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

Sediment quality in three south-western Australian estuaries

A technical report for the project Tackling acid sulfate soils on the WA coast

Looking after all our water needs

Water*Science*
technical series

Report no. WST 18
January 2010

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Tackling acid sulfate soils on the WA coast

Looking after all our water needs

KL Kilminster

Department of Water
Water science technical series
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January 2010

ISSN 1836-2869 (print)
ISSN 1836-2877 (online)

ISBN 978-1-921675-84-3 (print)
ISBN 978-1-921675-34-8 (online)

Australian Government

Acknowledgements

The Department of Water would like to thank the following people for their contribution to this publication. Dr Kieryn Kilminster wrote the report. Work contained within the report was performed by Department of Water staff (Dr Kieryn Kilminster, Dr Helen Astill, Dr Helen Nice, Ms Melinda Ranaldi, Ms Sarah Evans, Mr George Foulsham, Mr Luke Riley and Mr Alex Burgoyne) and the Marine and Freshwater Laboratory of Murdoch University. This project had collaborative links with the Swan River Trust-funded project *A baseline study of contaminants in the sediments of the Swan and Canning estuaries* and the *Baigup Reserve action plan*. We appreciate the advice received from our technical working group (Dr Jeff Turner, Professor Jeff Spickett, Dr Brad Degens, Mr Warren Hicks, Dr Jenny Stauber, Dr Jes Sammut and Professor Richard Norris) and the review provided by Dr Stuart Simpson.

Reference details

The recommended citation for this publication is:
Kilminster, KL 2010, *Sediment quality in three south-western Australian estuaries*, Water Science technical series, Report no. 18, Department of Water, Western Australia.

For more information about this report, contact Dr Kieryn Kilminster, Water Science branch, Department of Water.

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Summary

The creation of acid and mobilisation of metals is the likely result when acid sulfate soils are disturbed within the landscape (e.g. by dewatering, digging, excavation or lowering of watertables). Contamination of sediment within an estuary may occur when metal-rich acidic water (i.e. acidic drainage) discharges into the pH-buffered waters and results in the precipitation of metals. Sediment from 20 sites within the Swan-Canning estuary, six sites within the Peel-Harvey estuary and 10 sites within the Leschenault Inlet were analysed for signs of contamination by acidic drainage from disturbed acid sulfate soils.

The Swan-Canning estuary had the most variable sediment quality. Sediments from estuary sites near Claisebrook, Burswood, Maylands, Belmont and Perth's central business district posed the most risk to aquatic organisms with ANZECC & ARMCANZ[1] (2000) guidelines exceeded for zinc, lead, copper and mercury. Site-specific ecotoxicological testing could determine whether these contaminant concentrations are likely to be causing ecological harm.

Evidence from sediment quality did not suggest a significant impact from acid sulfate soils in any of the estuaries. Metal concentrations rarely exceeded ANZECC & ARMCANZ (2000) guidelines; where they did (in the Swan-Canning estuary) they were likely to reflect anthropogenic and/or historical contamination. However, concentrations of iron and aluminium were relatively high near the Yunderup dredge spoil site within the Peel-Harvey estuary (compared with the other estuaries), and high concentrations of monosulfides were also present around this area. Further sediment testing in the Peel-Harvey estuary could determine whether these sediment qualities are localised to the sites investigated, and if so, this would indicate probable impact from acid sulfate soils.

Sediment quality from these estuaries seemed similar to what was reported in previous studies undertaken approximately 20 years ago (although methodological differences made comparisons difficult). In addition, sediment appeared relatively uncontaminated compared with that from a number of estuaries worldwide and for most metals (except aluminium and iron, which were on the higher end of concentrations reported worldwide).

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[1] Australian and New Zealand Environment Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand

1 Introduction

1.1 Background to project

This study was part of *Tackling acid sulfate soils on the Western Australian coast* – a statewide project surveying indicators of acidic drainage in coastal water resources – funded by the Natural Heritage Trust and the National Plan for Salinity and Water Quality. Project funding was administered through the State Natural Resource Management Office and the Department of Water was the lead agency for the project.

1.2 Sediments in aquatic systems

Sediments are an important influence on water quality within estuaries and other aquatic systems. Sediments may act as both a sink and a source of nutrients and/or other contaminants. The physical and chemical properties of sediment will affect its ability to bind contaminants. Some of these physical and chemical properties affecting contaminant binding are a permanent characteristic of the sediment; for example, carbonate-rich sediments strongly bind phosphorus through adsorption onto calcium carbonate particles (McGlathery et al. 1994; Koch et al. 2001) and sediments with smaller particle sizes will adsorb more contaminants due to their larger surface area to volume ratio (Simpson et al. 2005). Other sediment characteristics may vary on diurnal or seasonal timescales and these include variables such as redox potential, oxygen concentration (of bottom waters or interstitial water within the sediment), sulfide content and organic matter content. Subsequent changes in these sediment characteristics may result in contaminants previously bound to the sediment being released into the water column.

Sediment quality is also important for benthic biota. Small sediment particles may be digested by sediment-dwelling organisms such as polychaetes. Contaminants including metals may then bioaccumulate within the polychaetes and potentially trophically transfer within the food chain. Where contaminants are present in sediment, growth and/or reproduction of organisms may be inhibited. Additionally, factors such as oxygen content, redox potential and organic content can affect the livelihood of animals that feed and burrow through the sediment.

1.3 Acid sulfate soil signals

The generation of acidity and mobilisation of metals is the likely result when acid sulfate soils are disturbed within the landscape (e.g. by dewatering, digging, excavation or lowering of watertables). Our conceptual understanding of how these contaminants (acidity and metals) are conveyed to estuarine waterbodies involves post-generation transport via surface water (freshwater streams) and/or groundwater. Fresh water and groundwater are typically less saline than estuarine waters. Estuarine water also has a greater acid-buffering capacity than fresh water due to the carbonate-bicarbonate equilibrium.

When metal-rich acidic water (i.e. acidic drainage) discharges into an estuary, the pH of this water is buffered to more neutral conditions by the estuarine water. Metals are typically more soluble in acid conditions, so as neutralisation of the water occurs the metals precipitate (forming mainly oxides and hydroxides) and may flocculate. These flocculated metal precipitates can accumulate on sediment surfaces.

Processes by which sediment may become contaminated by acidic drainage are summarised in the conceptual diagram shown in Figure 1. If acidic drainage is transported through groundwater, the area of sediment contamination is most likely to be localised to the area of groundwater intrusion. If transport of acidic drainage involves surface freshwater inflows, then the area of contamination would most probably occur adjacent to the drain discharge area where mixing of fresh and more saline water occurs. Contamination associated with drainage has been observed previously in the Swan River, where concentrations of lead were significantly higher adjacent to drains than in areas without drain influence (Rate et al. 2000). Physical processes such as sediment re-suspension, scouring and dispersion may act to redistribute these contaminated sediments spatially within the estuary.

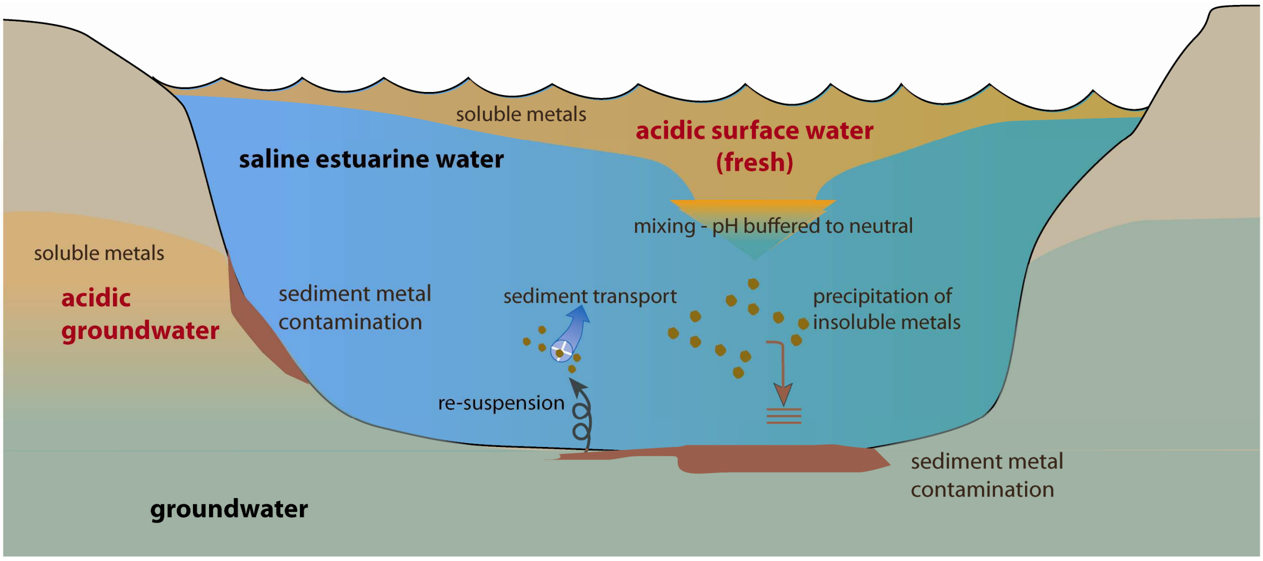

Figure 1 *Conceptual diagram of sediment contamination from acidic drainage.*

2 Aims and scope

2.1 Objective

This study's objective was to determine the sediment quality of three estuaries in the south-west of Western Australia, namely the Swan-Canning estuary, the Peel-Harvey estuary and the Leschenault Inlet. The study's primary aim was to investigate sediment quality with reference to signals of acidic drainage from disturbed acid sulfate soils, although the comparative study of sediment quality may have broader relevance.

2.2 Study sites

Sediment from 20 sites within the Swan-Canning estuary, six sites within the Peel-Harvey estuary and 10 sites within the Leschenault Inlet were analysed for signs of contamination from acidic drainage (Figure 2).

The Swan-Canning estuary is located in the Perth metropolitan area (population approximately 1.5 million) and receives river flow from both the Avon and Swan coastal catchments. Within these catchments are urban, agricultural and industrial land uses. The estuary is variable in depth (up to 20 m) and has a low tidal range. Heavy rainfall in the winter results in the whole estuary becoming fresh (Hill et al. 1991).

The Peel-Harvey estuary is located near Mandurah (population approximately 68 000) about 75 km south of Perth. The estuary system connects two coastal lagoons, the Peel Inlet (an almost circular basin) and the Harvey Estuary, and is fed by the Serpentine, Murray and Harvey rivers. The catchments are dominated by agriculture and increasing urbanisation. The Peel-Harvey estuary itself is typically shallow (<1.5 m) and highly eutrophic (Lavery et al. 1991; McComb et al. 1998). The construction of the Dawesville Channel (a man-made connection to the ocean completed in 1994) resulted in a greater flushing and marine influence on the Peel-Harvey estuary. The channel also reduced the frequency of algal blooms which were previously common (i.e. several per year).

The Leschenault Inlet (also known as the Leschenault Estuary) is located near Bunbury (population approximately 58 000) about 180 km south of Perth. The estuary is fed by the Preston and Collie rivers, from mostly agricultural catchments. There is increasing urban pressure on the estuary, with septic tanks rather than infill sewerage common in the Australind region. The estuary is approximately 11 km long and 2 km wide, with an average depth of <2 m (McComb et al. 2000).

The study sites were chosen according to selection criteria appropriate to investigations associated with each estuarine system. The Swan-Canning estuary sites linked with the Swan River Trust-funded project *A baseline study of contaminants in the sediments of the Swan and Canning estuaries* (Nice 2009). The Peel-Harvey estuary sites linked with a project assessing metal bioaccumulation effects on caged mussels, and the Leschenault Inlet sites linked with a project assessing metal bioaccumulation of seagrasses.

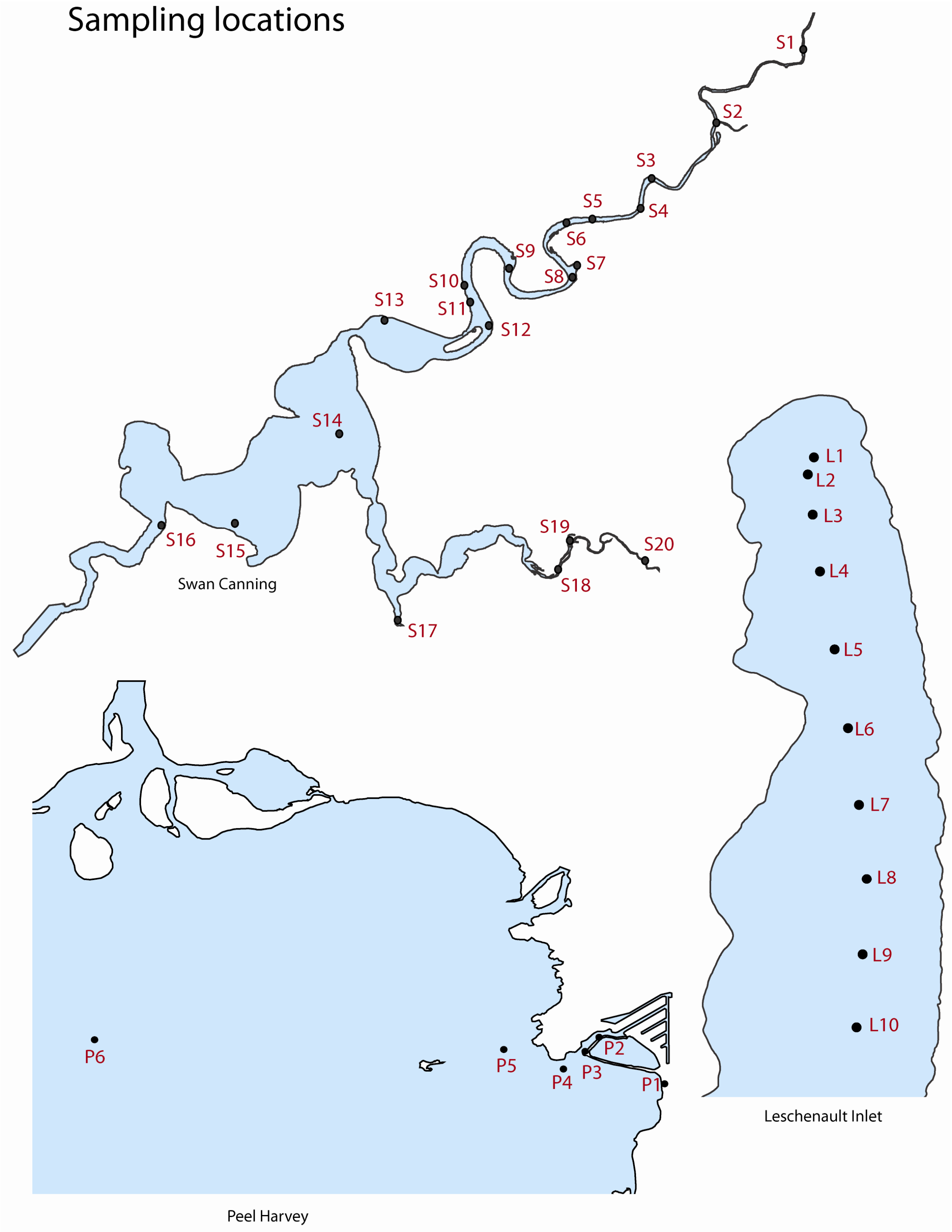

Figure 2 *Study sites sampled for sediment within the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet.*

2.3 Sampling and analysis

Sediment quality was investigated during the late spring to late summer of 2007–08. The Swan-Canning estuary was sampled in November 2007, the Peel-Harvey estuary in December 2007 and Leschenault Inlet in February 2008. All samples for a site were collected within a 20 m^2 area. Divers collected the samples using 9.4 cm diameter polycarbonate cores pressed gently into the sediment to minimise disturbance to the sediment surface layer. Rubber stoppers were inserted to seal the top of the core, allowing the sediment cores to be retrieved. Cores were transported upright to the boat for processing. The top 3 cm from five cores (collected within a 1 m^2 area) were composited to form a single sample. Five replicate samples were collected at each site. Sampling the top 2 cm of sediment is recommended for determining contamination associated with recent sedimentation (Simpson et al. 2005), but in this study the top 3 cm of sediment was sampled to allow comparisons with previous studies.

A subsample of sediment from each site was analysed in the field for redox potential (and pH for the Peel-Harvey estuary) using an intermediate junction redox sensor and pH electrode (TPS, Aust.). Samples were placed in plastic zip-lock bags with air excluded before sealing. Samples from the Swan-Canning estuary were kept on ice and delivered the same day to the National Measurement Institute (NMI) where analysis was performed. NMI analysed sediment for all variables (Table 1) except particle size, which was carried out by the Commonwealth Scientific and Industrial Research Organisation (CSIRO). Sediment samples from the Peel-Harvey estuary and Leschenault Inlet were kept on ice in the field and then frozen before transport to Southern Cross University (Environmental Analysis Laboratory) for all analyses (Table 1). The design of these studies varied slightly between locations, as each study had independent objectives. Sampling protocol was identical and many parameters analysed were consistent across the three estuarine systems studied (Table 1). All laboratories used are National Association of Testing Authorities (NATA) accredited and quality control and quality assurance results are reported in Appendix B.

2.4 Rationale for analytes measured

Metals and metalloids may accumulate within the sediment when contaminated groundwater or surface water is discharged into the estuary. Two commonly used methods to measure the quantity of metal and metalloid contamination in sediments both involve analysing an acid extract from the sediment using inductively coupled plasma techniques. ‘Total metals’ is an exhaustive acid extraction with aqua regia digestion, and may also dissolve a significant proportion of the sediment matrix. A more biologically relevant measure is HCl-extractable metals (sometimes referred to as ‘bioavailable metals’, although this analysis does not provide information about bioavailability to organisms). HCl-extractable metals are extracted with a dilute acid (1 M HCl for 1 hour), and thus the extract contains the most readily mobilised metals associated with the sediment matrix. Metals and metalloids measured in this study were: silver, aluminium, arsenic, cadmium, chromium, copper, cobalt, iron, mercury, manganese, molybdenum, nickel, lead, selenium and zinc.

Table 1 *Sediment analysis matrix for sampling within the three estuaries.*

	Swan Canning	Peel Harvey	Leschenault
Number of sites	20	6	10
Replicates	5	5	5
Field measurements			
Redox potential	✓	✓	✓
pH		✓	
Laboratory analyses			
Chromium reducible sulfur (S_{Cr})	✓	✓	✓
Acid volatile sulfur (AVS)		✓	✓
Acid neutralising capacity (ANC)	✓		✓
HCl-extractable metal suite[a]	✓	✓	✓
Total metals suite[b]		✓	✓
Total organic carbon	✓	✓	✓
Total sulfur	✓	✓	✓
Total nitrogen, Total phosphorus	✓		✓
Moisture content	✓	✓	✓
Particle size[c]	✓	✓	✓

[a] HCl-extractable metals – 1M HCl for 1 hour (Ag, Al, As, Cd, Cr, Cu, Co, Fe, Hg, Mn, Mo, Ni, Pb, Se, Zn). Silver was not analysed for Swan Canning sediments

[b] total metals – aqua regia digest (Ag, Al, As, Cd, Cr, Cu, Co, Fe, Hg, Mn, Mo, Ni, Pb, Se, Zn)

[c] particle size analysis – results are displayed as % sand (>63 µm) and % mud (<63 µm) although finer-scale data exists for the Swan Canning sediments

Reduced sulfur, in the form of sulfide minerals, may be generated within the estuary or washed (without the complete re-oxidation of the reduced sediments) from drains and rivers into the sediment of the main estuary. It also may be possible for reduced sulfur to be carried as bedload in some systems. Acid sulfate soil materials within sediments are comprised of two types of reduced sulfur compounds: monosulfides and pyrite. Iron monosulfides ($FeS_{(s)}$) vary in form and include the (semi)amorphous sulfides, mackinawite and greigite. These iron sulfides are formed under reducing conditions, and have traditionally been considered as precursors for pyrite formation (although recent research suggests that another pathway mechanism exists that does not require iron sulfide as a precursor for pyrite formation (Rickard & Morse 2005)). Acid volatile sulfur (AVS) and chromium reducible sulfur (S_{Cr}) are measures that determine the reduced sulfur within sediments. AVS determines the sulfide concentration within the sediment that is soluble in acid (cold 9 M HCl, 18 hr). These are typically considered to be metastable monosulfides, and are dominated by the dissolved sulfide species aqueous FeS clusters, but may include HS^-, H_2S, mackinawite, greigite and polysulfides (Rickard & Morse 2005). Some evidence suggests that the solubility of monosulfides under weakly acidic conditions varies for different metal sulfides (Cooper & Morse 1998), so the determination of AVS does not completely characterise all metal monosulfides within a sediment sample.

Chromium reducible sulfur provides a measure of reduced sulfur that includes pyrite ($FeS_{2(s)}$), elemental sulfur, and the more stable monosulfide fractions (some FeS and H_2S are likely to be lost on drying of sediment before analysis). Within-estuary production of these sulfidic materials may be enhanced by eutrophication, where an imbalance of organic matter in the system leads to high rates of mineralisation by sulfate-reducing bacteria.

Acid neutralising capacity (ANC) provides a measure of the internal buffering capacity of a sediment (or soil) to withstand acidification. The ANC within estuarine sediments is most commonly provided by carbonate minerals (shells, limestone). This is an important consideration for dredging activities involving sediment disposal, where knowledge of the ANC is required as part of the calculation of the net acid-generating capacity of the sediment.

Particle size: contaminants that accumulate via adsorption to particles will have the highest concentration on the finest particles within the sediment, as these have relatively more surface area than coarse particles (Simpson et al. 2005).

Redox potential is the oxidative/reductive potential of a sediment measured as the potential difference between an inert indicator electrode and a reference cell. Results are reported relative to the hydrogen half-cell (Eh). Raw data may require an adjustment for the reference half-cell actually used in the field measurement. Field measurements of Eh must be regarded as an integrated variable, as actual redox potential is highly heterogeneous when measured within sediment microprofiles (i.e. at a finer scale than measured in this study). It provides information about the dominant sedimentary microbial reductive processes occurring within the sediment profile: above 300 mV microbial processes are typically oxic, from 300 mV to -50 mV the processes are typically facultative with O_2, NO_3^-, Mn^{4+}, Fe^{3+} successively the preferred electron acceptors. Below -50 mV, sulfate-reduction and methanogenesis dominates. Additionally, redox condition affects many aspects of geochemistry as the cycling of nutrients and metals are commonly redox-dependent processes. For example, Fe- and Mn- bound phosphorus within the sediment is released into solution under low Eh conditions (Olila & Reddy 1997).

Total organic carbon is a measure of the percentage of carbon by weight within a dried sediment sample. Organic matter enrichment of sediment may be associated with either eutrophication or monosulfidic black ooze production.

Total sulfur is expressed as the percentage of sulfur by weight within a dried sediment sample. It is important to consider in estuarine systems, because the concentration of sulfur available to be converted into 'reduced sulfur' is likely to vary spatially within the estuary due to tidal influence and the mixing of sulfate-rich ocean water.

Total nitrogen and phosphorus provide a measure of the nutrient concentrations bound to the sediments. These parameters are not directly related to indicators of acidic drainage, but may reflect eutrophication pressures.

Moisture content is the percentage of water by weight present in the sediment sample and is determined gravimetrically by measuring the mass of water lost following drying at 110℃ to constant weight. Although it is usual to report concentrations of analytes in sediment as relative to the dry weight, it may be preferable to perform contaminant analysis on wet sediment because drying may alter the chemistry and/or increase volatisation of contaminants, thus resulting in losses of contaminants. Water content measurements are therefore required to convert the data to conventional dry weight units.

2.5 Derived parameters

Estimates of the degree to which reduced inorganic sulfurs are converted to pyrite may be used to describe the nature of the sedimentary depositional environment (Leventhal & Taylor 1990; Macdonald et al. 2004; Smith & Melville 2004). For these measures, chromium reducible sulfur (S_{Cr}) is converted to the amount of sulfur present within pyrite (S_{Cr} – AVS) and assumes that pyrite is the only stable sulfide mineral not liberated in the AVS. For clarity, this term will henceforth be referred to as $S_{Cr\text{-}py}$. The calculations for degree of pyritisation (DOP) and degree of sulfidisation (DOS) also require measurements of reactive iron in the depositional environment. Reactive iron (Fe_{HCl}) is usually measured following a 1 M hydrochloric acid extraction of the sediment for 24 hours. Fe_{HCl} is mainly non-silicate-bound iron, including amorphous iron oxides and oxyhydroxides, some crystalline iron oxides and iron monosulfides. The DOP (Equation 1) estimates the percentage of the total reactive iron that has been converted into pyrite, and assumes $S_{Cr\text{-}py}$ contains only pyrite and neither other metal monosulfides nor elemental sulfur. The DOS (Equation 2) estimates the percentage of the total reactive iron converted into either iron monosulfides (FeS) or pyrite. DOS is often used for environments with high concentrations of iron monosulfides present, and may provide a better indication of iron-limiting conditions in these environments.

Equation 1

$$\mathrm{DOP} = 100 \times \frac{\mathrm{Fe}_{\mathrm{SCr\text{-}py}}}{(\mathrm{Fe}_{\mathrm{SCr\text{-}py}} + \mathrm{Fe}_{\mathrm{HCl}})}$$

where $Fe_{SCr\text{-}py}$ *is the concentration of iron associated with sulfur from* $S_{Cr\text{-}py}$*, and* Fe_{HCl} *is the concentration of acid-extractable iron (with all concentrations as %).*

Equation 2

$$\mathrm{DOS} = 100 \times \frac{(\mathrm{Fe}_{\mathrm{SCr\text{-}py}} + \mathrm{Fe}_{\mathrm{AVS}})}{(\mathrm{Fe}_{\mathrm{SCr\text{-}py}} + \mathrm{Fe}_{\mathrm{HCl}})}$$

where Fe_{AVS} *is the concentration of iron associated with sulfur from AVS,* $Fe_{\mathrm{SCr\text{-}py}}$ *is the concentration of iron associated with sulfur from* $\mathrm{S}_{\mathrm{Cr\text{-}py}}$*, and* Fe_{HCl} *is the concentration of acid-extractable iron (with all concentrations as %).*

2.6 Data analysis

Results from each laboratory measurement were checked for normality and log-transformed if necessary. The computer software package PRIMER 6 + PERMANOVA was used to explore multivariate data relationships in sediment chemistry. Further details about the statistical routines employed in PRIMER (Plymouth Routines in Multivariate Ecological Research) and PERMANOVA (Permutational Multivariate Analysis of Variance) can be found in Clarke and Warwick (2001) and Anderson et al. (2008). Data was standardised within PRIMER (normalise function) before further multivariate data analysis (e.g. principal components analysis and PERMANOVA). Sigmaplot version 10 (Systat Software Inc.) was used for graphical representations of data, which were then applied to maps in Adobe Illustrator (CS3).

3 Results

3.1 Spatial distribution

Data for HCl-extractable metals, carbon and sulfur were transformed and normalised and the resultant euclidian-distance-based resemblance matrix was analysed with Permutational Multivariate Analysis of Variance (PERMANOVA) for the effect of region and site (nested within region). The PERMANOVA gave significant results for both region ($p<0.0001$, $F=7.2$) and site ($p<0.0001$, $F=22.6$). Differences in dispersion may have contributed to the regional effect as the Leschenault Inlet sites were highly clustered and the Swan-Canning estuary had the largest variation between sites (Figure 3). Replicate samples from a single site were generally close to each other in the multidimensional scaling (MDS) plot (Figure 3), suggesting that differences between sites were often larger than the heterogeneity observed within replicate sediment samples. The large variation in samples from the Swan-Canning estuary could be due to the variable physical nature of the Swan-Canning estuary (in terms of expected hydrodynamics, water depth, flow and riverine inputs). Sites in the Peel-Harvey estuary and Leschenault Inlet had more constant physical properties, with little tidal influence and fairly constant salinity and depth. Additionally, the Swan-Canning estuary has considerable urban pressure, with a surrounding population more than 20 times greater than the populations of the other regions. This urban pressure may also have been a substantial influence on the measured variables. Average values for particle size, TOC, Eh, S_{Cr} and TS measured at each site have been displayed spatially in figures 4–7. Average acid-extractable concentrations for the metals Cr, Zn, Cu, Pb, Fe and Al are displayed spatially in figures 10–12. Averages for all variables are reported in Appendix A (tables 8 and 9).

Particle size

Sediment particle size distribution (% sand: proportion greater than 63 μm, and % mud: proportion less than 63 μm) was compared across the estuaries (Figure 4). Sediment from the Leschenault Inlet sites generally had the greatest proportion of mud relative to the other estuaries with an average of 48% of the sediment particles less than 63 μm. The Peel-Harvey estuary was sandier, with almost 70% of sediment sampled having a grain size greater than 63 μm. The Swan-Canning estuary was the sandiest of the estuaries, with more than 80% of sediment sampled having a grain size greater than 63 μm.

Total organic carbon (TOC)

Total organic carbon (TOC) was most variable within the Swan-Canning estuarine sediments, ranging from 0.4–17% (Figure 5) with the highest loading of organic matter at the Perth central business district site (S13). Moderately-high loads of TOC were also measured near Belmont (S9), Maylands (S10), and Claisebrook (S11) (4.5–5.3%). Moderately high concentrations of TOC (5–8%) were also observed at sites near Yunderup in the Peel-Harvey estuary. In contrast only about 2% TOC was observed at the site furthest away from land (P6) in the Peel-Harvey estuary basin. The organic matter concentration measured within sediments in the Leschenault Inlet was more consistent, ranging from 2.5–4.9% for all sites.

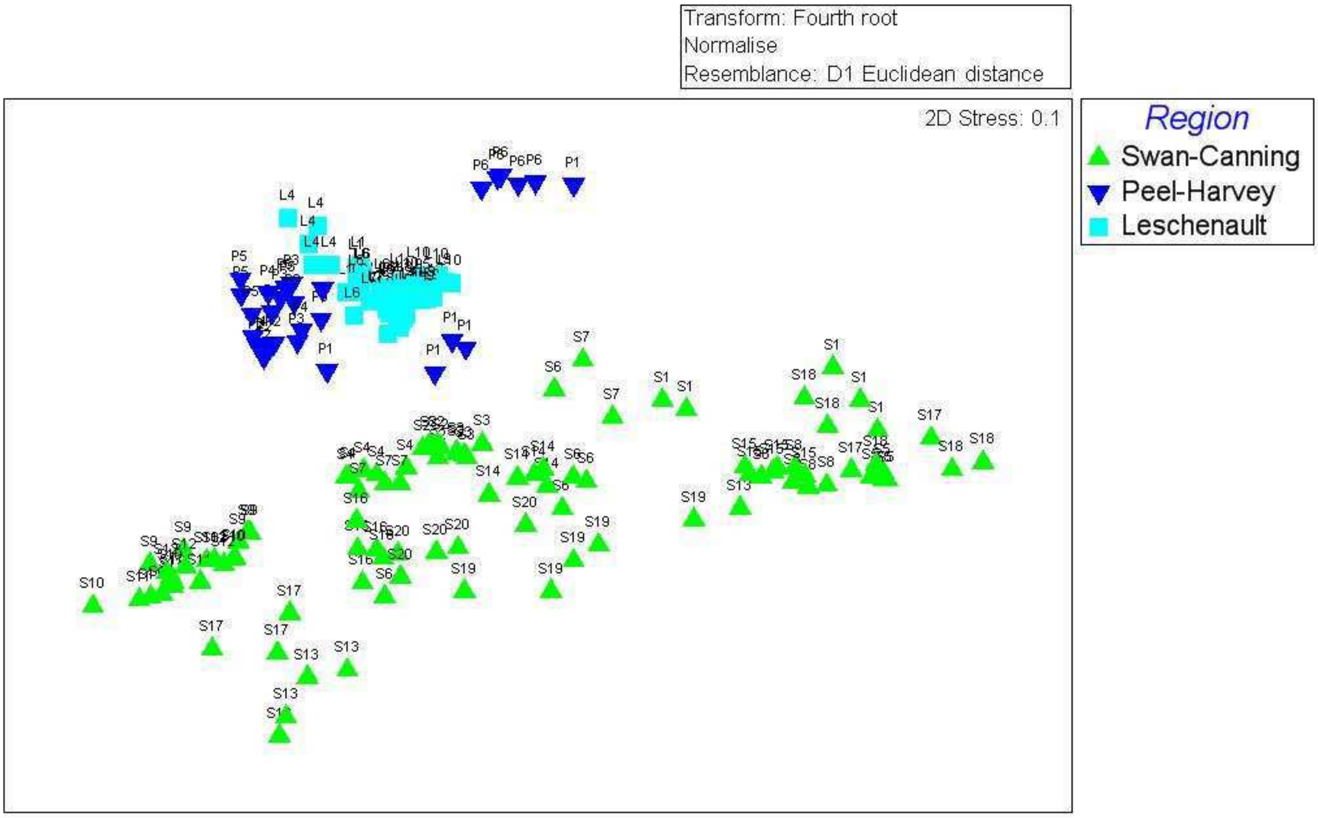

Figure 3 *Multidimensional scaling (MDS) plot of replicate samples within the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet (with HCl-extractable metals, carbon and sulfur measurements as variables).*

Redox potential (Eh)

Redox potential, measured in situ, ranged from -160 mV to 200 mV across sediment sampled within the three estuaries (Figure 6). These measures are an integrated redox potential for the top 3 cm and we would expect this to be the most oxic sediment zone in unvegetated sediment, with the sediment becoming progressively more anoxic with depth.

Sediment redox potential (Eh) was generally positive for the Swan-Canning estuary sites with a maximum Eh of 190 mV at S8. The exception was the Perth central business district (S13) where the Eh measured was -99 mV, suggesting that sulfate-reduction may be occurring near the sediment surface at this site.

Eh measured within the Peel-Harvey estuary sediments was negative for all sites (-54 to -160 mV), again suggesting that sulfate-reduction and perhaps methanogenesis may be occurring in the top few centimetres of the sediment. The sites near the shore (P1–P5) had more negative Eh than site P6.

The Eh measured in the Leschenault Inlet sediments was mostly positive. It is probable that the value for L1 is actually an artefact of the sampling method because the sediment was transported by wading (the water depth was too shallow to reach by boat). This delayed the measurement of Eh at L1 and may have resulted in an artificially high value.

The inlet's negative Eh measurements were for sites L3 and L4 (-90 and -120 mV respectively). The aquatic vegetation changed from being dominated by *Ruppia megacarpa* to *Halophila ovalis* between sites L4 and L5. Both sites also had drift macroalgae present. From stable carbon isotope analysis and bacterial biomarkers, macroalgae has previously been shown to be a preferential carbon source for bacterial decomposition to seagrass (*Posidonia oceanica*) (Holmer et al. 2004). The macroalgae, mainly present as the charophyte *Lamprothamnium papulosum*, may have provided a more labile source of organic matter (compared with the macrophytes) and resulted in increased microbial mineralisation. Lower Eh would result in increased rates of microbial activity ultimately dependent on the more 'unfavourable' electron acceptors such as Fe(II), Mn(IV) and SO_4^{2-}.

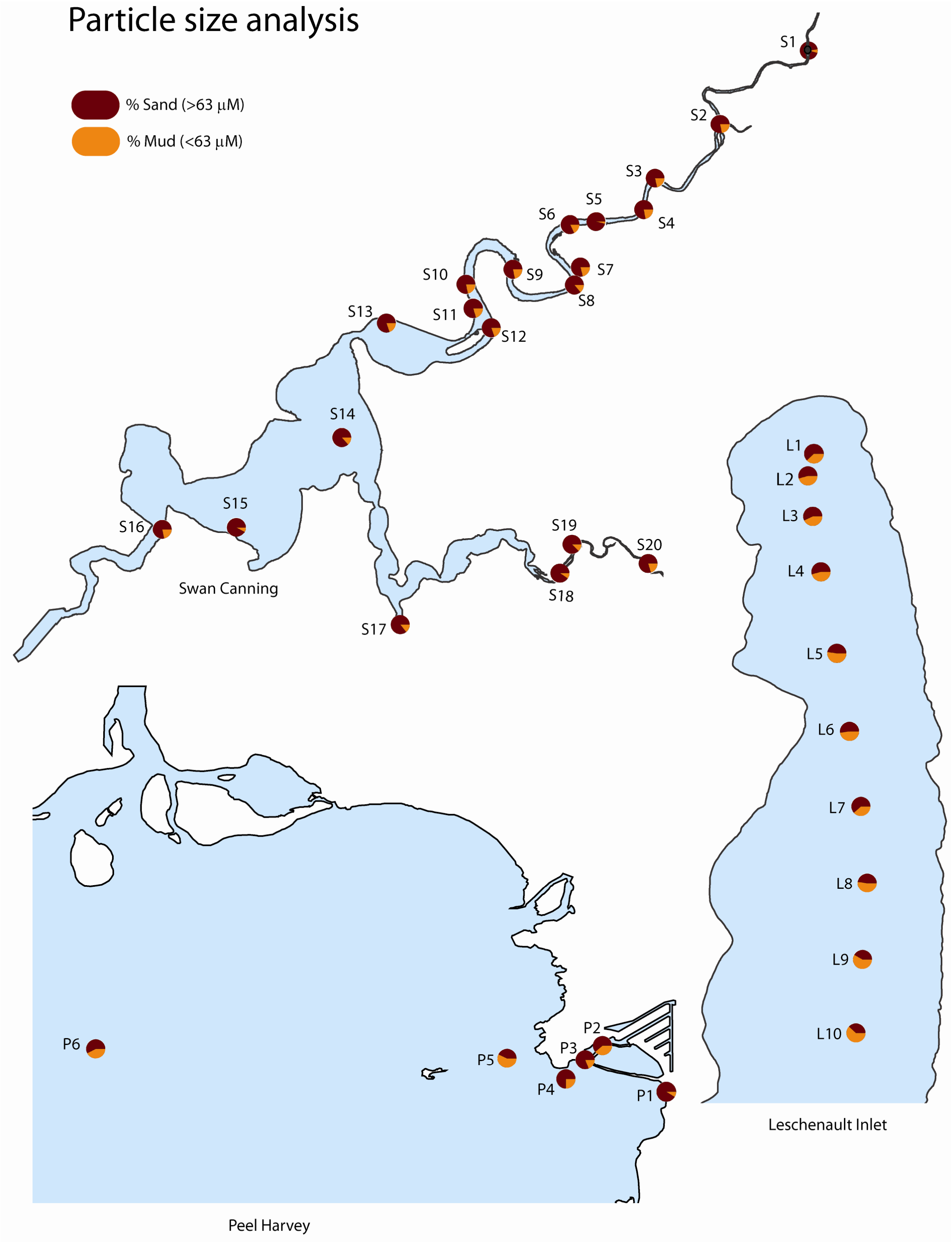

Figure 4 *Average particle size distribution for sediment sampled within the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The proportion of sand to mud is shown by the relative shaded areas of colour in each of the circles.*

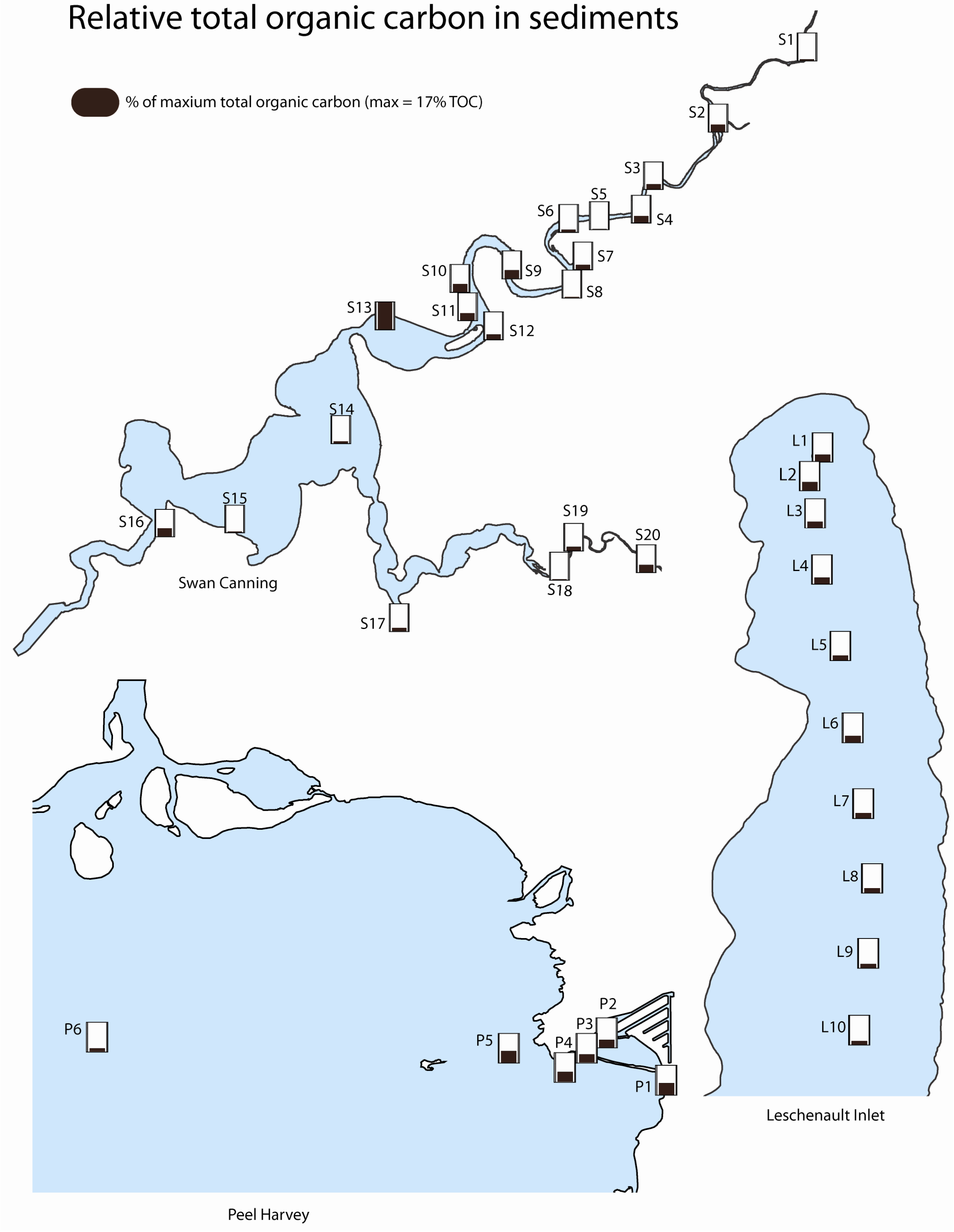

Figure 5 *Average total organic matter (as a percentage of maximum organic matter observed) within sediment from the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The size of the bar that denotes the TOC content is normalised to the highest measured concentration at any site (i.e. 17 % at S13).*

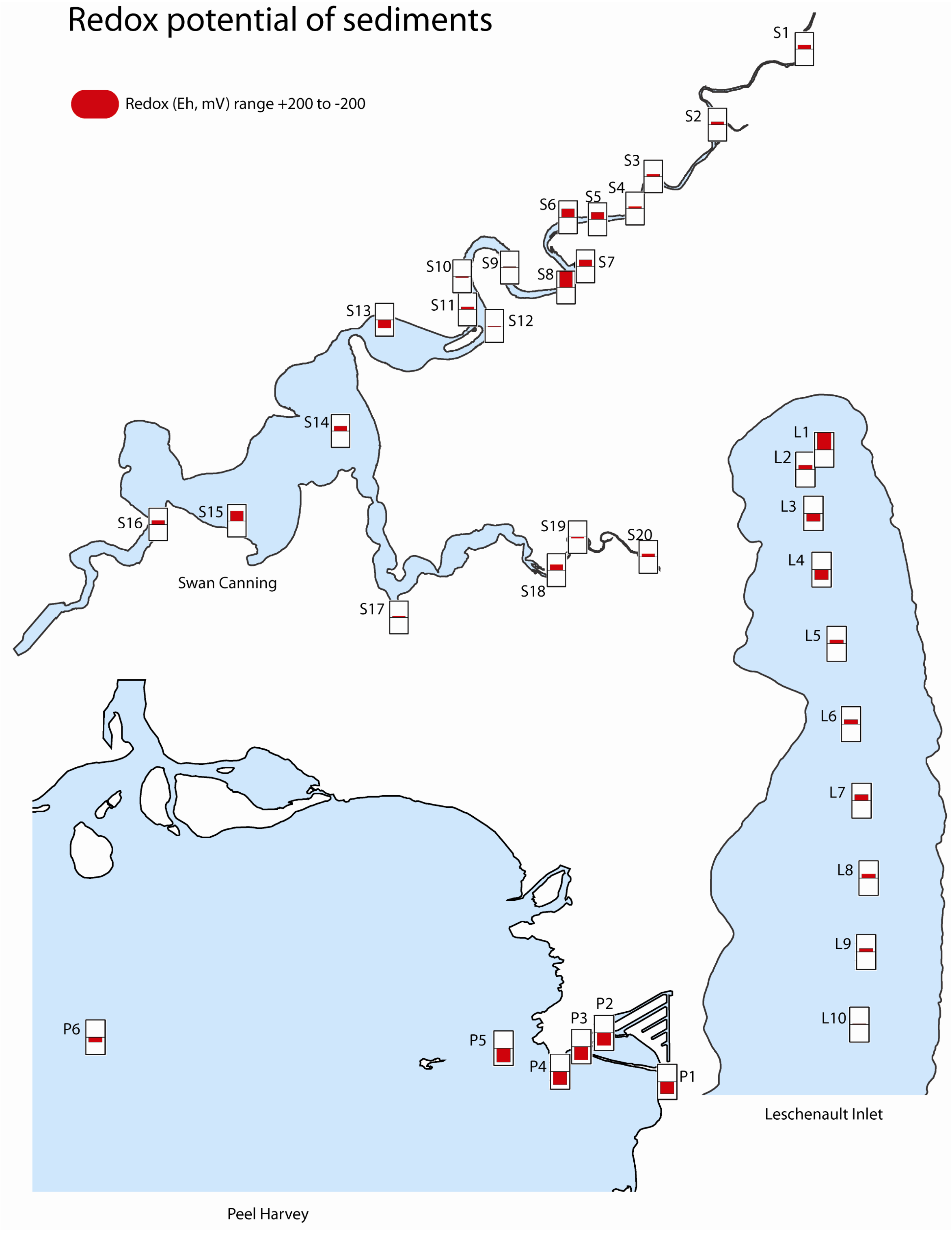

Figure 6 *Average redox potential (Eh range +200 to -200 mV) within sediments from the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The scale of the bar denotes the redox potential of sediments between -200 mV and +200 mV, with the highest Eh recorded at L1 (198 mV at S8), although this is probably an artefact of sampling (see text).*

Chromium reducible sulfur and total sulfur

The mineralisation of organic matter by bacterial sulfate-reduction produces ‘free’ sulfide (S^{2-}), which then forms an equilibrium in water with HS^- and H_2S. However, the availability of the free reduced sulfides in sediment porewater is a function of the availability and redox state of sulfide-precipitable cations (such as ions of iron, manganese, copper and other transition metals) within the sediment (Billon et al. 2001). Measurements of chromium reducible sulfur (S_{Cr}) are a measure of the pools of precipitated sulfides (and elemental sulfur) and are indicative of the capacity and history of the sediment to bind free sulfides. These are sometimes also reported as TRS; that is, total reduced sulfur. For estuarine systems, it may be important to consider the S_{Cr} in conjunction with the total sulfur (TS) concentration because spatial variability in the availability of sulfur may influence the formation of reduced inorganic sulfur.

The Swan-Canning estuary showed the greatest variation in water-column salinity (from 4.2 to 34 ppt at the time of sampling) among the sites selected for sediment analysis, relative to the other two estuaries investigated. TS concentrations co-vary with salinity. However, it appears that the availability of sulfur does not drive S_{Cr} abundance because no upstream/downstream gradient of S_{Cr} was associated with TS concentration (Figure 7). For all sediments sampled, more than half the TS in sediments was present as reduced sulfur. In the Swan-Canning estuary, on average 54 ± 23% of the TS was measured as S_{Cr}. Sites S14 (Melville Water), S15 (Applecross) and S16 (Blackwall Reach) showed a lower proportion of reduced sulfur to TS (14 ± 1%, 28 ± 4%, 22 ± 6% respectively), probably because these are the most marine-influenced sites within the estuary and sulfur would be abundantly available. For sites in the Peel-Harvey estuary and Leschenault Inlet, the proportion of TS present as reduced sulfur was slightly higher and less variable than the Swan-Canning estuary at 57 ± 9% and 65 ± 9% respectively (mean ± standard deviation).

Spatially, the Swan-Canning estuarine sediments showed highly variable sulfur concentrations. Sites in the upper Swan River appear to have higher S_{Cr} and TS than those in the upper Canning. The highest S_{Cr} (1.17%) in the Swan-Canning estuary was measured at the central Belmont site (S7) and the lowest (0.03%) measured at the Applecross site (S15). For the Peel-Harvey estuary, the highest concentrations of S_{Cr} and TS were observed near Yunderup, and these sites (P2, P3, P4, P5) generally had higher reduced sulfur concentrations (0.95–1.70%) than in the other estuaries. Sulfur concentrations were more consistent in the Leschenault Inlet: the lowest S_{Cr} measured was 0.60% at site L10, and the highest 1.07% at site L4.

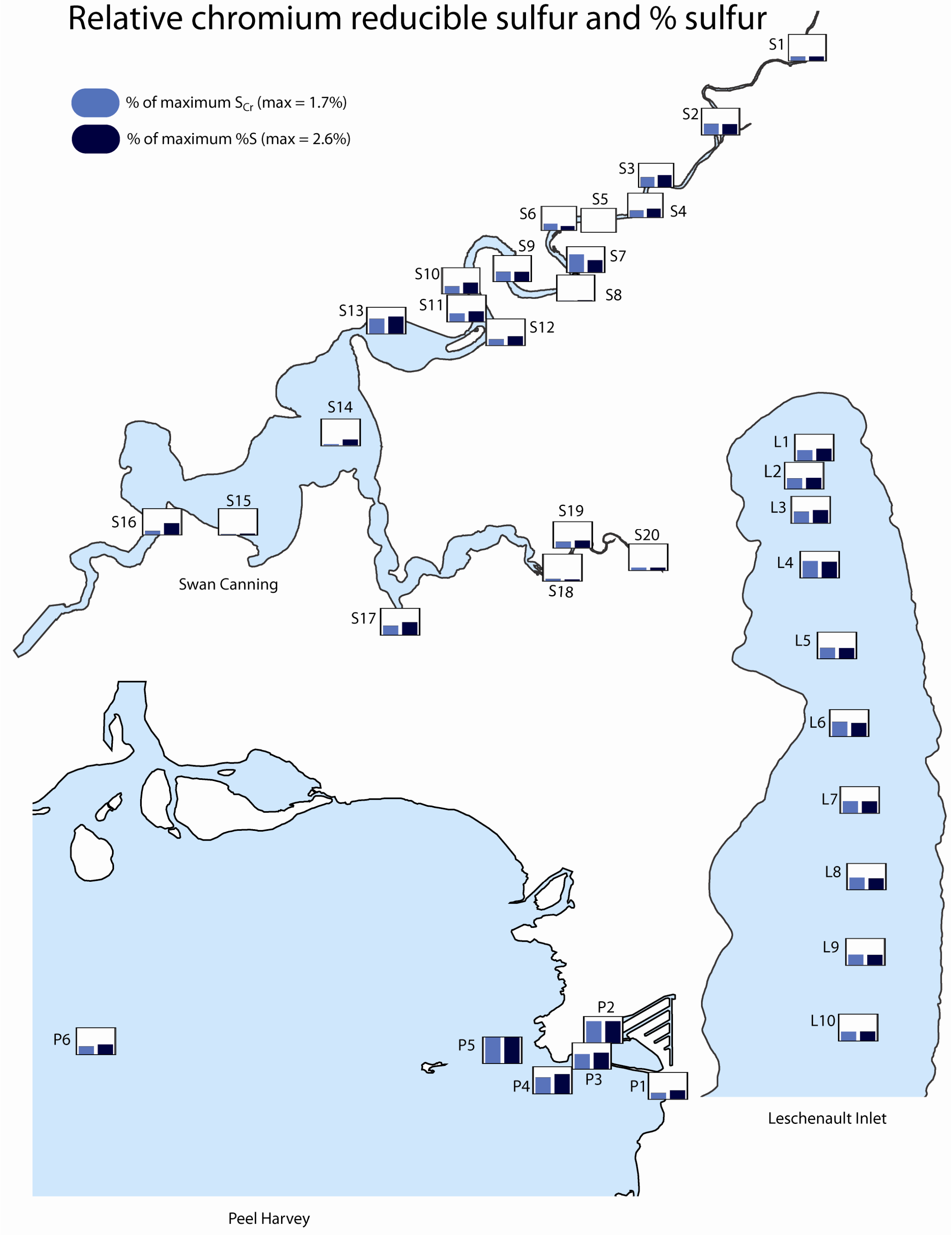

Figure 7 *Average chromium reducible sulfur and total sulfur within sediments of the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet as a percentage of the highest concentration observed (1.7% and 2.6% respectively at site P5).*

Acid volatile sulfur

Acid volatile sulfur (AVS) was only measured for the Peel-Harvey estuary and Leschenault Inlet samples, with much greater concentrations present in the Peel-Harvey estuary (Figure 8). The ratio of AVS to S_{Cr} (figures 9A and B) was significantly higher ($p<0.0001$, t-test) in the Peel-Harvey estuary samples than the Leschenault Inlet samples (0.29 and 0.09 respectively) indicating that more of the reduced sulfur is present as monosulfides such as FeS, rather than being converted to pyrite (FeS_2).

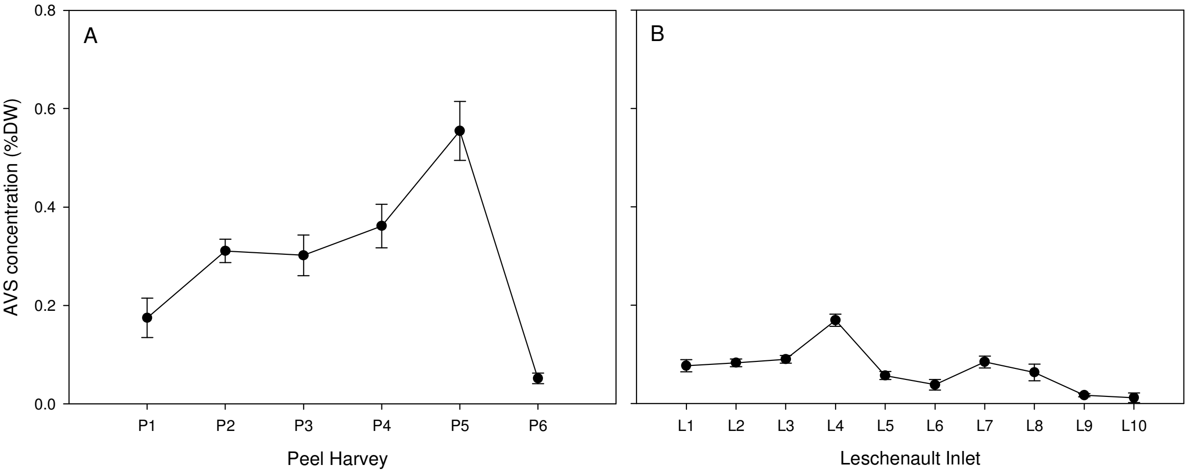

Figure 8 *Acid volatile sulfur (AVS) concentration in sediment collected from (A) Peel-Harvey estuary and (B) Leschenault Inlet (mean ± st. err).*

Conversion of iron monosulfides to pyrite

The degree of pyritisation (DOP) and degree of sulfidisation (DOS) were calculated for samples from the Peel-Harvey estuary and Leschenault Inlet, but not the Swan-Canning estuary (as acid volatile sulfur was not measured in these samples). Here the reactive iron (Fe_{HCl}) was determined by an acid digest with 1M HCl for 1 hour (HCl-extractable metals). This might have underestimated the reactive iron present, as the recommended digest was 1M HCl for 24 hours (Canfield 1989; Leventhal & Taylor 1990). The methodological difference needs to be kept in mind when comparing DOP and DOS with reported values in the literature, as lower Fe_{HCl} would overestimate DOP and DOS. Relative differences in DOP and DOS between sites and locations will not be affected.

The ratio of AVS to $S_{Cr\text{-}py}$ was much higher and much more variable in the Peel-Harvey estuary sediments than in the Leschenault Inlet sediments (figures 9A and B). At both estuaries, there was a trend for decreasing ratio the higher the site number (i.e. lower in the estuary). Larger ratios of AVS to $S_{Cr\text{-}py}$ could either be due to higher concentrations of AVS, or lower concentrations of $S_{Cr\text{-}py}$. From the data displayed in Figure 8, we can conclude that the change in the ratio is dominated by higher concentrations of AVS in the Peel-Harvey estuary than in the Leschenault Inlet.

DOP was similar across all sites within the Peel-Harvey estuary and Leschenault Inlet, where pyrite associated iron was (on average) equal to 35% of the available reactive iron, with a range of 27–43% (figures 9C and D). DOS was more variable across sites and was much higher in the Peel-Harvey estuary where iron in monosulfides or pyrite was equal to approximately 62% of available reactive iron compared with only 44% for the Leschenault Inlet (figures 9C and D).

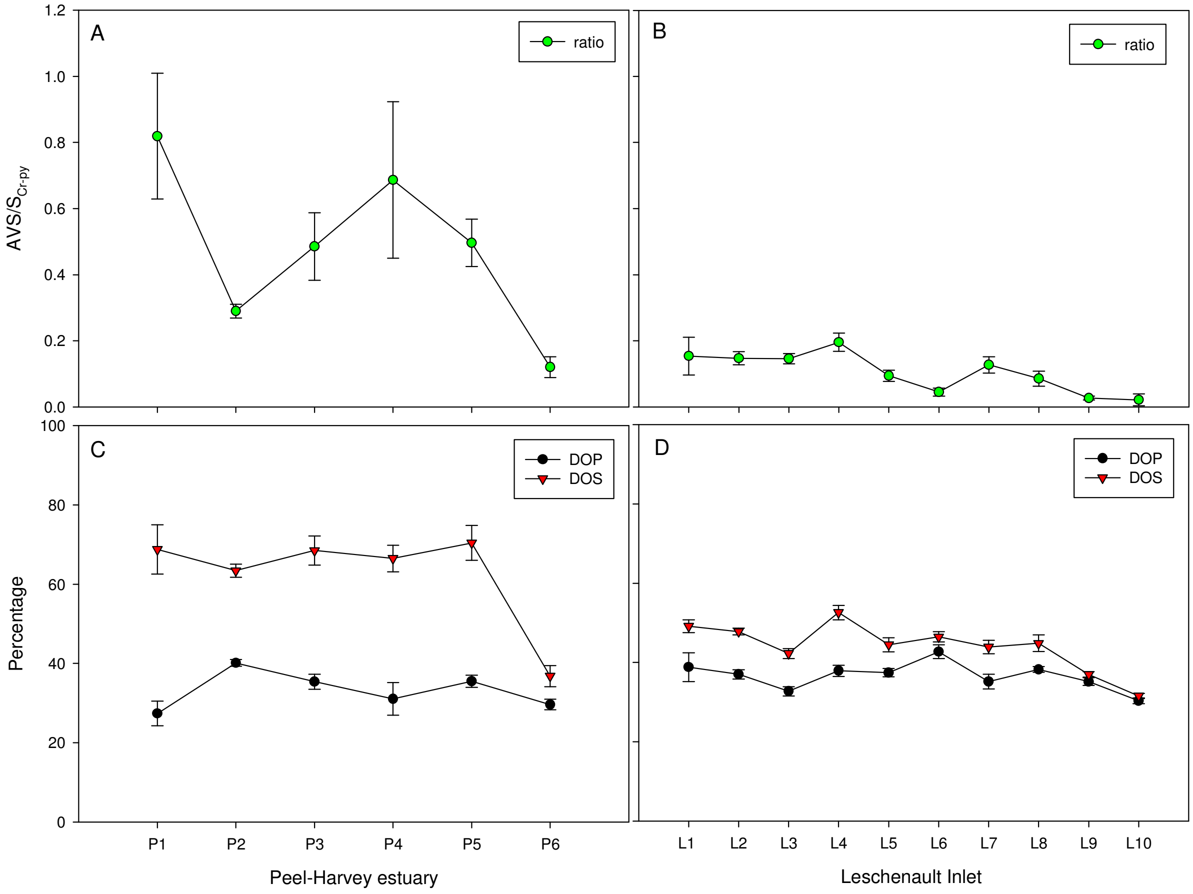

Figure 9 *Plots of the ratio of AVS to $S_{Cr\text{-}py}$ for the Peel-Harvey estuary sites (A) and the Leschenault Inlet (B), and degree of pyritisation (DOP) and degree of sulfidisation (DOS) for sites in the Peel-Harvey estuary (C) and Leschenault Inlet (D).*

HCl-extractable iron and aluminium

Iron and aluminium are metals commonly associated with disturbance of acid sulfate soils in Australia (Willett et al. 1993; Cook et al. 2000). Figure 10 shows the relative metal concentrations calculated as the percentage of the maximum concentration recorded. This enables spatial distribution of iron and aluminium to be assessed on the same relative axes. The sites with the highest HCl-extractable iron also exhibit the highest HCl-extractable aluminium concentrations; in fact these two parameters are strongly correlated (R=0.9).

Spatial distribution of iron and aluminium within the Swan-Canning estuary was highly varied. The greatest concentrations were found among sites S9–S12 and ranged from 21 900–25 600 mg kg^{-1} for iron and 3280–3760 mg kg^{-1} for aluminium. Sites with low concentrations of iron and aluminium were found in all reaches of the estuary. The highest concentrations of iron and aluminium in the Peel-Harvey estuary were found in the Yunderup sites (P2–P5) and ranged from 10 300–18 100 mg kg^{-1} for iron and 2390–3350 mg kg^{-1} for aluminium. Iron and aluminium showed no clear spatial pattern within the Leschenault Inlet (iron ranged from 8130–12 700 mg kg^{-1} and aluminium ranged from 2330–3070 mg kg^{-1}).

HCl-extractable chromium and zinc

Zinc is a metal that is commonly leached from acid sulfate soils (Cook et al. 2000; Åström & Deng 2003), however zinc pollution may also be due to other sources such as paint, agricultural chemicals and galvanised steel used for roofing materials. Chromium is less often associated with acid sulfate soil drainage (Cook et al. 2000; Åström & Deng 2003; Miller et al. 2010) but is more commonly associated with industrial sources such as combustion of fossil fuel, steelworks, chromium plating and brick making. The relative metal concentrations calculated as the percentage of the maximum concentration recorded at any site are shown in Figure 11.

The spatial distribution of chromium and zinc within the Swan-Canning estuary was highly varied. The highest concentrations were found among sites S9–S12 and ranged from 11–18 mg kg^{-1} for chromium and 304–444 mg kg^{-1} for zinc. Slightly elevated zinc concentrations were also measured at sites S19 and S20 in the upper Canning River (236–231 mg kg^{-1} zinc). Slightly elevated concentrations of chromium in the Peel-Harvey estuary were found at sites P1–P4 (9.0–10.6 mg kg^{-1}). Concentrations of HCl-extractable chromium in the Leschenault Inlet were all below 8 mg kg^{-1}. Zinc was low in both the Peel-Harvey estuary (<42 mg kg^{-1}) and Leschenault Inlet (<12 mg kg^{-1}).

HCl-extractable copper and lead

Copper is commonly reported as being leached from acid sulfate soils (Åström & Corin 2000; Nordmyr et al. 2008), however both copper and lead also have major anthropogenic and industrial sources. The relative metal concentrations calculated as the percentage of the maximum concentration recorded at any site are shown in Figure 12. In the Swan-Canning estuarine sediments the highest concentrations of copper were measured at sites S10, S11 and S12 (48–69 mg kg^{-1}) while the highest concentrations of lead were measured at sites S10, S11 and S13 (104–126 mg kg^{-1}). Concentrations of copper appeared somewhat elevated around the Yunderup sites (P2–P5: 20–29 mg kg^{-1}) in the Peel-Harvey estuary.

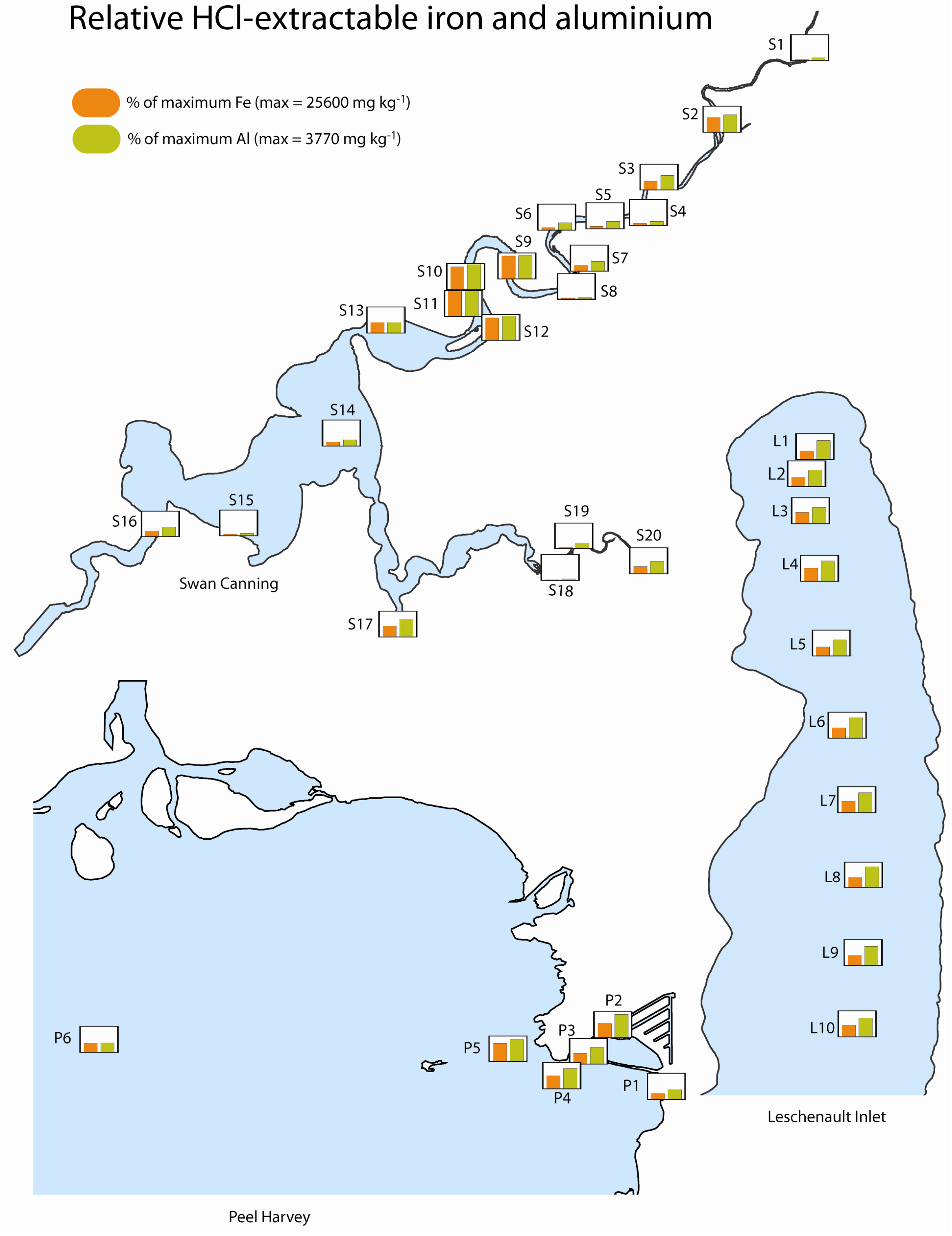

Figure 10 *Average HCl-extractable iron and aluminium, as a percentage of the maximum HCl-extractable metals observed, within sediment from the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The size of the bar that denotes the metal concentration is normalised to the highest measured concentration of each at any site (i.e. 25 600 mg kg^{-1} of iron at S11).*

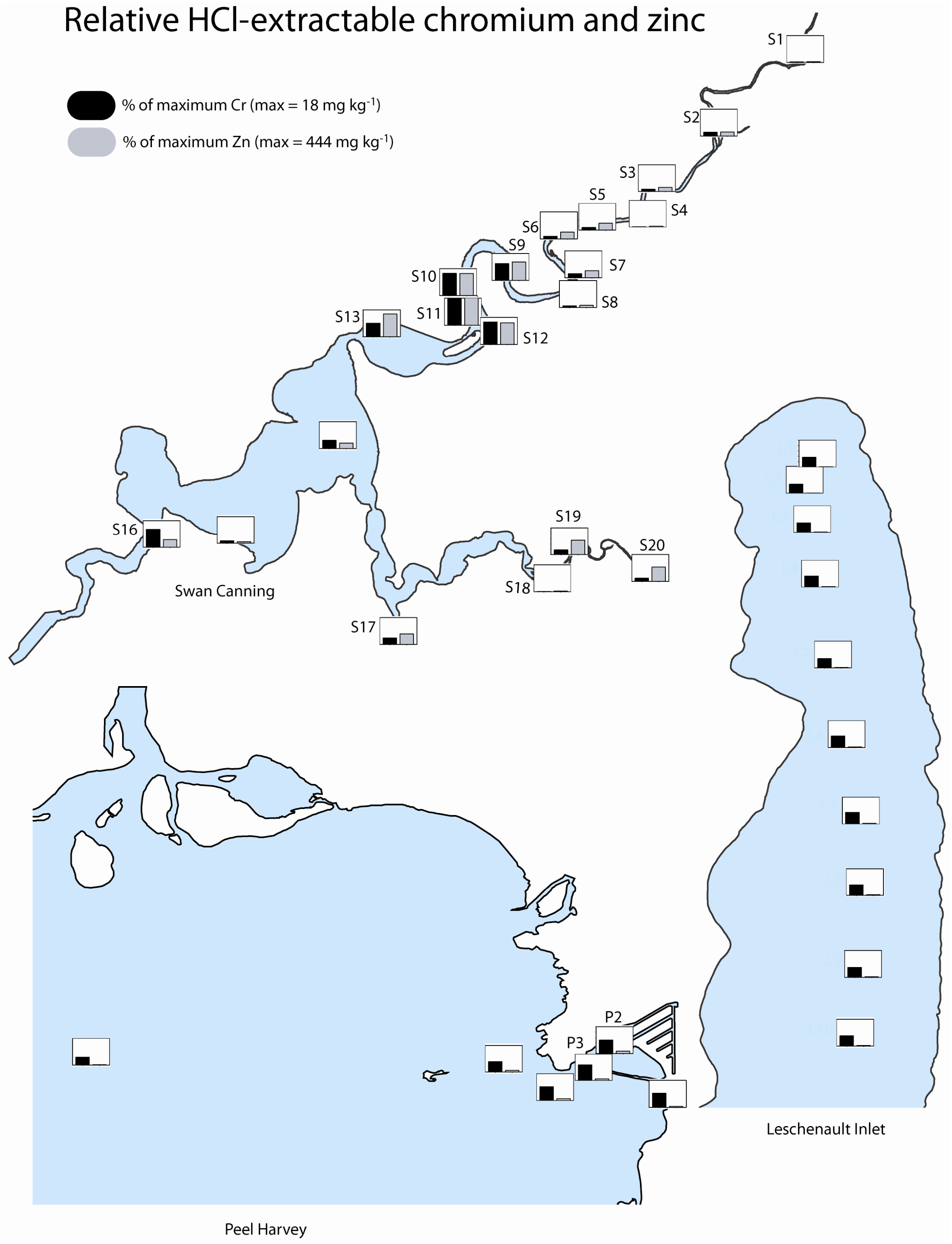

Figure 11 Average HCl-extractable chromium and zinc, as a percentage of the maximum HCl-extractable metals observed, within sediment from the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The size of the bar that denotes the metal concentration is normalised to the highest measured concentration of each at any site (i.e. 18 mg kg^{-1} of chromium at S11).

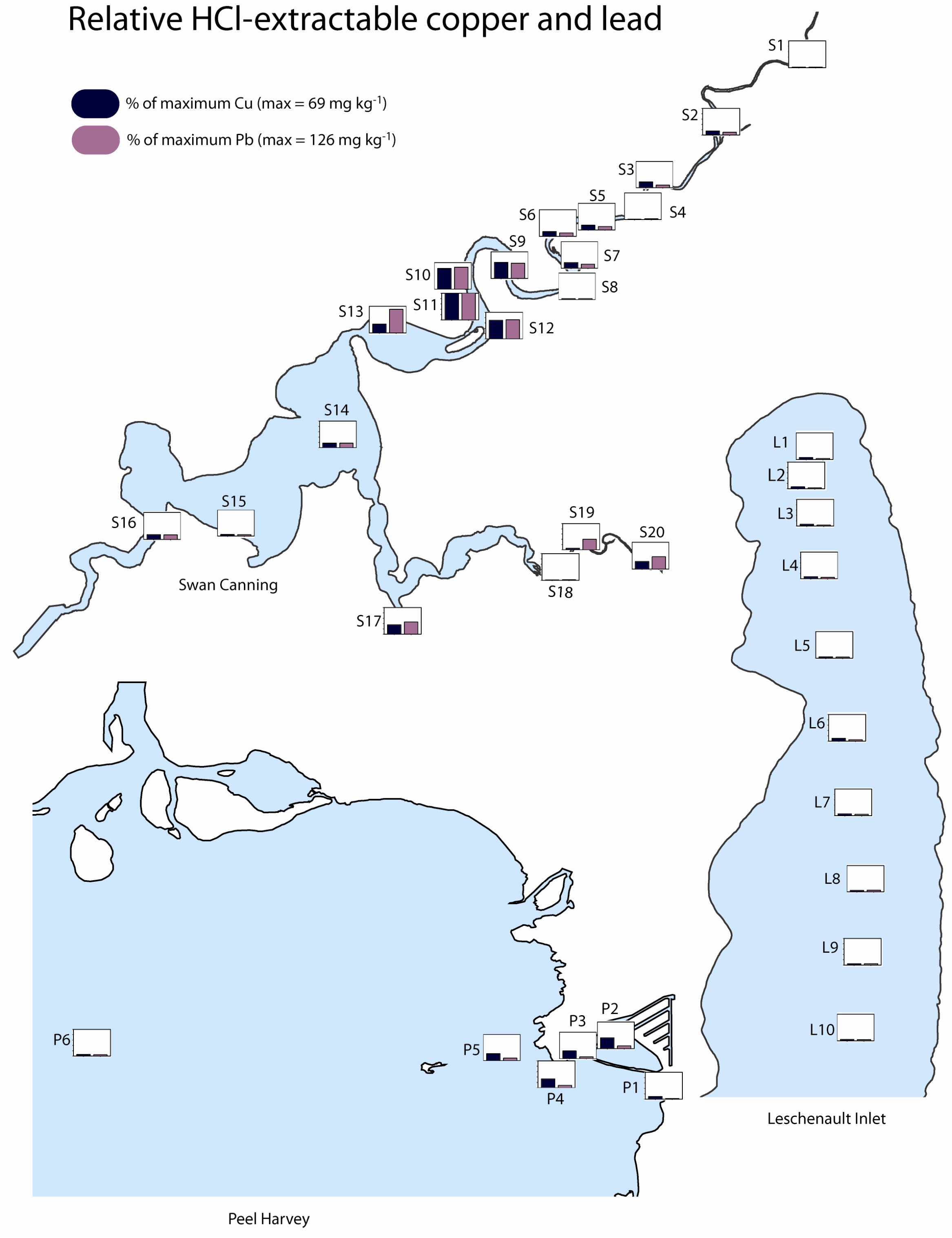

Figure 12 *Average HCl-extractable copper and lead, as a percentage of the maximum HCl-extractable metals observed, within sediment from the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. The size of the bar that denotes the metal concentration is normalised to the highest measured concentration of each at any site (i.e. 69 mg kg^{-1} of copper at S11).*

3.2 Data relationships

Correlations

Strong to very strong positive correlations were observed between HCl-extractable and total metal concentrations for arsenic, cobalt, copper, manganese, molybdenum and zinc in the Peel-Harvey estuary and the Leschenault Inlet (Table 2). Total metals were not measured for the Swan-Canning estuary sediments. This strong correlation indicates that the higher the total concentration of these metals in a sediment sample, the higher the concentration of HCl-extractable metals present. Yet not all metals followed this trend: only moderate to weak correlations were observed for aluminium, iron, chromium and nickel (Table 2). The concentrations measured for HCl-extractable metals were often positively co-correlated with other metals, with Table 3 showing the metals that exhibited strong correlations ($R>0.7$) with a significant positive slope ($p<0.05$).

Moderately strong to strong correlations were observed for many HCl-extractable metals versus moisture content. For example, $R=0.83$ for HCl-extractable aluminium versus moisture content. Similar relationships ($R>0.6$) with moisture content were observed for many other variables including TOC, TN, TP, S_{Cr}, AVS, TS and HCl-extractable cobalt, chromium, copper, iron and nickel. However, moisture content was not correlated to % sand, or to % mud, and total metal concentrations were rarely correlated to moisture content.

Table 2 *Correlations between total metal concentrations and HCl-extractable metal concentrations measured in the Peel-Harvey estuary and Leschenault Inlet sediments.*

Metal	Correlation (R)	Correlation strength	*p* value
Aluminium	0.67	Moderate	<0.0001
Arsenic	0.88	Strong	<0.0001
Cobalt	0.79	Strong	<0.0001
Chromium	0.26	Weak	<0.01
Copper	0.91	Very strong	<0.0001
Iron	0.24	Weak	<0.05
Manganese	0.94	Very strong	<0.0001
Molybdenum	0.93	Very strong	<0.0001
Nickel	0.49	Moderate	<0.0001
Zinc	0.89	Strong	<0.0001

Table 3 *Correlation coefficient (R) for HCl-extractable metals exhibiting strong correlation (R>0.7, p<0.05).*

	Aluminium	**Arsenic**	**Cobalt**	**Chromium**	**Copper**	**Iron**	**Nickel**
Arsenic	0.73						
Cobalt	0.76	0.84					
Chromium	0.70	0.76	0.70				
Copper			0.70				
Iron	0.89	0.73	0.82	0.73	0.72		
Nickel	0.73	0.78	0.87	0.82	0.85	0.81	
Lead					0.83		0.80
Zinc					0.81		0.79

3.3 Comparison to guideline values

The results were compared with the Australian and New Zealand Environment Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC & ARMCANZ 2000) *Interim sediment quality guideline* trigger values, which are also described in the *Handbook for sediment quality assessment* (Simpson et al. 2005). In the *Interim sediment quality guideline*, ISQG-low is a threshold concentration below which the frequency of adverse biological effects is expected to be very low. ISQG-high represents a concentration above which adverse biological effects are more likely.

Guideline values only exist for a subset of the metals analysed; that is, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc. The concentrations of metals in sediments were generally highly variable and often slightly skewed in distribution. The mean of the five replicates for each site was chosen for comparison with guideline values and the sites that exceeded guideline values are shown in Table 4. If median rather than mean was used for comparison with the guidelines, then only two sites would be affected: ISQG-low for zinc would be exceeded at site S17, and ISQG-high would be exceeded at site S13. Appendix A (Table 8) reports average HCl-extractable and total metals for all sites and highlights those above guideline values.

Table 4 *Sites where* Interim sediment quality guideline *values for metals were exceeded. In most cases ISQG-low was exceeded. Instances where ISQG-high was exceeded have been shown in bold type.*

Estuary	Sites	Guidelines exceeded
Swan Canning	S9, S10, S12, S13, S19, S20	Lead, zinc
	S11	Copper, lead, **zinc**
	S16, S17	Mercury, lead
Peel Harvey	P1, P2, P3, P4, P5, P6	Silver*
Leschenault Inlet		Contaminants present but not exceeding guidelines for any site.

** guideline value exceeded for total metals, but not exceeded for HCl-extractable metals*

3.4 Nitrogen and phosphorus

Total nitrogen (TN) and total phosphorus (TP) were measured in sediment for the Swan-Canning estuary and the Leschenault Inlet. Average TN ranged from 10–420 mM (140–5880 mg kg^{-1}) in the Swan-Canning estuary and 240–420 mM (3360–5880 mg kg^{-1}) in the Leschenault Inlet (Figure 13). Average TP ranged from 2.4–53 mM (74–1640 mg kg^{-1}) in the Swan-Canning estuary and 8.8–11.9 mM (270–370 mg kg^{-1}) in the Leschenault Inlet (Figure 13). The concentrations of TP were much less variable across sites in the Leschenault Inlet sediment than in the Swan-Canning estuary (Figure 13). The stoichiometric ratio of nitrogen to phosphorus (N:P) is often used to indicate nutrient limitation, based on the ratio of C:N:P of 106:16:1 suggested by Redfield (1934). N:P ratios were typically lower in the Swan-Canning estuary (with an average of approximately 9:1) compared with the Leschenault Inlet (with an average of approximately 32:1) (Figure 14). These results show that on average, phosphorus is more depleted relative to nitrogen in sediments from the Leschenault Inlet when compared with the Swan-Canning estuary. Nutrients within sediments are likely to originate from a number of sources including organic material such as living and dead microbial communities, detritus, as well as inorganic nutrients bound to sediments. As such, processes such as denitrification, nitrogen fixation, mineralisation and redox changes will alter the concentration and speciation of nutrients within a sediment. Site S13 shows a higher N:P ratio than the other sites in the Swan-Canning estuary, perhaps as a result of the extremely high amount of organic matter (17%) present at the site. Alternatively the ratio might indicate enhanced phosphorus release associated with low redox potential.

There are currently no ANZECC & ARMCANZ (2000) guidelines for nutrient concentrations in sediments. Instead nutrients within these sediments were compared with historical records of sediment nutrient data collected between 1988–1990 in the Leschenault Inlet and Swan-Canning estuary (McComb et al. 2000). In this previous study TP ranged from 9.3–12.5 mM for the Leschenault Inlet and 6.8–54 mM for the Swan-Canning estuary – values very similar to those measured in the current study. TN was not determined in the study by McComb et al. (2000).

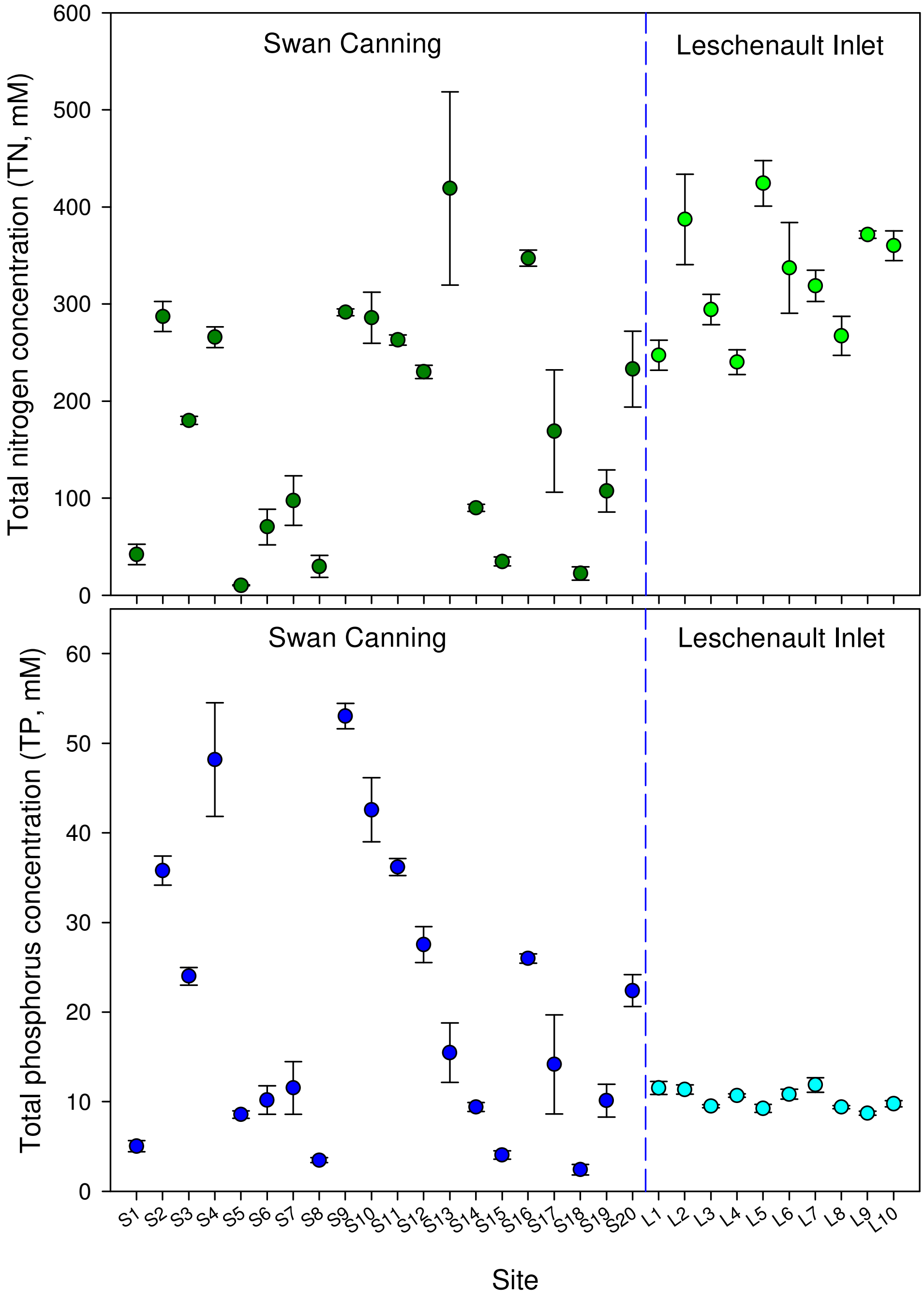

Figure 13 *Total nitrogen and total phosphorus measured in sediment from the Swan-Canning estuary and Leschenault Inlet (mean ± standard error).*

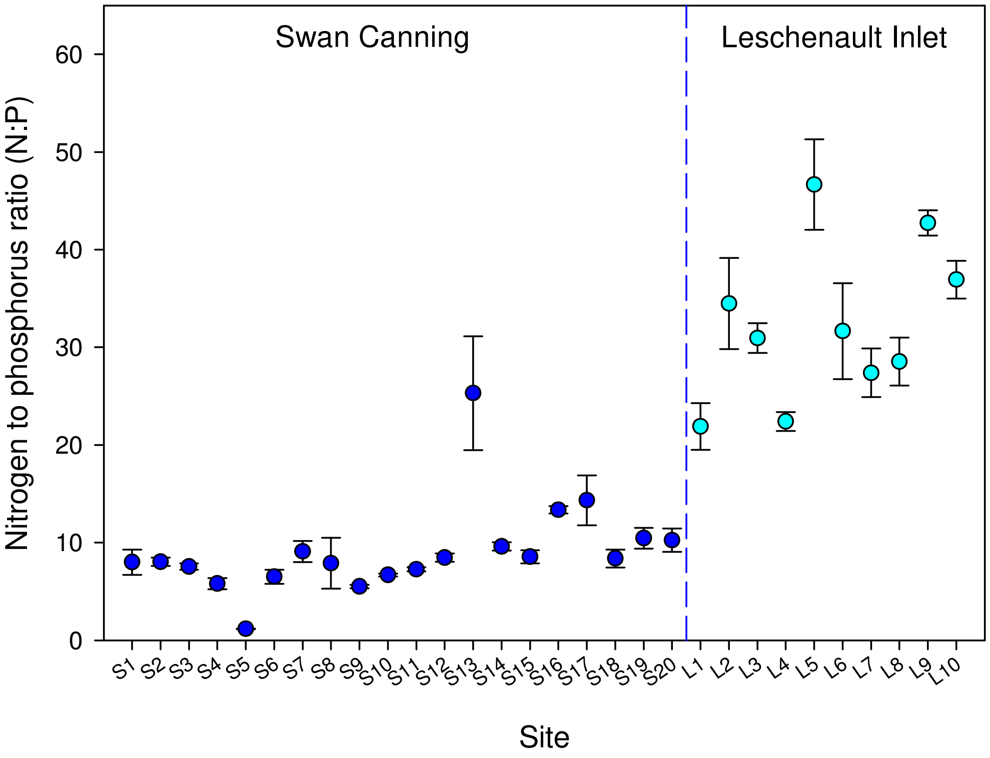

Figure 14 *Ratio of nitrogen to phosphorus (N:P) for sediment sampled in the Swan-Canning estuary and Leschenault Inlet (mean ± standard error).*

4 Discussion

4.1 Acid sulfate soil indicators

Acid sulfate soil material within sediment refers to the reduced sulfur components of the sediment that once oxidised can generate acid. These reduced sulfur compounds can be operationally quantified by two common techniques: measurement of acid volatile sulfur (AVS) and chromium-reducible sulfur (S_{Cr}). AVS was initially believed to be predominantly composed of iron monosulfide minerals (e.g. mackinawite and greigite) and thought of as a precursor for pyrite ($FeS_{2(s)}$) formation. More recent research suggests that AVS is dominated by aqueous FeS clusters but also may include HS^-, H_2S, mackinawite, greigite and polysulfides. The mineral forms of AVS (e.g. mackinawite and greigite) are not direct precursors to pyrite formation because they must be dissolved before the formation reaction can proceed (Rickard & Morse 2005).

The typical concentration of AVS in unpolluted coastal marine sediments is 0.06–0.29%, with freshwater sediments even lower (Troelsen & Jørgensen 1982; Leonard et al. 1993). In contrast, AVS concentrations of up to 6.2% of sediment within acid sulfate soil environments have been reported (Table 5). Average concentrations of AVS recorded in the top 3 cm for sediment in the Peel-Harvey estuary and Leschenault Inlet were 0.3% and 0.07% respectively. These results suggest the Leschenault Inlet is unlikely to be significantly impacted, and that the Peel-Harvey estuary may be on the high end of natural (unpolluted) concentrations and lower end of potential impact from acid sulfate soils.

Low values for the degree of pyritisation (DOP) (5–7%) and degree of sulfidisation (DOS) (10–15%) have been observed in the Tweed River floodplain, NSW (Smith & Melville 2004). Similarly low DOP (0.6–4%) and DOS (5–13%) have been measured in surficial sediments of the Cudgen Lake floodplain, NSW (Macdonald et al. 2004). These values of DOP and DOS indicate that iron was not limiting the formation of acid sulfate soil materials for these sediments. The values of DOP and DOS observed in the Peel-Harvey estuary (35% DOP, 62% DOS) and Leschenault Inlet (35% DOP, 44% DOS) are high by comparison. As discussed earlier, in this study the reactive iron (Fe_{HCl}) was determined by an acid digest with 1M HCl for 1 hour, which may have underestimated the reactive iron present (as the recommended digest is 1M HCl for 24 hours (Canfield 1989; Leventhal & Taylor 1990)).

For the samples of marine shale analysed by Leventhal and Taylor (1990), digesting with 1M HCl for 1 hr resulted a concentration of reactive iron approximately 50–60% of that obtained if the samples were digested for 24 hours. This probable underestimation of Fe_{HCl} must be considered when comparing DOP and DOS with other reported values, because lower Fe_{HCl} would give overestimated values of DOP and DOS. Relative differences between sites and locations are still applicable. If we assume that the acid-extraction method underestimated the reactive iron by 50% – based on Leventhal and Taylor (1990) – then the average DOP observed would be approximately 22% for both systems, with the DOS approximately 37% and 27% for the Peel-Harvey estuary and Leschenault Inlet respectively. Even with these corrections, the DOP and DOS values were higher in this study than determined for the studies from NSW (Macdonald et al. 2004; Smith & Melville 2004). These higher values for DOP and DOS suggest that a greater proportion of the iron present in sediments had been converted to reduced sulfides.

Table 5 *Reported chemical qualities of sulfidic materials within sediments of drains affected by acid sulfate soil drainage waters.*

Location	% AVS	% S_{Cr}	% C	% Fe	% Al	Reference
Sandy Creek, NSW (Australia)	0.1–0.9	1.1–6.9[a]	2–14	n.d.	n.d.	(Bush et al. 2004)
Tuckean Swamp, NSW (Australia)	0.7–6.2	0.9–8[a]	6–49	n.d.	n.d.	(Bush et al. 2004)
Rock Mouth Creek, NSW (Australia)	0.6–2.8	1.2–4.4[a]	9–23	n.d.	n.d.	(Bush et al. 2004)
Tweed, Richmond and Clarence rivers, NSW (Australia)	0.4–3.3	2.1–6.4	n.d.	23.9[b]	n.d	(Burton et al. 2006)
McLeods Creek, NSW (Australia)	0.75	0.98	4.05	8.3[c]	6.1[c]	(Smith 2004)
McLeods Creek and Richmond River floodplain, NSW (Australia)	n.d.	2.0–5.4	1.7–11.8	0.5–1.6[d]	n.d.	(Ward et al. 2004)
Tweed River floodplain, NSW (Australia)[e]	0.14–0.3	1.3–2.8	6.3–7.4	3.9–5.5[f]	n.d.	(Smith & Melville 2004)
Cudgen Lake floodplain, NSW (Australia)	0.6–1.0	0.9-1.3	4–6	8.2–9.5[g]	3.8-4.1[g]	(Macdonald et al. 2004)

[a] *2-step analytical method used so results reported as % S_{Cr} are S_{py} + AVS to approximate 1-step S_{Cr} procedure*

[b] *oxalate-extractable iron*

[c] *aqua-regia digestion*

[d] *citrate/dithionate extractable iron*

[e] *data from top 4 cm of sediment core only considered (as most closely reflects the current study)*

[f] *reactive iron (present as Fe monosulfides, Fe oxyhydroxides and some Fe-bearing silicates)*

[g] *acid-extractable metals using concentrated nitric acid*

Iron and aluminium (and other metals) are commonly exported from disturbed acid sulfate soils and redistributed in downstream sediments (Åström & Corin 2000; Cook et al. 2000; Nordmyr et al. 2008). The concentrations of iron and aluminium measured in the sediment of drains affected by acid sulfate soils range from 0.5–24% for iron and 3.8–6.1% for aluminium (Table 5). In the current study the maximum HCl-extractable iron concentrations were 2.6% and the maximum HCl-extractable aluminium concentrations were 0.38% (at site S11; refer to Figure 2 for site locations). However, comparison of sediment metal concentrations with literature values is confounded due to the variation in extraction and digestion methods used in these studies.

The analytes that exceeded the guidelines tended to be those commonly associated with industrial sources, such as lead, zinc, copper and mercury, although these elements are also known to occur naturally (NHMRC 2008). There were a few sites where acidic drainage was suspected from previous water quality monitoring and/or the history of the surrounding landscape. These included Parkfield drain at the Leschenault Inlet's northern end (closest to site L1), and the dredge disposal site near Yunderup in the Peel-Harvey estuary (closest to sites P3 and P4). However, there was no highly convincing trend or gradient for potential signals of acidic drainage (iron, aluminium, S_{Cr}, etc.) for sediment at these sites compared with other 'non impacted' sites.

Site P1 was situated at the Peel-Harvey estuary's edge within a drain that periodically discharges acidic water (pH <3) directly to the estuary. The lower concentrations of some metals at this site are likely to be explained by the dissolution of sediment-bound metals under acidic conditions, as well as the transport of the soluble fraction through porewater exchange associated with the acidic water frequently draining to the estuary. Slightly lower concentrations of most metals at site P6 may be due to the site's relative remoteness from terrestrial sources (this site was located towards the centre of the Peel Inlet's basin). Total organic carbon (TOC) was significantly lower at site P6 (1.8% TOC) relative to other sites in the Peel-Harvey estuary (average 6.4% TOC). Unfortunately there is insufficient data within this study to determine whether the higher concentrations of S_{Cr} and some metals at sites P1–P5 (relative to P6) is due to the effect of acidic drainage from the dredge spoil site and localised to this area, or whether it is an effect of distance from land and the possible terrestrial sources of these contaminants. Sampling sediment from more sites (including sites in the Peel Inlet's basin and sites adjacent to the estuary's edge but at some distance from the dredge spoil site) would help resolve whether sediment quality in this region is likely to be impacted by acid sulfate soils.

Generally, low concentrations of metals (for which guideline values exist) were measured in the sediments of the Peel-Harvey estuary, because all HCl-extractable metals were lower than *Interim sediment quality guideline* values. These sediments were highly reducing with significant quantities of reduced sulfur and organic carbon. Together, these findings suggest that the dominant influence on sediment quality for the Peel-Harvey estuary is organic enrichment – perhaps driven mostly by eutrophication.

4.2 Role of sediment type

Sediments can act as both a sink and a source of nutrients and other contaminants affecting both estuarine water quality and biological productivity. The interrelationship of sediment and water quality has been recognised in a number of studies (Risgaard-Petersen & Jensen 1997; Radke et al. 2004; Smith et al. 2007). The distribution of organic-rich muds in the Swan-Canning estuary is spatially variable, but nonetheless important because significant fluxes of nutrients can be released from these sediment types relative to more sandy sediments (Smith et al. 2007). The current sediment survey also revealed significant variation in sediment type, and associated contaminants spatially within the Swan-Canning estuary. In contrast, sediment sampled in the Leschenault Inlet and Peel-Harvey estuary was more consistent in terms of particle size, organic content and metal contamination, because organic-rich fine sediments dominated both estuaries.

The phosphorus retention index (PRI) of a sediment (or soil) is a measure of how much phosphorus the sediment can retain. In a recent study, the PRI of sediment from the Vasse-Wonnerup wetlands was strongly positively correlated with smaller sediment particles (Wilson et al. 2008). Concentrations of sediment phosphorus were higher and more variable in the Swan-Canning estuary than in the Leschenault Inlet (see Figure 13). Phosphorus concentrations were not correlated to particle size when considering sediments from both estuaries together. However for the Swan-Canning estuary data alone, total phosphorus concentration was correlated to sediment particle size (R=0.74).

Nitrogen concentrations were positively correlated to particle size (R=0.73) in sediments from both the Swan-Canning estuary and Leschenault Inlet. The variable N:P ratios of sediment seen in both these systems may reflect variation in catchment inputs of nutrients to the estuaries, or alternatively differences in nutrient processes within the sediment.

4.3 Potential effects on aquatic organisms

The sediment quality reported in this study for the three estuaries (Swan-Canning estuary, Peel-Harvey estuary and Leschenault Inlet) presents only minor concern for possible adverse biological effects. The potential biological effects are likely to be different for each estuary sampled and are discussed separately here, based on the variables determined from the sediment in each case.

Swan-Canning estuary

The metals lead, copper and mercury were present in concentrations that exceeded the ISQG-low trigger values (ANZECC & ARMCANZ 2000) while zinc concentrations also exceeded the ISQG-high trigger value (ANZECC & ARMCANZ 2000). Bioaccumulation of non-essential metals poses a threat to aquatic organisms, and metal concentrations may then potentially transfer across trophic levels (Phillips & Rainbow 1994).

Total organic matter was particularly high at one site in the Swan-Canning estuary (S13) and was also associated with reduced sediments. If sulfide is generated in these sediments from enhanced sulfate-reduction due to the high concentrations of organic matter, the anoxic sediments may be rendered unfavourable for benthic flora and fauna (Raven & Scrimgeour 1997; ANZECC & ARMCANZ 2000; Azzoni et al. 2001). An additional risk for this site is deoxygenation of the water column when sediment is re-suspended.

Concentrations of phosphorus were relatively high within Swan-Canning estuary sediments with an average TP of 636 mg kg^{-1}. Sediment-bound nutrients can be a potential source of nutrients to the overlying water by diffusing into the sediment porewater (interstitial water within the sediment) and then reaching the overlying water when porewater concentrations are sufficiently high (ANZECC & ARMCANZ 2000). Nutrient release from sediments may thereby potentially drive nuisance algal blooms within the estuary.

Peel-Harvey estuary

Moderate to high concentrations of organic matter, low redox potential (average -130 mV) and high concentrations of reduced sulfur (S_{Cr}) characterised most sites within the Peel-Harvey estuary. In addition, high concentrations of acid volatile sulfur (AVS) were also measured within surficial sediments. As the estuary is shallow (<2 m in general), these sediments, if re-suspended, pose the risk of rapid deoxygenation of the water column – potentially affecting the survival of fish and other oxygen-consuming organisms. Highly reducing sediments, such as those observed in the Peel-Harvey estuary, are likely to affect the survival of benthic organisms adapted to more oxic or slightly hypoxic surficial sediments.

Nutrients were not determined in the Peel-Harvey estuary sediments, although they have been assessed in previous investigations (DoW 2006).

Leschenault Inlet

Sediment in the Leschenault Inlet did not exceed guideline concentrations for any metal or metalloid, and redox potential indicated that oxic to slightly anoxic sediments prevail. While the concentrations of aluminium and iron in the inlet's sediment appear elevated relative to the lowest concentrations measured, there are no guideline values for these metals, and these concentrations may reflect background concentrations for the estuary. Abundant aquatic flora (seagrasses) and fauna (in particular crabs) were also observed during sampling, suggesting the estuary is providing a relatively good habitat for aquatic organisms.

The concentration of nitrogen in sediments was high, particularly relative to the concentration of phosphorus retained in the sediments. The Leschenault Inlet is commonly believed to be nitrogen limited (McKenna 2007), so additional inputs of nitrogen could drive excessive primary production. Without further investigation, it is not known whether the nitrogen within the sediment is available or if it is 'locked up' in more recalcitrant organic matter.

4.4 Comparison with historical data

Table 6 shows historical data from regions of the estuaries relevant to the current study. For example, a number of the historical studies investigated the far upper reaches of the Swan and Canning rivers, but only the data from the spatial extent of the current study have been reported in Table 6.

Some historical data exists for the metal content of sediment within the estuaries studied. However, direct comparison of this data with the current data is confounded by the evolution of both sampling and chemical analysis methodologies in recent times. Methods for determining iron and aluminium are variable (and unknown) for the historical data and likely to differ from the methods used in the current study. The variations in methodology make it impossible to say with any certainty whether there has been a recent increase in metal concentration within the sediments (e.g. due to anthropogenic activities including, among others, disturbance of acid sulfate soil). However, there does not appear to be a clear increase in any of the variables tested for which there is historical data. Total organic carbon content has not changed markedly within the estuaries investigated.

Table 6 *Summary of sediment quality historical data for the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. Concentrations are reported per dry weight of sediment.*

Location	Parameter	Range	Year sampled	Reference	Current study
Swan Canning	TOC (%)	0.3–22.6	1988–89	(Hill et al. 1991)	0.2–19.7
	TOC (%)	2.5–8.5	1998	(Gerritse et al. 1998)	
	TOC (%)	0.7–5.8	1996–97	(Rate et al. 2000)	
Peel Harvey	TOC (%)	0.6–14.5	1988–89	(Hill et al. 1991)	1.7–7.4
Leschenault Inlet	TOC (%)	3.9–15.2	1988–89	(Hill et al. 1991)	2.4–4.9
Swan Canning	Al (%)	0.4–9.7	1988–89	(Hill et al. 1991)[1]	0.1–0.38[B]
	Al (%)	1.5–3.8	1991	(Gerritse et al. 1998)[2]	
Peel Harvey	Al (%)	0.2–2.8	1988–89	(Hill et al. 1991)[1]	0.14–0.33[B]
Leschenault Inlet	Al (%)	1.5–3.6	1988–89	(Hill et al. 1991)[1]	0.23–0.31[B]
Swan Canning	Fe (%)	0.4–7.0	1988–89	(Hill et al. 1991)[1]	0.06–2.6[B]
	Fe (%)	0.5–1.3	1991	(Gerritse et al. 1998)[2]	
Peel Harvey	Fe (%)	0.1–2.0	1988–89	(Hill et al. 1991)[1]	0.52–1.8[B]
Leschenault Inlet	Fe (%)	1.9–4.4	1988–89	(Hill et al. 1991)[1]	0.81–1.3[B]

Location	Parameter	Range	Year sampled	Reference	Current study
Swan Canning	Zn (mg kg^{-1})	18–2190	1980	(Chegwidden 1980)[3]	11.2–444[B]
	Ni (mg kg^{-1})	5–38	1980	(Chegwidden 1980)[3]	0.2–6.6[B]
	Cu (mg kg^{-1})	2.7–327	1980	(Chegwidden 1980)[3]	0.8–69[B]
	Cu (mg kg^{-1})	2.6–300	1996–97	(Rate et al. 2000)[4]	
	Cr (mg kg^{-1})	2.4–275	1980	(Chegwidden 1980)[3]	0.3–18[B]
	Cd (mg kg^{-1})	0–0.9	1996–97	(Rate et al. 2000)[4]	
	Cd (mg kg^{-1})	0.3–4.4	1980	(Chegwidden 1980)[3]	
	Pb mg kg^{-1})	4.9–180	1996–97	(Rate et al. 2000)[4]	2.2–126[B]
Swan Canning	TP (mg kg^{-1})	800–1700	1998	(Gerritse et al. 1998)	75–1640
	TP (mg kg^{-1})	210–1700	1988–90	(McComb et al. 2000)	
Peel Harvey	TP (mg kg^{-1})	140–290	1988–90	(McComb et al. 2000)	n.d.
Leschenault Inlet	TP (mg kg^{-1})	290–390	1988–90	(McComb et al. 2000)	270–370

[1] analytical method not reported

[2] digestion of sediment – acid extractable 10% HCl for 24 hours

[3] digestion of sediment with nitric, perchloric and sulfuric acid digest

[4] sequential acid extraction

[B] HCl-extractable metals extraction

4.5 Results in a global context

Sediment quality is commonly analysed and reported for many estuaries worldwide. Results from a small selection of those for which metal concentrations have been reported are collated in Table 7. Again the variability in methods used for the extraction of metals from sediments before analysis makes it difficult to compare the current study and the data from estuaries worldwide. More commonly reported were data from total metal digestions of sediment (although the acids used and the time of digest varied between all reports). In the current report, total metal determinations were made for the Peel-Harvey estuary and the Leschenault Inlet, but not the Swan-Canning estuary.

The highest concentration of iron measured in the current study was 4.9% (total) and 2.6% (HCl-extractable). These concentrations are of a similar order to those reported for iron in Ria of Huelva (Spain), Vörå River Estuary (Finland) and Laguna Madre (USA) (Table 7). The highest concentration of aluminium measured in the current study was 3.3% (total) and 0.36% (HCl-extractable). Aluminium was only reported for the study in Vörå River Estuary (Finland), where aluminium (total) ranged from 1.8–5%.

In contrast, much higher maximum concentrations of total copper, lead and zinc were reported in these previous studies (Table 7) compared with those observed in either the Peel-Harvey estuary or Leschenault Inlet (where total metals were determined). This was particularly the case for Gao-ping River (Taiwan), Ria of Huelva (Spain) and Sydney Harbour (Australia), with copper concentrations up to 3720 mg kg^{-1}, lead concentrations up to 3210 mg kg^{-1} and zinc concentrations up to 8820 mg kg^{-1} (Table 7).

Table 7 *Sediment quality reported for metal contaminants in estuaries worldwide. n.d. = not determined*

Location	**Fe (%)**	**Al (%)**	**Cu (mg kg^{-1})**	**Cr (mg kg^{-1})**	**Pb (mg kg^{-1})**	**Zn (mg kg^{-1})**	**Reference**
Gao-ping River, Taiwan[1]	n.d.	n.d.	14.5–197	35.7–2714	18.3–92.9	65.9–1535	(Doong et al. 2008)
Ria of Huelva, south-western Spain[2]	5–13	n.d.	341–3718	n.d.	232–3212	22–3998	(López-González et al. 2006)
Vörå River Estuary, Finland[3]	3.0–3.5	1.8–5.0	28–63	40–45	n.d.	200–444	(Nordmyr et al. 2008)
Lower Laguna Madre, Texas, USA[4]	0.7–1.8	n.d.	6.3–13.9	n.d.	2.8–10.1	34.5–80.9	(Whelan III et al. 2005)
Sydney Harbour, Australia[5]	n.d.	n.d.	20–701	n.d.	78–1050	75–8820	(Birch et al. 2008)
Victoria Harbour, Pearl River Estuary, China[6]	n.d.	n.d.	21.2–173	n.d.	19.6–30.7	55–176	(Tang et al. 2008)
Swan Canning[7]	0.6–2.6	0.1–0.38	0.8–69	0.3–18	2.2–126	11.2–444	This study
Peel Harvey[3]	0.88–3.7	0.59–2.7	8.2–31	17–32	5.4–16	15–44	This study
Leschenault Inlet[3]	2.2–4.9	2.0–3.4	8.9–43	27–42	9.2–16	16–27	This study

[1] *total metal digestion method with nitric, hydrochloric and hydrofluoric acids*

[2] *total metal digest with hydrofluoric and chloric acids*

[3] *total metal digest with aqua regia*

[4] *bioavailable metal digest with hydrogen peroxide and nitric acid*

[5] *total metals digest with perchloric acid and nitric acid 2:1*

[6] *total metal digest with perchloric acid and nitric acid*

[7] *HCl-extractable metal digest with hydrochloric acid*

5 Conclusion and recommendations

Sediment quality within the three estuaries does not appear to be particularly degraded overall, although some clear differences exist between them. The quality of present-day sediments from these estuaries was similar to what was reported in previous studies (although methodological differences made comparisons difficult).

Sediments from certain sites within the Swan-Canning estuary posed the highest potential risk to aquatic organisms with ANZECC & ARMCANZ (2000) guideline values being exceeded for zinc, lead, copper and mercury. Site-specific ecotoxicological testing could determine whether these contaminant concentrations are likely to be causing ecological harm.

There was no conclusive evidence from sediment quality to suggest impacts from acid sulfate soils in any of the estuaries. Metal concentrations rarely exceeded ANZECC & ARMCANZ (2000) guidelines, and where they did (in the Swan-Canning estuary) could likely be attributed to anthropogenic and/or historical contamination. Concentrations of iron and aluminium were relatively high near the Yunderup dredge spoil site within the Peel-Harvey estuary (compared with the other estuaries), and high monosulfides were also present around this area. However little direct toxicity is expected from the high concentration of iron, as similar concentrations (around 2.2%) have been tested previously as control sediments (with no ecotoxicological effect) (Spadaro et al. 2008). Additionally, the presence of high concentrations of AVS may also reduce the toxicity risk of metals to organisms (Hansen et al. 2005). Further sediment testing in the Peel-Harvey estuary might determine whether these sediment characteristics are localised to the sites investigated, and if so, this would indicate probable impact from acid sulfate soils related to the dredge spoil.

Overall, the sediment appeared relatively uncontaminated compared with results from a number of estuaries worldwide. However, the highest concentrations of iron and aluminium observed in this study were on the higher end of the range reported for sediments worldwide.

Based on these findings the following recommendation is made:

Recommendation: Site-specific ecotoxicological testing within the Swan-Canning estuary should be undertaken for sites that exceeded ANZECC & ARMCANZ guideline values for HCl-extractable metals.

Appendices

Appendix A — Average values measured in sediment at each site

Table 8 *Average HCl-extractable (b) and total (t) metals (mg kg^{-1}dry weight) for sediments from sites within the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. n.d. = not determined, n = 5. Above ISQG-low, above ISQG-high*

Site		Ag	Al	As	Cd	Cr	Cu	Co	Fe	Hg	Mn	Mo	Ni	Pb	Se	Zn
Swan-Canning estuary																
ISQG-low trigger		*1*		*20*	*1.5*	*80*	*65*			*0.15*			*21*	*50*		*200*
ISQG-high trigger		*3.7*		*70*	*10*	*370*	*270*			*1*			*52*	*220*		*410*
S1	*(b)*	n.d.	392	<0.5	<0.5	<0.5	1.2	0.6	1610	<0.2	49	0.7	<0.5	2.2	<0.5	11
S2	*(b)*	n.d.	2470	0.72	<0.5	2.5	11	2.5	14 300	<0.2	100	<0.5	1.9	13	<0.5	66
S3	*(b)*	n.d.	2150	0.61	<0.5	1.5	15	2.6	8720	<0.2	100	<0.5	1.5	13	<0.5	67
S4	*(b)*	n.d.	3350	1.8	<0.5	3.2	18	3.8	21 100	<0.2	130	<0.5	2.5	23	<0.5	130
S5	*(b)*	n.d.	566	0.65	<0.5	<0.5	1.0	<0.5	1720	<0.2	7.0	<0.5	<0.5	3.6	<0.5	16
S6	*(b)*	n.d.	1000	1.3	<0.5	1.8	12	3.7	2450	<0.2	630	<0.5	1.9	16	<0.5	110
S7	*(b)*	n.d.	1350	2.1	<0.5	2.7	15	2.3	5510	<0.2	81	<0.5	2.1	19	0.5	120
S8	*(b)*	n.d.	178	<0.5	<0.5	1.1	2.9	0.6	750	<0.2	83	<0.5	<0.5	5.5	<0.5	37
S9	*(b)*	n.d.	3280	7.5	<0.5	11.	42	7.9	22 100	<0.2	360	<0.5	5.4	73	1.5	300
S10	*(b)*	n.d.	3570	8.6	<0.5	15	54	7.6	21 900	<0.2	330	<0.5	6.2	100	1.8	360
S11	*(b)*	n.d.	3760	8.4	<0.5	18	69	7.2	25 600	<0.2	230	<0.5	6.6	130	1.7	440
S12	*(b)*	n.d.	3520	8.8	<0.5	15	48	7.6	22 100	<0.2	370	<0.5	5.9	91	1.6	360
S13	*(b)*	n.d.	1500	1.2	<0.5	9.0	23	1.2	10 100	<0.2	67	<0.5	3.4	110	0.8	380
S14	*(b)*	n.d.	994	1.3	<0.5	5.4	12	2.0	4500	<0.2	140	<0.5	1.5	22	<0.5	90

S15	*(b)*	n.d.	292	<0.5	<0.5	1.6	4.2	<0.5	1200	<0.2	64	<0.5	<0.5	7.4	<0.5	25
S16	*(b)*	n.d.	1420	3.0	<0.5	12	35	1.7	5520	0.24	190	<0.5	3.0	69	0.8	130
S17	*(b)*	n.d.	2530	4.1	<0.5	4.4	24	2.1	10 600	0.57	62	<0.5	2.3	58	2.5	170
S18	*(b)*	n.d.	183	<0.5	<0.5	<0.5	0.8	<0.5	556	<0.2	8.0	<0.5	<0.5	2.2	1.1	12
S19	*(b)*	n.d.	888	1.1	<0.5	3.1	4.6	0.7	2090	<0.2	9.4	<0.5	2.2	50	1.7	240
S20	*(b)*	n.d.	1770	1.2	<0.5	2.2	19	3.2	7000	<0.2	100	<0.5	3.7	58	2.2	240
Peel-Harvey estuary																
P1	*(b)*	<0.5	1380	1.6	<0.5	9.4	6.9	3.2	5160	<0.2	110	<0.5	2.4	3.2	nd	14
	(t)	2.4	5890	3.1	<0.5	22	10	5.4	8800	<0.2	140	1.5	4.2	5.4	0.7	21
P2	*(b)*	<0.5	3350	2.1	<0.5	9.0	28	2.8	13 900	<0.2	70	1.3	2.6	13	nd	42
	(t)	3.6	27 200	4.2	<0.5	32	31	7.0	29 300	<0.2	100	6.7	8.7	15	1.5	44
P3	*(b)*	<0.5	2390	2.0	<0.5	11	21	2.1	10 300	<0.2	44	1.9	2.3	10	nd	26
	(t)	2.3	18 500	3.7	<0.5	30	23	4.9	22 900	<0.2	69	7.3	6.6	11	0.9	30
P4	*(b)*	<0.5	2890	2.2	<0.5	9.3	23	2.1	12 800	<0.2	60	1.7	2.3	11	nd	30
	(t)	2.2	21 300	3.8	<0.5	26	25	5.3	24 500	<0.2	91	7.5	7.0	12	1.1	33
P5	*(b)*	<0.5	3150	2.5	<0.5	7.2	19	2.4	18 100	<0.2	59	1.8	2.6	14	nd	27
	(t)	2.3	27 400	5.7	<0.5	30	25	6.4	37 300	<0.2	100	10	8.6	16	1.4	34
P6	*(b)*	<0.5	1450	4.4	<0.5	5.3	4.0	1.2	9470	<0.2	68	<0.5	1.3	6.4	nd	6.7
	(t)	1.6	12 300	7.0	<0.5	17	8	2.7	21 800	<0.2	110	2.4	3.8	8.4	0.4	15
Leschenault Inlet																
L1	*(b)*	<0.5	2650	3.5	<0.5	6.5	5.2	3.1	8130	<0.2	320	1.1	2.7	5.0	1.1	6.4
	(t)	<0.5	28 400	8.0	<0.5	33	14	9.9	40 300	<0.2	590	4.8	14	9.2	1.6	18
L2	*(b)*	<0.5	2360	3.7	<0.5	6.1	4.9	3.1	8590	<0.2	340	0.7	3.2	4.9	1.1	6.1
	(t)	<0.5	33 900	9.8	<0.5	40	16	12	48 900	<0.2	770	5.1	18	11	1.9	21

L3	*(b)*	<0.5	2330	3.5	<0.5	6.4	4.7	3.2	11 100	<0.2	250	0.6	2.3	5.4	1.0	6.4
	(t)	<0.5	22 780	6.9	<0.5	30	12	8.9	22 900	<0.2	430	3.0	13	9.7	1.2	16
L4	*(b)*	<0.5	2890	3.8	<0.5	7.4	5.5	3.9	12 700	<0.2	210	2.7	2.6	7.4	1.0	9.7
	(t)	<0.5	27 050	9.0	<0.5	36	13	10	35 800	<0.2	370	9.3	14	12	1.3	23
L5	*(b)*	<0.5	2330	4.6	<0.5	6.2	4.0	3.3	8970	<0.2	180	<0.5	2.2	5.8	0.8	7.9
	(t)	<0.5	22 500	11.1	<0.5	30	10	8.2	33 900	<0.2	310	2.5	12	9.3	1.1	18
L6	*(b)*	<0.5	2960	5.8	<0.5	7.6	7.2	3.9	10 100	<0.2	230	0.7	2.6	6.8	1.0	9.8
	(t)	<0.5	31 380	17.8	<0.5	41	13	11	46 500	<0.2	420	3.6	16	14	1.5	25
L7	*(b)*	<0.5	2850	5.7	<0.5	7.8	4.7	4.2	11 300	<0.2	220	<0.5	2.5	6.8	1.0	11
	(t)	<0.5	32 040	18.3	<0.5	42	14	12	49 000	<0.2	400	2.3	16	14	1.4	27
L8	*(b)*	<0.5	3070	4.4	<0.5	7.2	3.9	3.7	10 400	<0.2	150	0.5	2.2	7.5	0.6	10.
	(t)	<0.5	24 840	12.8	<0.5	35	11	9.3	34 000	<0.2	260	2.4	13	12	1.1	22
L9	*(b)*	<0.5	2800	4.3	<0.5	6.7	3.5	3.4	10 500	<0.2	160	<0.5	2.2	6.8	0.6	9.7
	(t)	<0.5	29 830	16.0	<0.5	41	14	11	45 900	<0.2	350	2.3	16	16	1.3	26
L10	*(b)*	<0.5	2690	6.4	<0.5	6.9	3.6	3.5	11 700	<0.2	220	<0.5	2.1	6.4	0.6	11
	(t)	<0.5	19 690	17.3	<0.5	27	9	7.4	32 800	<0.2	280	1.2	11	9.5	0.8	19

Table 9 *Average values for other analytes in sediments from sites within the Swan-Canning and Peel-Harvey estuaries and the Leschenault Inlet. n.d. = not determined, n = 5.*

Site	**ANC (% $CaCO_3$)**	**TOC (%)**	**Redox (Eh, mV)**	**Moisture content (% dw)**	**TN (mg kg^{-1})**	**TP (mg kg^{-1})**	**S_{Cr} (%)**	**AVS (%)**
Swan-Canning estuary								
S1	0.96	0.94	52	27.9	588	156	0.27	n.d.
S2	2.5	4.48	35	76.3	4020	1110	0.68	n.d.
S3	1.7	3.10	33	63.7	2520	744	0.68	n.d.
S4	2.2	4.18	27	74.4	3720	1494	0.49	n.d.
S5	0	0.23	87	18.7	142	266	0.01	n.d.
S6	2.1	1.52	100	37.2	984	316	0.47	n.d.
S7	1.6	2.88	80	56.9	1360	358	1.2	n.d.
S8	0.53	0.58	190	21.6	414	108	0.03	n.d.
S9	4.3	5.24	11	76.7	4080	1644	0.64	n.d.
S10	4.2	5.04	-15	73.5	4000	1320	0.47	n.d.
S11	2.6	4.48	34	73.1	3680	1122	0.53	n.d.
S12	3.1	3.12	-8	72.1	3220	854	0.39	n.d.
S13	5.3	17.1	-98	64.3	5870	480	0.94	n.d.
S14	8.6	1.30	60	47.8	1260	292	0.08	n.d.
S15	1.0	0.61	120	26.7	486	126	0.03	n.d.
S16	36	5.16	52	66.2	4860	806	0.25	n.d.
S17	1.8	2.32	20	52.0	2370	440	0.59	n.d.
S18	0.63	0.41	72	20.8	313	75	0.12	n.d.

S19	0.76	2.50	-17	50.2	1504	314	0.40	n.d.
S20	1.6	4.56	39	62.4	3260	694	0.17	n.d.

Peel-Harvey estuary

P1	n.d.	6.80	-130	55.6	n.d.	n.d.	0.41	0.17
P2	n.d.	7.42	-140	75.2	n.d.	n.d.	1.4	0.31
P3	n.d.	4.98	-160	68.0	n.d.	n.d.	0.95	0.30
P4	n.d.	5.81	-150	69.1	n.d.	n.d.	1.0	0.36
P5	n.d.	7.22	-160	74.9	n.d.	n.d.	1.70	0.55
P6	n.d.	1.88	-53	47.5	n.d.	n.d.	0.50	0.05

Leschenault Inlet

L1	8.3	4.42	200	62.1	3460	358	0.68	0.08
L2	2.9	4.86	49	59.6	5420	352	0.67	0.08
L3	8.4	3.82	-89	59.7	4120	295	0.71	0.09
L4	5.2	3.97	-120	63.1	3360	331	1.1	0.17
L5	6.8	3.07	45	55.5	5940	287	0.67	0.06
L6	4.6	3.72	52	60.7	4720	336	0.91	0.04
L7	2.7	3.29	70	62.2	4460	368	0.79	0.08
L8	3.6	2.65	51	55.7	3740	291	0.80	0.06
L9	3.4	2.48	40	53.5	5200	270	0.67	0.02
L10	2.8	2.42	11	50.7	5040	303	0.60	0.01

Appendix B — Quality assurance and quality control

All data was obtained from National Association of Testing Authorities (NATA) accredited laboratories: the National Measurement Institute for the Swan Canning data and the Environmental Analysis Laboratory of Southern Cross University for the Peel Harvey and Leschenault data.

Table 10 *Summary of spike recovery data showing range observed where multiple samples were analysed.*

Analyte	**Swan Canning** % recovery	**Peel Harvey** % recovery	**Leschenault** % recovery
ANC	89–100	n/a	101
Al	100–103	110	118
As	96–104	92	113
Ag	n/a	88	121
TOC	100–120	93	n/a
Cd	98–101	86	110
Co	99–101	84	87
Cr	97–101	101	115
Cu	99–103	100	106
Fe	101–103	94	106
Hg	101–109	96	89
Mn	97–104	104	107
Mo	101–105	85	91
TN	95–101	n/a	n/a
Ni	100–103	90	118
TP	100–107	n/a	88
Pb	97–103	101	85
S_{Cr}	96–118	95	94
S	100–108	98	n/a
Se	93–107	95	105
Zn	100–105	99	108

Table 11 *Summary of lab duplicate data showing the percentage difference between duplicates for the HCl-extractable metal suite, with data for the total metal suite shown in parentheses.*

Analyte	**Swan Canning** mg kg^{-1}	**Peel Harvey** mg kg^{-1}	**Leschenault** mg kg^{-1}
Al	0–11.8	1.1–3.5 (0–16)	0 (1.9)
As	1.4–3.8	3.7–4.5 (0–4.3)	2.3–7.1 (3.6)
Cd	<LOR	0.5 (0–48)	0 (n.d.)
Co	14	4.6–7.3 (0–10)	9.7–10 (2.2)
Cr	19	6.6–11 (1.6–3.9)	2.1–2.8 (20)
Cu	1.1–14	1.3–1.6 (0.3–6.0)	14–20 (4.5)
Fe	2.3–13	0–2.6 (10–16)	0–1.2 (0.7)
Hg	<LOR	0 (0)	0 (14)
Mn	0–9.5	4.3–6.0 (2.5–3.4)	7.4–8.2 (0.4)
Mo	<LOR	1.9–28 (2.2–20)	0 (3.0)
Ni	6.9	3.4–9.7 (4.5–7.6)	1.0–5.4 (9.3)
Pb	2.8–24	4.9–6.4 (2.7–5.8)	0 (6.1)
Se	7.1	n.d. (13–18)	17 (0.4–11)
Zn	0–14	4.4–16 (0–9.4)	5.7–8.0 (7.3)

Acronyms

ANZECC	Australian and New Zealand Environment Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DEC	Department of Environment and Conservation
DoE	Department of Environment (before it was amalgamated with the Department of Conservation and Land Management to form DEC in 2006)
DoW	Department of Water
NATA	National Association of Testing Authorities
PERMANOVA	Permutational Multivariate Analysis of Variance
PRIMER	Plymouth Routines in Multivariate Ecological Research

Glossary

Acid-buffering capacity	A measure of the resistance to changes in pH following the addition of an acid.
Acid sulfate soils	Naturally occurring, these are soils containing significant quantities of reduced sulfur (pyrite and other sulfides). When these soils are disturbed the reduced sulfur is oxidised, resulting in the release of acidity and often toxic metals.
Acidification	The process by which soil or water becomes more acidic (decreasing pH).
Algal blooms	The rapid excessive growth of algae, generally caused by high nutrient levels and favourable conditions. Can result in water-column deoxygenation when the algae die.
Anthropogenic	Originating from the activity of humans.
Benthic	Related to or happening on the bottom of a body of water.
Contaminants	A substance (either biological or chemical) that is either present in an environment where it does not belong or is capable of producing an adverse response.
Correlation	Indicates the strength and direction of the linear relationship between two random variables.
Hypoxic	Water with a low concentration of oxygen (typically 1–30% of oxygen saturation).
Neutralisation	The chemical reaction in which an acid and a base react to produce salt and water (H_2O).
Oxidation	The loss of electrons by a chemical species 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. (The negative log of the hydrogen ion concentration.)
Phytoplankton	Photosynthesising microorganisms in aquatic ecosystems which include diatoms, cyanobacteria and dinoflagellates.
Precipitate	The solid formed when two ionic solutions are mixed together to produce an insoluble product.
Redox potential	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 by a chemical species accompanied by a decrease in oxidation state.
Stratification	Stratification in water occurs when waters of high and low salinity (halocline), and/or cold and warm water (thermocline), form layers which act as barriers to water mixing.
Sulfate-reduction	In the aquatic environment, the microbially catalysed process which converts sulfate to sulfide.
Terrestrial	Refers to an organism (or ecosystem) being of land origin.

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