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 38% total; 18% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Samples above guideline: 4% total; 0% soluble.
Copper (total and soluble) (mg L^{-1})	≥0.0014	Samples above guideline: 21% total; 14% soluble.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 68% total; 21% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0006	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.

Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Samples above guideline: 7% total; 0% soluble.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)

E4. *Comparison of Scott Coastal Plain catchment water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV, unless otherwise stated. N = 28. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.*

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 86% total; 54% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 25% total; 25% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Samples above guideline: 11% total; 4% soluble.
Copper (total and soluble) (mg L^{-1})	≥0.0014	Samples above guideline: 4% total; 4% soluble.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 46% total; 29% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0006	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Samples above guideline: 4% total; 4% soluble.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.
Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.

Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Guideline not exceeded.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Guideline not exceeded.

[A] Low reliability ANZECC & ARMCANZ guideline value.
[B] Ambient water quality guidelines for iron, Province of British Columbia (2008)

E5. Comparison of south coast catchment water quality with ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection high-reliability TV, unless otherwise stated. N = 29. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc.

Variable (units)	Trigger level	Samples exceeding trigger values
Aluminium (total and soluble) (mg L^{-1})	≥0.055 (pH>6.5) ≥0.008 (pH<6.5)[A]	Samples above guideline: 97% total; 93% soluble.
Arsenic (total and soluble) (mg L^{-1})	≥0.013	Guideline not exceeded.
Cadmium (total and soluble) (mg L^{-1})	≥0.0002	Guideline not exceeded.
Cobalt (total and soluble) (mg L^{-1})[A]	≥0.0014	Samples above guideline: 14% total; 14% soluble.
Chromium (using Cr (VI) trigger) (total and soluble) (mg L^{-1})	≥0.001	Samples above guideline: 17% total; 10% soluble.
Copper (total and soluble) (mg L^{-1})	≥0.0014	Samples above guideline: 3% total; 0% soluble.
Iron (total and soluble) (mg L^{-1})[B]	≥1.000 (total) ≥0.35 (soluble)	Samples above guideline: 83% total; 72% soluble.
Mercury (total and soluble) (mg L^{-1})	≥0.0006	Guideline not exceeded.
Manganese (total and soluble) (mg L^{-1})	≥1.900	Guideline not exceeded.
Molybdenum (total and soluble) (mg L^{-1}) [A]	≥0.034	Guideline not exceeded.

Nickel (total and soluble) (mg L^{-1})	≥0.011	Guideline not exceeded.
Lead (total and soluble) (mg L^{-1})	≥0.0034	Guideline not exceeded.
Selenium (total and soluble) (mg L^{-1})	≥0.0011	Guideline not exceeded.
Vanadium (total and soluble) (mg L^{-1})	≥0.006	Samples above guideline: 3% total; 0% soluble.
Zinc (total and soluble) (mg L^{-1})	≥0.008	Samples above guideline: 3% total; 3% soluble.

[A] *Low reliability ANZECC & ARMCANZ guideline value.*
[B] *Ambient water quality guidelines for iron, Province of British Columbia (2008)*

Appendix F — Guideline trigger values exceeded by site

F1. *Catchment sites at which metals and nutrients exceeded ANZECC & ARMCANZ guideline trigger values. The ANZECC & ARMCANZ (2000) trigger values for freshwater 95% species protection and lowland river ecosystem stress are used. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc. Normal text indicates value exceeded trigger value,* ***bold*** *text indicates value was 2x trigger value, and* ***red*** *text indicates 10x trigger value.*

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
BBDSMP	5	Swan Canning	**Al,** Fe	**Al, Fe**	TN
BCBW	5	Swan Canning	**Al**	**Al,** Cr	**NOx**, TN, **TP**, FRP
BCRUS	5	Swan Canning	**Al**	**Al**, Fe	-
BICKBK 05	5	Swan Canning	Al	**Al**	**NOx**
BICKBKEDS	5	Swan Canning	-	**Al**	**NOx**
BLACMDS	4a	Swan Canning	-	Fe	NOx
BNCADEN	5	Swan Canning	**Al**	**Al**	**NOx**, TN, **TP**, FRP
BSMDO	5	Swan Canning	**Al**	**Al**	**NOx**, TN
BWD9	5	Swan Canning	**Al, Co**, **Zn**	**Al, Co**, Fe, **Zn**	**NOx**, **TN**, **TP**, **FRP**
BWMDBI	5	Swan Canning	n.d.	**Al**	**NOx**
BWMDBPI	5	Swan Canning	**Al, Co, Fe**	**Al, Co,** Cr, **Fe**	**NOx**, **NH$_4^+$**
BWMDBR	5	Swan Canning	Al	**Al**	**NOx**
CAMDOUT	5	Swan Canning	-	**Al**, **Fe**	NOx

Site name	**Iso-group**	**Region**	**Exceeded metals (soluble)**	**Exceeded metals (total)**	**Exceeded nutrients**
EBBHDS	2	Swan Canning	**Al**,	**Al, Fe**	**TN**, **TP**, **FRP**
EBMBUS	2	Swan Canning	**Al**, Fe	**Al**, **Fe**	**TN**, **TP**, **FRP**
HRDSMW	2	Swan Canning	-	Al	-
HRES	5	Swan Canning	-	Al, Fe	NOx, NH_4^+
JBDG	4a	Swan Canning	-	-	NOx
JBSDS	2	Swan Canning	-	Al	-
LACDD	5	Swan Canning	-	-	**NOx**, TN
LIEP6	5	Swan Canning	-	-	**NOx**, TN, **TP**, **FRP**
MSCWW	5	Swan Canning	-	Al	**NOx**, TN, **NH4**, **TP**, FRP
PAS01	5	Swan Canning	**Al**, Cu, Zn	**Al**, Cu, Zn	NOx, TN
SBMD4	5	Swan Canning	-	Al	TP, FRP
SCCIS10	5	Swan Canning	**Al**,	**Al**, Fe	**NOx**, TN, **TP**, **FRP**
SLMBAIGIN	5	Swan Canning	-	Al	NOx, TP, FRP
SRBDS	3	Swan Canning	-	Al	NOx
WBHW	5	Swan Canning	-	-	**NOx**, TN
WCEBDS	4a	Swan Canning	-	-	-
YBRPUS	5	Swan Canning	-	-	**NOx**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
613014	4a	Peel Harvey	**Al**	**Al**	-
613027	2	Peel Harvey	**Al**, Fe	**Al**, Cr, **Fe**	TN, **TP**, **FRP**
613029	2	Peel Harvey	**-**	Al	TN
613031	2	Peel Harvey	**-**	**Al**, Fe	**TP**
613052	5	Peel Harvey	**Al**	**Al**, Fe	TP
613053	5	Peel Harvey	**Al**	**Al**, Cr	TN, NH_4^+, **TP**, **FRP**
614030	5	Peel Harvey	**-**	**Al**, Fe	TP, FRP
614063	4a	Peel Harvey	**Al**, **Fe**	**Al**, **Fe**	TN, **TP**, **FRP**
614065	2	Peel Harvey	**-**	**Al**	-
614094	5	Peel Harvey	Al	**Al**, Fe, Cr	-
614120	n.d.	Peel Harvey	**Al**, Fe	**Al**, Cu, Fe	TN, NH_4^+, **TP**, **FRP**
614121	5	Peel Harvey	**-**	Al, Fe, **Zn**	TN, **TP**, **FRP**
AMRL3	2	Peel Harvey	**Al**, **Fe**	**Al**, **Fe**	TN, **TP**, **FRP**
HR01012 (WRC1)	4a	Peel Harvey	**Al**	**Al**	NOx
HR01014	2	Peel Harvey	Al, Fe	**Al**, **Fe**	TP
HR02005	4a	Peel Harvey	**Al**, Cu	**Al**, Cr	TN, **TP**, **FRP**
MPH003	3	Peel Harvey	**Al, Co**, Zn	**Al, Co**	-
MR01002	2	Peel Harvey	**Al**	**Al**	TN
MR01010	2	Peel Harvey	Al, Fe	**Al**, Co, **Fe**, V	TN, **TP**, **FRP**
MR01012	1	Peel Harvey	**Al**	**Al**, Fe	TN, **TP**, **FRP**
MR03017	4b	Peel Harvey	**-**	**Al**	TN
MR04014	2	Peel Harvey	Al, Co	**Al**, Co, **Fe**	TN, NH4, **TP**
MR04019	2	Peel Harvey	V	**Al**	TN, **TP**, **FRP**
MR05004	2	Peel Harvey	**Al**, Fe	**Al**, Fe	TN, **TP**, **FRP**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
MR05005	n.d.	Peel Harvey	**Al**, **Fe**, V	**Al**, **Fe**, V	TN, **NH_4^+**, **TP**, **FRP**
MR05010	2	Peel Harvey	**Al**, **Fe**, **Zn**	**Al**, **Fe**, **Zn**	TN, **TP**, FRP
NYUND	2	Peel Harvey	**-**	Al	TN, TP
PATRDTRIB	4b	Peel Harvey	Al**, Co**, **Fe**, Mn	**Al, Co**, Cu, **Fe**, Mn, V	TN, **NH_4^+**, **TP**, **FRP**
PHM3	2	Peel Harvey	**-**	Al, Fe	-
PHS7	2	Peel Harvey	**Al**, Fe, V	**Al**, Cr, Fe, V	TN, NH_4^+, **TP**, **FRP**
SR04014	1	Peel Harvey	**Al**, **Fe**, V	**Al**, **Fe**, V	TN, NH_4^+, **TP**, **FRP**
ACID01	4a	Leschenault	Al	**Al**	-
ACID02	5	Leschenault	**Al**	**Al**, Co, **Fe**	**TN**, **NH_4^+**, TP, **FRP**
ACID03	2	Leschenault	Al, **Co**, Fe	**Al**, **Co**, **Fe**	**TN**, **NH_4^+**, TP, **FRP**
ACID04	2	Leschenault	**Al**, Co, Cu, Fe	**Al**, **Co**, Cu, **Fe**, V	NOx, **TN**, **NH_4^+**, TP, **FRP**
ACID05	5	Leschenault	**Al**	**Al**	NOx
ACID06	4a	Leschenault	**Al**	**Al**, Fe	NOx
ACID07	1	Leschenault	Al, **Co**	**Al**, **Co**	-
ACID08	2	Leschenault	**-**	**Al**	-
ACID09		Leschenault	**Al**	**Al**, **Fe**	TN, NH_4^+, TP, **FRP**
ACID10	4a	Leschenault	**Al**	**Al**, Fe	NOx, **TN**, **NH_4^+**, TP, **FRP**
ACID11	4b	Leschenault	Al	**Al**, Co, Fe	**NOx,** TN, **NH_4^+**, TP
ACID12	2	Leschenault	**Al**	**Al**	**-**
ACID13	4a	Leschenault	**Al**, Cu	**Al**, Cr, Cu, Fe	NOx

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
ACID14	4a	Leschenault	**Al**	**Al**	NOx
ACID15	1	Leschenault	**Al**	**Al**	NOx
ACID16	5	Leschenault	**Al**, Cu, **Fe**	**Al**, Co, Cu, **Fe**, V	**TN**, NH_4^+, TP, **FRP**
ACID17	2	Leschenault	**Al**, **Co**, **Fe**	**Al**, **Co**, **Fe**	TN, **NH_4^+**
BRUN6	4b	Leschenault	**Al**	**Al**, Fe	NOx, TN, TP
GBC01	4a	Leschenault	**Al**, Cu, Fe	**Al**, Co, Cu, **Fe**	NOx, **TN**, **NH_4^+**, TP, **FRP**
GBC02	5	Leschenault	**Al**	**Al**, Co, **Fe**	TP
GBC03	4a	Leschenault	**Al**	**Al**, Fe	NOx
LESCH01	4b	Leschenault	**Al**	**Al**, Cu	-
LESCH02	4b	Leschenault	**Al**, Co	**Al**, **Co** Fe	NOx, TN, TP
LESCH03	4a	Leschenault	**Al**	**Al**, Cu, Fe	**NOx**
LESCH04	4b	Leschenault	**Al**	**Al**, Fe	TP
LESCH05	3	Leschenault	**Al**,	**Al**, Co, **Fe**	NOx, **TN**, **NH_4^+**, TP, **FRP**
LESCH06	2	Leschenault	**Al**, Fe	**Al**, Fe	**TN**, **NH_4^+**, **TP**, **FRP**
LESCH07	1	Leschenault	**-**	Al	NOx, TN, NH_4^+
608003	2	Scott Coastal Plain	-	Al, Fe	-
608147	2	Scott Coastal Plain	Al	**Al**	**-**
608171	2	Scott Coastal Plain	**Al**, Cu	**Al**, **Cu**	**-**
609022	4b	Scott Coastal Plain	**-**	Al	**-**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
609041	2	Scott Coastal Plain	**-**	**-**	-
609060	5	Scott Coastal Plain	-	-	**-**
6081009	2	Scott Coastal Plain	Al	**Al**	-
6081010	2	Scott Coastal Plain	-	Al, **Fe**	-
6081026	2	Scott Coastal Plain	**Al**, Fe	**Al**, **Fe**	-
6081040	2	Scott Coastal Plain	**Al**	**Al**	**-**
6081053	2	Scott Coastal Plain	**Al**	**Al**, Cr	**-**
6091008	2	Scott Coastal Plain	**-**	Al	**-**
6091044	2	Scott Coastal Plain	**Fe**	**Fe**	-
6091222	4b	Scott Coastal Plain	**Al**, Co, Cr, **Fe**	**Al**, Co, Cr, **Fe**	TN, **TP**
6091223	2	Scott Coastal Plain	**Al**, Co, **Fe**, Mn	**Al**, Co, **Fe**, Mn	**TN**, **TP**
6091224	5	Scott Coastal Plain	Co	Al, Co	**NOx**, TN, NH_4^+
6091302	2	Scott Coastal Plain	**Al**	**Al**, Fe	-
6091305	4a	Scott Coastal Plain	Al	**Al**, Fe	**NOx**
6091408	2	Scott Coastal Plain	**Al**	**Al**	**-**
6091596	2	Scott Coastal Plain	**Al**, Co, **Fe**	**Al**, Co, Cr, **Fe**	-
6091735	1	Scott Coastal Plain	**Al**	**Al**	**-**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
6091752	1	Scott Coastal Plain	Al, Fe	**Al**, **Fe**	TN, **TP**
6091753	2	Scott Coastal Plain	**-**	**-**	NOx
6091754	4a	Scott Coastal Plain	**-**	**Al**	NOx
6091755	3	Scott Coastal Plain	**Al**, Co, Fe	**Al**, Co, **Fe**	**TP**
6091756	2	Scott Coastal Plain	**Al**	**Al**	TN
6091757	n.d.	Scott Coastal Plain	Co	Al, Co, **Fe**	**TN**, NH_4^+, **TP**
6091758	5	Scott Coastal Plain	**Al**, **Co**, **Fe**	**Al**, **Co**, **Fe**	**-**
CHE	4b	Albany	**-**	Al	**NOx**
DML	2	Albany	**Al**	**Al**	-
FREEBOROUGH	4b	Albany	**Al**, **Fe**	**Al**, **Fe**	**TN**, NH_4^+, **TP**, **FRP**
HAY	2	Albany	**Al**	**Al**	**-**
HENNING	2	Albany	**Al**, Fe	**Al**, Fe	-
INFLOW	2	Albany	**Al, Fe**	**Al**, **Fe**	TN, NH_4^+, **TP**, FRP
KR	2	Albany	Al, Fe	**Al**, **Fe**	TP
LEAY	4b	Albany	**Al**, **Fe**	**Al**, **Fe**	NH_4^+
LIT	4a	Albany	**Al**, Fe	**Al**, **Fe**	TP
LOWKG	3	Albany	**Al,** Fe	**Al,** Fe	TN, **TP**, **FRP**
MANCK	2	Albany	**Al, Fe**	**Al**, **Fe**	**TN**, **TP**, **FRP**
MIT	4b	Albany	**Al**, Co	**Al**, **Co**	-
MRD	3	Albany	**Al**, Fe	**Al**, Fe	TN, **TP**, FRP
MTBARKRD	3	Albany	**Al,** Cr, Fe	**Al,** Cr, Fe	-

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
RD	5	Albany	**Al**	**Al, Fe**	**NOx**, TN, NH_4^+, **TP**, FRP
RZ7	2	Albany	**Al**, **Fe**	**Al**, **Fe**	**TN**, **TP**, **FRP**
SCO	4a	Albany	**Al**, Fe	**Al**, **Fe**	-
SLE	4b	Albany	**Al**, Fe	**Al**, **Fe**	TP
SUN	4b	Albany	**Al**, **Fe**	**Al**, **Fe**	TN, **TP**, FRP
TILP001	3	Albany	**Al**, Co**, Fe**	**Al**, **Co,** Cu, **Fe**	TN, **TP**, FRP
TILP006	2	Albany	**Al**	**Al**, Fe	TN, NH_4^+, **TP**, FRP
TILP008	2	Albany	**Al**, Fe	**Al**, Fe	NOx, TP
TILP012	5	Albany	**Al**, **Co, Fe**,	**Al**, **Co**, **Fe**	**TN**, **NH_4^+**
TILP013	2	Albany	**Al,** Cr, Fe	**Al,** Cr, Fe	**TN**, TP
TILP047	2	Albany	**Al**, **Fe**, **Zn**	**Al, Cr**, **Fe**, V, **Zn**	TN, TP
WCWF	2	Albany	**Al**, Fe	**Al**, **Fe**	NOx, TP
WOOD1	5	Albany	**Al**, **Co,** Cr, **Fe**	**Al**, **Co**, Cr, **Fe**	**-**
YAK1	5	Albany	**Al**,	**Al**, Cr, **Fe**	**NOx**, TN, NH_4^+, **TP**
YU	5	Albany	Al	Al	NOx, TN, TP

F2. *Estuarine sites at which metals and nutrients exceeded ANZECC & ARMCANZ trigger values. The ANZECC & ARMCANZ (2000) trigger values for 95% species protection - freshwater or marine (see Section 7.3) - and estuarine ecosystem stress were used. Trigger values were adjusted by the hardness algorithm for cadmium, chromium, copper, nickel, lead and zinc. Normal text indicates value exceeded trigger value,* ***bold*** *text indicates value was 2x trigger value, and* ***red*** *text indicates 10x trigger value.*

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
616094-s	4b	Swan Canning	-	n.d	TP, **FRP**
616094-w	2	Swan Canning	-	**Al**,	**NO$_x$**, TN, **NH$_4^+$**, **TP**, **FRP**
ARM-s	5	Swan Canning	-	n.d	TP, **FRP**
ARM-w	4a	Swan Canning	-	-	**FRP**
BAC-s	4b	Swan Canning	-	n.d	**TP**, **FRP**
BAC-w	1	Swan Canning	-	**Al**,	**NO$_x$**, TN, **NH$_4^+$**, TP
BLA-s	4a	Swan Canning	-	n.d	TP, **FRP**
BLA-w	n.d.	Swan Canning	-	-	NH$_3$
CAS-s	5	Swan Canning	-	n.d	TN, **TP**, **FRP**
CAS-w	1	Swan Canning	-	**Al**	**NO$_x$**, TN, **NH$_3$**, **TP**, **FRP**
ELL-s	5	Swan Canning	-	n.d	TN, **TP**, **FRP**
ELL-w	5	Swan Canning	-	**Al**, Fe,	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**
KIN-s	5	Swan Canning	-	n.d	TN, **TP**, **FRP**
KIN-w	n.d.	Swan Canning	-	Al	NO$_x$, TN, **NH$_4^+$**, TP, **FRP**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
MAY-s	5	Swan Canning	-	n.d	TN, **TP**, **FRP**
MAY-w	4a	Swan Canning	-		NH_4^+, TP, **FRP**
NAR-s	4a	Swan Canning	-	n.d	TP, **FRP**
NAR-w	1	Swan Canning	-	Al,	**FRP**
NIC-s	4b	Swan Canning	-	n.d	**TP**, **FRP**
NIC-w	5	Swan Canning	Cu	**Al**, Cu	**NO_x**, TN, **NH_4^+**, TP, **FRP**
NIL-s	5	Swan Canning	-	n.d	TN, NH_4^+, **TP**, **FRP**
NIL-w	1	Swan Canning	-	-	NH_4^+, TP, **FRP**
RIV-s	5	Swan Canning	-	n.d	TN, **TP**, **FRP**
RIV-w	1	Swan Canning	-	-	NH_4^+, TP, **FRP**
RON-s	4a	Swan Canning	-	n.d	TN, **TP**, **FRP**
RON-w	1	Swan Canning	-	-	NO_x, TN, **NH_4^+**, TP, **FRP**
SAL-s	4a	Swan Canning	-	n.d	**TP**, **FRP**
SAL-w	1	Swan Canning	-	-	NH_4^+, TP, **FRP**
STJ-s	4a	Swan Canning	-	n.d	TN, NH_4^+, **TP**, **FRP**
STJ-w	4b	Swan Canning	-	-	NH_4^+, TP, **FRP**
SUC[S]	2	Swan Canning	-	n.d	TN, **TP**, **FRP**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
SUC-w	1	Swan Canning	-	Al	NO_x, TN, **NH_4^+**, TP, **FRP**
MPH001-w	1	Peel Harvey	-	**Al**, Co	**TN**, **TP**, **FRP**
MPH002-w	2	Peel Harvey	-	**Al**	**TN**, **TP**, **FRP**
MPH003-w	1	Peel Harvey	-	Al	**NO_x**, TN, **NH_4^+**, **TP**, **FRP**
MPH006-s	4a	Peel Harvey	-	n.d.	**-**
MPH006-w	n.d.	Peel Harvey	-	Al, **As**	**-**
MPH015-s	1	Peel Harvey	-	n.d.	TP
MPH015-w	3	Peel Harvey	Al	**Al**, **As**	TN, **TP**
MPH019-s	1	Peel Harvey	-	n.d.	TN, TP
MPH019-w	1	Peel Harvey	**Al**	**Al**, **As**	TN, **TP**
MPH025-s	5	Peel Harvey	-	n.d.	**-**
MPH025-w	1	Peel Harvey	-	**Al**, **As**	-
MPH040-s	4b	Peel Harvey	-	n.d.	**TN**, **TP**
MPH040-w	4b	Peel Harvey	-	Al	TN, NH_4^+, TP, **FRP**
MPH044-s	2	Peel Harvey	-	n.d.	TN, TP, FRP
MPH044-w	2	Peel Harvey	-	Al, **As**	TP
MPH061-s	1	Peel Harvey	-	n.d.	**FRP**
MPH061-w	2	Peel Harvey	-	**As**	-
MPH071-s	1	Peel Harvey	-	n.d.	**FRP**
MPH071-w	4a	Peel Harvey	-	**Al**, **As**	**-**
MPH083-s	2	Peel Harvey	-	n.d.	TP, **FRP**
MPH083-w	2	Peel Harvey	Al	**Al**, **As**	**-**
MPH091-s	4a	Peel Harvey	-	n.d.	TP, FRP

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
MPH091-w	1	Peel Harvey	**Al**, Fe	**Al**, Fe	**NO$_x$**, TN, **NH$_4^+$**, **TP**, **FRP**
MPH155-s	4b	Peel Harvey	-	n.d.	TN, TP
MPH155-w	2	Peel Harvey	Al	**Al**	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**
MPH158-s	1	Peel Harvey	-	n.d.	TN, **TP**, **FRP**
MPH158-w	2	Peel Harvey	Al	**Al**	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**
PHE01-s	1	Peel Harvey	-	n.d.	TP, **FRP**
PHE01-w	5	Peel Harvey	-	**Al**	NO$_x$, **NH$_4^+$**, **SRP**
PHE02-s	4b	Peel Harvey	-	n.d.	**FRP**
PHE02-w	5	Peel Harvey	-	Al	**-**
PHE04-s	1	Peel Harvey	-	n.d.	**FRP**
PHE04-w	4a	Peel Harvey	-	**Al**	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**
PHE07-s	1	Peel Harvey	-	n.d.	**FRP**
PHE07-w	4a	Peel Harvey	-	**Al**	NH$_3$, FRP
PHE31-s	1	Peel Harvey	-	n.d.	TN, TP, **FRP**
PHE31-w	4a	Peel Harvey	-	**Al**	NH$_4^+$, **FRP**
PHE58-s	2	Peel Harvey	-	n.d.	**FRP**
PHE58-w	n.d.	Peel Harvey	-	Al	FRP
PHRM2-s	4a	Peel Harvey	Al	n.d.	TN, **TP**, **FRP**
PHRM2-w	2	Peel Harvey	-	**Al**	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**
PHRM4-s	4a	Peel Harvey	-	n.d.	**FRP** *(TN/TP n.d.)*
PHRM4-w	2	Peel Harvey	-	**Al**	**NO$_x$**, TN, **NH$_4^+$**, TP, **FRP**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
PHRM9-s	2	Peel Harvey	-	n.d.	**FRP** *(TN/TP n.d.)*
PHRM9-w	2	Peel Harvey	-	**Al**	**NO_x**, TN, **NH_4^+**, TP, FRP
PHRS4-s	3	Peel Harvey	-	n.d.	TN, **NH_4^+**, **TP**, **FRP**
PHRS4-w	1	Peel Harvey	-	Al	FRP
PHRS6-s	4a	Peel Harvey	-	n.d.	**TN**, **NH_4^+**, **TP**, **FRP**
PHRS6-w	1	Peel Harvey	-	-	TN, TP, FRP
PHRS7-s	1	Peel Harvey	Co	n.d.	**TN**, **NH_4^+**, **TP**, **FRP**
PHRS7-w	4a	Peel Harvey	-	Al	**TN**, **TP**, FRP
6111043-s	4a	Leschenault	-	n.d.	NH_4^+, **FRP**
6111043-w	5	Leschenault	Al, Fe	**Al**, Fe	**NO_x**, **TN**, **NH_4^+**, **TP**, **FRP**
6121130-s	2	Leschenault	-	n.d.	FRP
6121130-w	4a	Leschenault	Al, Fe, Cd	Al, Cd	**NO_x**, TN, FRP
6121161-s	1	Leschenault	-	Al (only Al, Fe analysed)	NO_x, TN, **NH_4^+**, **TP**, **FRP**
6121161-w	3	Leschenault	**Al**, **Fe**	**Al**, Co, Fe, Cu	**NO_x**, **TN**, **NH_4^+**, **TP**, **FRP**
6121162-s	2	Leschenault	-	n.d.	NO_x, TN, **TP**, **FRP**
6121162-w	3	Leschenault	Al, Co, Fe	**Al**, Co, Fe	**NO_x**, **TN**, **NH_4^+**, **TP**, **FRP**
6121166-s	4b	Leschenault	-	Al (only Al, Fe analysed)	**NH_4^+**, TP, **FRP**
6121166-w	4a	Leschenault	Al, Fe	**Al**, Fe	**NO_x**, **TN**, **NH_4^+**, TP, **FRP**
6121168-s	2	Leschenault	-	n.d.	NH_4^+, FRP
6121168-w	4a	Leschenault	**-**	**Al**, Fe	**NO_x**, TN, **NH_4^+**, TP, FRP

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
6121173-s	1	Leschenault	Co, V	n.d.	**TN**, **NH_4^+**, **TP**, **FRP**
6121173-w	3	Leschenault	-	Al	**TN**, **NH_4^+**, **TP**, **FRP**
6121203-s	4b	Leschenault	Al	n.d.	**NO_x**, TN, **NH_4^+**, **TP**, **FRP**
6121203-w	5	Leschenault	**Al**	**Al**, Fe, Cu, V	**NO_x**, **TN**, **NH_4^+**, **TP**, **FRP**
6121206-s	4a	Leschenault	-	n.d.	NH_4^+, **FRP**
6121206-w	4a	Leschenault	-	-	**FRP**
6121207-s	1	Leschenault	-	n.d.	**FRP**
6121207-w	5	Leschenault	-	-	NH_4^+, **FRP**
610019-s	1	Vasse Wonnerup	-	n.d.	TN, **NH_4^+**, **TP**
610019-w	4a	Vasse Wonnerup	-	-	**NO_x**, **TN**, **NH_4^+**, **TP**
610020-s	1	Vasse Wonnerup	**-**	n.d.	**NH_4^+**, TP
610020-w	5	Vasse Wonnerup	**Fe**	**Fe**, Zn	**NO_x**, **TN**, **NH_4^+**, **TP**
6101063-s	4b	Vasse Wonnerup	-	n.d.	**TN**, **TP**
6101063-w	4a	Vasse Wonnerup	-	-	**TN**, **NH_4^+**, **TP**
6101064-s	4b	Vasse Wonnerup	-	n.d.	**TN**
6101064-w	5	Vasse Wonnerup	**-**	Fe	**NO_x**, **TN**, **NH_4^+**, **TP**
6101065-s	2	Vasse Wonnerup	**-**	n.d.	NH_4^+
6101065-w	4a	Vasse Wonnerup	**Fe**	**Fe**	**NO_x**, **TN**, **NH_4^+**, **TP**

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
6101067-s	1	Vasse Wonnerup	-	n.d.	**TN**, **TP**
6101067-w	4a	Vasse Wonnerup	-	-	-
6101072-s	4b	Vasse Wonnerup	**-**	n.d.	TN, **TP**
6101072-w	4a	Vasse Wonnerup	-	**-**	NH$_4^+$
BRF01-w	2	Hardy	Al, Fe	**Al**	**NO$_x$**, TN, NH$_4^+$, **TP**, **FRP**
BRF02-w	2	Hardy	-	Al	**NO$_x$**, **TN**
HIF01-w	2	Hardy	-	-	**NO$_x$**, TN
HIF02-w	2	Hardy	-	Al	**NO$_x$**, TN
HIF03-w	2	Hardy	-	Al	**NO$_x$**, TN
HIF04-w	2	Hardy	-	Al	**NO$_x$**, TN
HIF05-w	2	Hardy	-	-	**NO$_x$**, **TN**
HIF06-w	2	Hardy	-	-	**NO$_x$**, TN
MIF01-w	2	Hardy	-	Al	**NO$_x$**, **TN**
MIF02-w	2	Hardy	-	Al	**NO$_x$**, TN, TP, FRP
MIF03-w	4a	Hardy	**Al**, Cu, Fe	**Al**	**NO$_x$**, **TN**, NH$_4^+$, **TP**, **FRP**
SRF01-w	4a	Hardy	**Al**, **Fe**	**Al**	**NO$_x$**, **TN**, **TP**, **FRP**
AOH 2-s	5	South coast estuaries	-	n.d.	FRP
AOH 2-w	4b	South coast estuaries	-	- (only Al, Fe analysed)	FRP
AOH 4-s	5	South coast estuaries	**-**	n.d.	FRP
AOH 4-w	n.d.	South coast estuaries	-	- (only Al, Fe analysed)	FRP

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
AOH 5-s	1	South coast estuaries	-	n.d.	FRP
AOH 5-w	1	South coast estuaries	-	- (only Al, Fe analysed)	FRP
APRH 2-s	1	South coast estuaries	-	n.d.	FRP
APRH 2-w	1	South coast estuaries	-	- (only Al, Fe analysed)	FRP
APRH 3-s	4a	South coast estuaries	-	n.d.	FRP
APRH 3-w	n.d.	South coast estuaries	-	(only Al, Fe analysed)	FRP
APRH 4-s	4a	South coast estuaries	-	n.d.	FRP
APRH 4-w	1	South coast estuaries	**-**	- (only Al, Fe analysed)	FRP
BRO001-s	1	South coast estuaries	Al	n.d.	-
BRO001-w	n.d.	South coast estuaries	**-**	Al	FRP
BRO002-s	1	South coast estuaries	Al	n.d.	-
BRO002-w	n.d.	South coast estuaries	Al	Al	FRP
BRO004-s	1	South coast estuaries	Al	n.d.	-
BRO004-w	n.d.	South coast estuaries	-	Al	**FRP**
IRW001-s	1	South coast estuaries	-	n.d.	FRP
IRW001-w	n.d.	South coast estuaries	-	-	**FRP**
IRW003-s	1	South coast estuaries	-	n.d.	FRP

Site name	Iso-group	Region	Exceeded metals (soluble)	Exceeded metals (total)	Exceeded nutrients
IRW003-w	n.d.	South coast estuaries	Al	Al	**FRP**
NI 10-s	1	South coast estuaries	-	n.d.	**-**
NI 10-w	n.d.	South coast estuaries	Al	**Al**	**FRP**
NI 5-s	2	South coast estuaries	-	n.d.	-
NI 5-w	n.d.	South coast estuaries	Al	Al	**FRP**
WAL001-s	4b	South coast estuaries	-	n.d.	**-**
WAL001-w	n.d.	South coast estuaries	**Al**	**Al**	TN, **TP**, **FRP**
WAL003-s	1	South coast estuaries	-	n.d.	NH_4^+
WAL003-w	n.d.	South coast estuaries	**Al**, Fe	**Al**	TP, **FRP**
WAL004-s	1	South coast estuaries	-	n.d.	**-**
WAL004-w	n.d.	South coast estuaries	Al	Al	**FRP**
WI12-s	2	South coast estuaries	-	n.d.	NH_4^+, FRP
WI12-w	2	South coast estuaries	(only Al, Fe analysed)	-	TN, NH_4^+, FRP
WI30-s	1	South coast estuaries	-	n.d.	**-**
WI30-w	1	South coast estuaries	(only Al, Fe analysed)	-	NH_4^+, FRP
WI6-s	2	South coast estuaries	-	n.d.	FRP
WI6-w	1	South coast estuaries	(only Al, Fe analysed)	-	**FRP**

Appendix G — Sulfur stable isotope ratios measured in fertilisers, detergent and rainfall

G1. *Sulfur stable isotope ratios (per mil, ‰) measured for various sources of 'oxidised sulfur'.*

Source	Manufacturer	Product name	del34S
Fertiliser	Yates	Thrive water soluble plant food	2.5
	Scotts	Osmocote multi-purpose	2.9
		Osmocote plus roses	2.0
		Lawn builder	8.3
	Cresco	Lawn fertiliser	0.7
	Richgro	Sulfate of potash	-0.1
	CSBP	Sulfate of ammonia	2.2
		Super phosphate	1.1
		Coastal super	2.3
		GSOP	18.7
Detergent	United Laboratories	Duo laundry detergent	21
Rainfall	(collected in Perth metropolitan area)		18.2-20.0

Acronyms

ANOVA	Analysis of variance
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASS	Acid sulfate soils
DEC	Department of Conservation and Environment
DoE	Department of Environment
DoW	Department of Water
MBO	Monosulfidic black ooze
PERMANOVA	Permutational multivariate analysis of variance

Glossary

Abiotic	Non-living chemical and physical factors in the environment.
Acids, fully dissociated	Acids that fully dissociate in water are called strong acids; for example, $H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$.
Acids, weak	Acids that do not fully dissociate when dissolved in water are called weak acids. Vinegar is a commonly known weak acid. These acids, when dissolved in water, form an equilibrium where both reactants and products are present. The equilibrium means that if some H^+ ions are removed (i.e. by neutralisation), more will be formed to maintain the equilibrium.
Acidification	The process by which soil or water becomes more acid (decreasing pH).
Alkalinity	A measure of a solution's ability to resist changes in pH due to the addition of an acid. In natural waters this usually relates to the amount of bicarbonate, carbonate, and hydroxide compounds present in the water.
Algal blooms	The rapid excessive growth of algae, generally caused by high nutrient levels and favourable conditions. Water-column deoxygenation may occur when the algae die.
Analyte	A substance or chemical constituent that is determined in an analytical procedure.
Anaerobic	Without air, where 'air' is generally used to mean oxygen.
Anoxic	An absence of oxygen, an extreme form of hypoxia or 'low oxygen' (anoxic 0% and hypoxia <40% dissolved oxygen saturation in solution).
Anthropogenic	Originating from the activity of humans.
Baseline data	Data or measurements collected as a starting point, generally before a program begins.
Bimodal distribution	A statistical distribution having two modes – indicating a mixing of two populations such as the salinity from a dataset containing a mix of fresh and marine waters.
Blackwater event	Rapid deoxygenation of a waterway due to the high oxygen demand of the mobilised organic-rich matter (may also contain monosulfides). Blackwater events are usually triggered by a rainfall event.
Blank sample	Clean samples of distilled de-ionised water prepared in the field or laboratory, treated as normal samples to determine if contamination occurs during sampling, handling or analysis.
Box plots	A graph summarising the distribution of a set of data values using

	summary data: minimum, lower quartile (25%), median, upper quartile (75%), maximum and often outliers observations. Also known as a box-and-whisker diagram or plot.
Buffering	Resisting changes in pH when a small amount of strong acid or base is added to a solution. Common buffering agents are carbonate or bicarbonates. Seawater contains high quantities of these compounds.
Chloride to sulfate ratio	The ratio of the mass of chloride to sulfate, used as an indicator of changes in sulfate. Chloride is considered a conservative ion that has few additional sources except seawater. The ratio of seawater is normally ~7.2:1. Additional sulfate from acidic drainage can reduce this ratio to <4:1. Sulfate removed by sulfate reduction can produce ratios of >25:1.
Correlation	Indicates the strength and direction of the linear relationship between two random variables.
Dewatering	The removal of groundwater during sewerage and other below-ground construction projects. This is often carried out during the site development phase of a major construction project due to a high water table.
Dredging	Dredging is an excavation activity carried out at least partly underwater, in shallow seas, estuaries or freshwater areas to keep waterways navigable. Bottom sediments are collected and disposed of at a different location.
Eutrophic	Waters rich in mineral and organic nutrients that promote plant life, especially algae, which can cause a reduction in dissolved oxygen as the algal population collapse and biological oxygen demand increases.
Fish kill	The sudden and mass death of aquatic animals due to the introduction of pollutants or the reduction of dissolved oxygen concentration in a waterbody.
Fractionation	A separation process in which a mixture (solid, liquid, solute, suspension or isotope) is divided up in a number of smaller quantities (fractions) and the composition changes according to a gradient. For example, fractionation of sulfur by sulfate-reducing bacteria, where bacteria use the lighter sulfur isotope (^{32}S) preferentially to the heavier sulfur isotope (^{34}S), which results in a change in isotopic composition of the resulting sulfide relative to the starting material.
Guidelines	Values or ranges of acceptable or unacceptable levels of a chemical, beyond which a management response is usually triggered.
Holocene period	A geological epoch at the end of the last Ice Age which began approximately 10 000 years ago and is characterised by the development of human civilisations.

Hotspots	In the context of this project: areas which show clear signals of acidity by either iso-group classification or extremely high concentrations of iron and/or aluminium
Hydrolysis	Chemical reaction involving water and the oxidation of a compound.
Iso-group	In the context of this project: groupings that categorise the signal of acidic drainage using a combination of both sulfur stable isotope and sulfate and chloride analysis.
Isotope	One of several nuclides having the same number of protons in their nuclei, but with different numbers of neutrons, resulting in a very slight variation in the mass of the element.
Isotopically light	The substance which is enriched in the lighter isotope relative to the composition of another substance; for example, low $\delta^{34}S$ value (relative to another).
Leaching	The loss of mineral and organic solutes from the soil matrix due to percolation. It is a mechanism of soil formation and acidic drainage.
LOR	Limit of reporting. The lower limit of reliability given by the laboratory responsible for carrying out the analysis. Greater than the limit of detection (LOD).
Median	The middle value of an ordered set of values. It indicates the centre line of a distribution, while the mean (average) can be skewed by a single high or low value.
Metal mobilisation	Metals such as aluminium, iron, cadmium and zinc that are bound to organic or mineral components of the soil matrix which when dissolved can be redistributed to other areas of the landscape.
Multi-dimensional scaling	A multivariate statistical technique which aims to develop spatial structure from numerical data by estimating the differences and similarities between analytical units. The resulting locations are commonly displayed in a 2D or 3D visualisation.
Multi-parameter probe	Often refers to a handheld water quality meter that measures parameters in the field (in situ). Parameters can include: pH, temperature, dissolved oxygen, electrolytic conductivity, redox, turbidity and salinity. Water quality data is collected by submersing the sensor in the water to indicate environmental conditions.
Non-parametric	Statistical procedures which are not based on the dimensional units of the measured observation, rather these procedures usually use the rank order of observations.
Oxidation	The loss of electrons accompanied by an increase in oxidation state. This process does not necessarily require the presence of oxygen.
pH	A log scale for indicating the acidity of a solution in terms of hydrogen

	ion concentration.
Precipitate	The solid formed when two solutions are mixed together which have an insoluble product.
Redox	In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons and is measured in volts (V), millivolts (mV), or Eh (1 Eh = 1 mV). Because the absolute potentials are difficult to accurately measure, reduction potentials are defined relative to the standard hydrogen electrode which is arbitrarily given a potential of 0.00 V.
Reduction	The gain of electrons accompanied by a decrease in oxidation state.
Replicate sample	A second sample taken from the same site at the same time, using exactly the same methods. They are representative of the same environmental condition and used to evaluate the variability of the environment and to establish how reproducible the sample is.
Salinity	Measures the concentration of dissociated salts in a solution (commonly Na^+, Ca^{+2}, Mg^{+2}, Cl^-, CO_3^{-2}), recorded in practical salinity units (psu) or parts per thousand (ppt). Salinity ranges from fresh 0-<5, brackish 5-25, and saline >25 ppt. Marine waters are generally 32-38 ppt.
Sulfides	Group of minerals that are compounds of one or more metallic elements combined with the non-metallic element sulfur; for example, pyrite FeS_2, or galena PbS.
Surface waters	Waterways that include estuaries, rivers, drains, lakes and wetlands. Does not include groundwater or pore water.
Sulfate-reduction	The microbially catalysed process which converts sulfate ($SO_4^{2-}{}_{(aq)}$) to sulfide ($S^{2-}{}_{(aq)}$).
Sulfur isotope	Forms of sulfur with the same number of protons but differing numbers of neutrons; for example, S^{34} with one additional neutron per molecule is the second-most abundant (4.2%) of sulfur isotopes (c.f. S^{32} abundant 95% – the common form).
Trophic web	A set of interconnected relationships by which energy and materials circulate within an ecosystem. The food web is divided into two broad categories: the grazing web - materials typically pass from plants to plant eaters (herbivores) to flesh eaters (carnivores) (plants) and the detrital web (organic debris); the detrital web - materials pass from plant and animal matter to bacteria and fungi (decomposers), then to detrital feeders (detritivores), and then to their predators (carnivores).

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