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A rapid protocol for assessing sediment condition in eutrophic estuaries

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The enrichment of sediments with nutrients and organic matter (eutrophication) is a key anthropogenic stressor of estuaries worldwide, impacting their sediment condition, ecology and ecosystem service provision. A key challenge for estuary managers and scientists is how to effectively quantify and monitor these changes in ecological condition in a timely and cost-effective manner. We developed a Rapid Assessment Protocol (RAP) for characterizing sediment condition based on the qualitative characteristics of sediment colour, odour and texture. We evaluated its utility for assessing sediment condition, and particularly the degree and effects of sediment enrichment (as quantified by complementary measurements of total C, organic C and total N) across 97 sites throughout a eutrophic microtidal estuary. RAP results were strongly and significantly correlated with the degree of sediment enrichment, with RAP scores correctly identifying the assigned enrichment class (low, medium, high) of 83.5% of sites. More enriched sediments exhibited poorer condition, manifested as significantly lower RAP scores for sediment colour, texture and odour, particularly (but not only) where enrichment coincided with elevated mud content. The RAP was particularly successful (<12% misclassification) at identifying sites with low levels of enrichment, indicating its promise as a first-pass survey approach for identifying potential reference or control sites to support impact assessments. RAP approaches based on qualitative sediment characteristics can provide a useful proxy for the degree and impacts of inorganic and organic enrichment, with potentially broad applicability for supporting timely, cost-effective assessment and monitoring of sediment condition in estuaries worldwide.

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Environmental significance

The enrichment of sediments with nutrients and organic matter is a key anthropogenic stressor that significantly impacts sediment condition in estuaries worldwide. Yet, estuary managers typically rely on intensive, costly and time-consuming approaches to quantify sediment condition, thereby limiting the extent to which these impacts may be quantified and monitored. We demonstrate that a rapid assessment protocol, based solely on qualitative assessments of sediment colour, texture and odour, provides an informative and robust proxy for the degree and effects of sediment enrichment. Rapid Assessment Protocols have considerable potential as tools for rapid, broad-scale monitoring and reporting of sediment condition, and are likely to be particularly useful in areas of the world in which technical and financial resources are limited.

1 Introduction

Estuaries are highly productive environments^{1,2} that support unique biodiversity and also human populations through their

provision of ecosystem goods and services.^{3,4} Yet the location and nature of estuaries often leave them vulnerable to a range of both natural and anthropogenic pressures, which degrade their ecological condition and undermine their ability to support these vital functions. A key challenge for estuary managers and scientists is how to effectively quantify and monitor these changes in ecological condition in a timely and cost-effective manner.

As transitional ecosystems situated at the receiving end of rivers and their catchments, many of which are important focal points for human settlement,⁵ estuaries often receive large inputs of allochthonous organic matter (OM),^{6,7} fine sediments⁸ and dissolved inorganic nutrients including nitrogen (N) and phosphorus (P).⁹ Widespread shifts to agricultural and industrial land uses over the last century, followed by rapid urbanization, have accelerated catchment exports of N, P and OM including both

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dissolved and particulate organic carbon (OC).^{6,10,11} Consequently, estuaries receive far greater inputs of nutrients per unit area than any other type of ecosystem.¹ Increasing concentrations of OM and/or nutrients in estuarine sediments, hereafter termed 'enrichment', are a significant and widespread outcome of this catchment clearance and eutrophication. Clearing of native vegetation has also enhanced the delivery of terrigenous silts and clays (*i.e.* mud) to rivers and estuaries worldwide,^{8,12} representing an additional stressor that often coincides and interacts with enrichment. The accumulation of these inputs is often particularly pronounced in the sediments of microtidal systems (tidal range <2 m), which typically have limited flushing and long residence times.¹³

Crucially, such enrichment is both a symptom and cause of degraded sediment condition (also referred to as 'sediment quality' or 'sediment health'), the mechanisms, manifestations and consequences of which are summarised in Fig. 1. Sediments containing low levels of OM and nutrients tend to support relatively low levels of biological production, be relatively well oxygenated and assimilate available nutrients from the water column through efficient nutrient processing pathways that utilize oxygen (Fig. 1a).^{14,15} The delivery of inorganic nutrients fuels increased primary production in estuaries (eutrophication), including phytoplankton and macroalgal

blooms,^{1,16} enhancing the supply of OM to sediments (Fig. 1b). Microbial decomposition of OM increases sediment metabolism and oxygen consumption, shifting sediment redox status towards hypoxic and anoxic conditions when oxygen consumption exceeds the rate of replacement through diffusion.^{15,17} Enriched sediments with high mud content are therefore particularly vulnerable to hypoxia due to reduced diffusion of oxygen through fine-grained sediments,^{18,19} and most notably where the salinity of the overlying water column is vertically stratified.^{16,17} Visible signs of oxygen deficiency include a change in sediment colour from orange/brown to grey/black, and an accompanying decrease in depth or disappearance of the apparent Redox Potential Discontinuity (aRPD) layer.^{20,21} As oxygen availability modulates many of the biogeochemical processes in sediments, these changes affect nutrient cycling between the sediment and overlying water. For example, microbially-mediated coupled nitrification–denitrification occurs in sediments with oxygen penetration depths of only a few mm, yet under frequent and/or sustained hypoxia these sediments may become reduced throughout their profile, inhibiting nitrification.²² Enriched, reducing sediments thus support limited nitrogen removal *via* denitrification,²³ act as net sources of inorganic nutrients such as phosphates and ammonium to the water column and accumulate potentially toxic

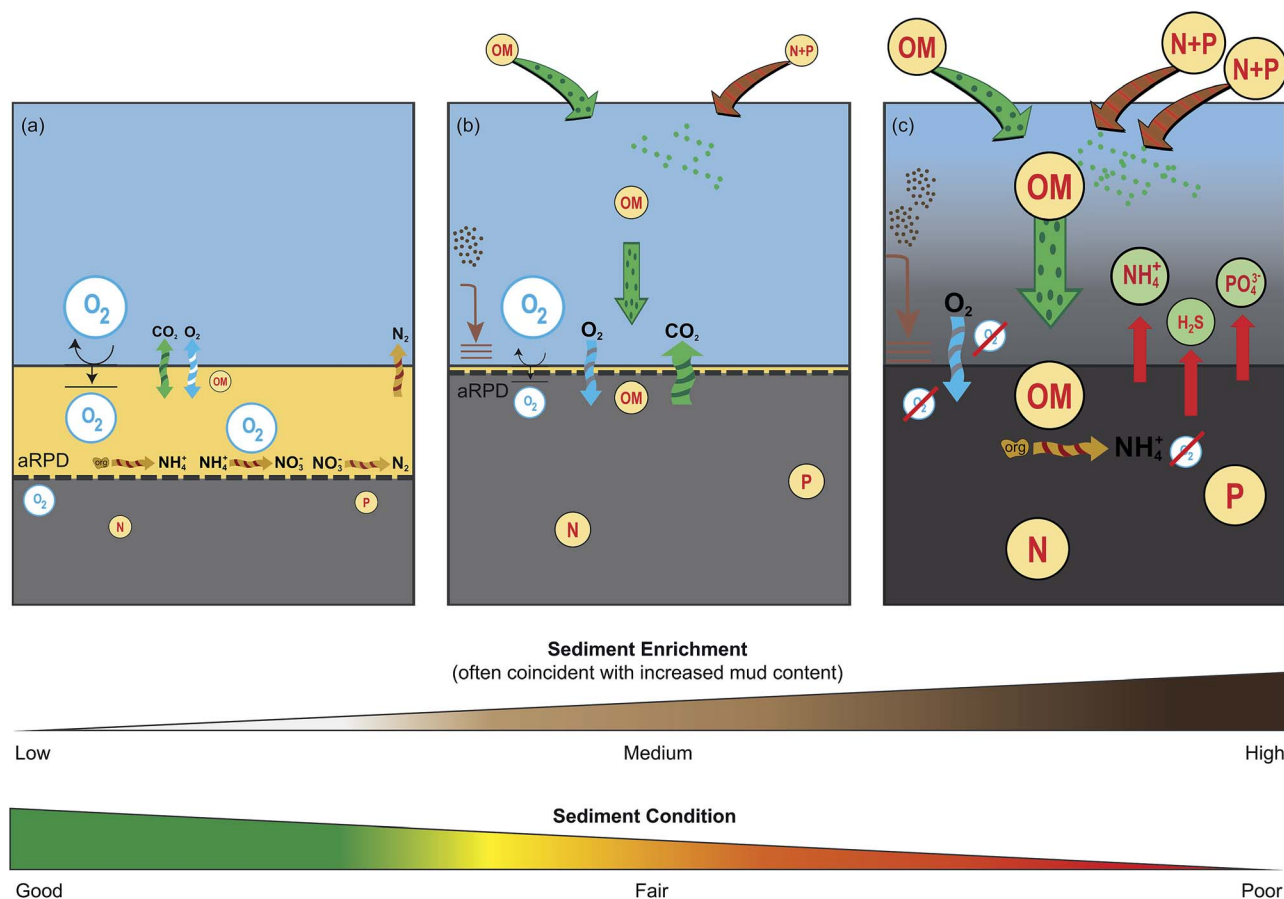


Fig. 1 Conceptual model of the effects of progressive enrichment with organic matter (OM) and nutrients on sediment condition. See text for detailed explanation. aRPD; apparent redox potential discontinuity.

sulfides, including free H_2S (Fig. 1c).^{22,24} At the extreme end of the enrichment continuum are strongly reducing, fine-grained and organic-rich monosulfidic sediments such as those found in estuaries draining acid sulfate soils.²⁵ These chronically anoxic sediments can be a significant source of methane, a potent greenhouse gas.¹⁸

Enrichment with organic and inorganic nutrients impacts not only sediment characteristics, biogeochemical processes and estuarine water quality, but also the biological communities, higher ecological functions and ecosystem services that estuaries provide.^{26,27} For example, benthic faunal communities in hypoxic, sulfidic sediments are widely known to be impoverished,^{28,29} and the release of phosphate and ammonium from hypoxic sediments can fuel algal blooms that may result in fish kills.^{30,31} Robust and cost-effective methods for quantifying the patterns, drivers and consequences of altered sediment condition in estuaries are thus imperative to better support the sustainable use of these systems.

Sediment condition, encompassing interconnected changes in the redox, OM, nutrient, and biological status of sediments, can be measured *via* a multitude of physical, chemical and/or biological approaches.^{32,33} In recent decades, such schemes have increasingly employed responses of specific species (bioassays), biotic communities (ecological assessment) or process measurements such as dissolved inorganic carbon effluxes to quantify impacts of contaminants^{34,35} or organic enrichment.^{23,36} However, as these approaches are time-consuming and expensive,³² the development of rapid, reliable and cost-effective alternatives for assessing sediment condition remains an important goal for research and management.³⁷ Rapid Assessment Protocols (RAP) have shown promise for identifying impacts of organic enrichment associated with fish farms^{38–40} and are fundamental first-pass components of habitat condition assessments for streams, rivers and wetlands worldwide.^{41–43} It is thus intuitive that similar approaches might hold considerable promise for classifying, mapping and monitoring sediment condition in estuaries. Here, we develop and test the utility of a RAP for assessing the condition of estuarine sediments, using the Peel–Harvey Estuary (Fig. 2), a highly modified, eutrophic system in south-western Australia as a case study.⁴⁴

Our primary aim is to evaluate the utility of a RAP for assessing sediment condition, and particularly the degree and effects of enrichment by organic and inorganic nutrients throughout the study system. Specifically, we address the following objectives:

- (1) Develop a RAP for characterizing sediment condition, based on the qualitative characteristics of sediment colour, odour and texture, across a large number of sites throughout the estuary.
- (2) Evaluate the degree to which RAP condition assessments provide a useful and robust proxy for the degree and effects of sediment enrichment, as reflected by complementary, quantitative measurements of TC, OC and TN.
- (3) Quantify the influence of water depth, % mud and enrichment on sediment condition, and summarise these relationships *via* spatially interpolated maps.

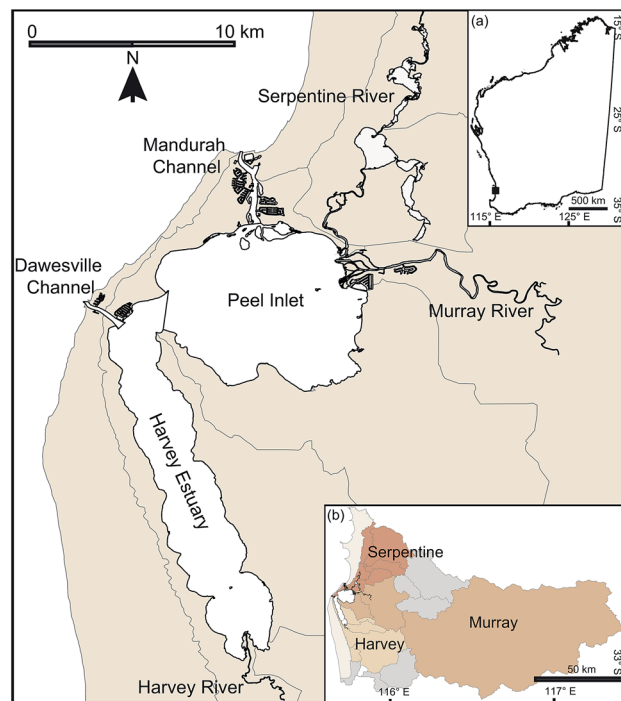


Fig. 2 Map of the Peel–Harvey Estuary, showing its two main basins, two entrance channels and three tributary rivers. Insets show (a) the location of the estuary in south-western Australia and (b) the catchments of the rivers.

We conclude by evaluating the strengths and limitations of the RAP approach, and its potential scope of application for assessing sediment condition in this and other estuaries worldwide.

2 Methods

2.1. Study location

The Peel–Harvey is a permanently-open, microtidal estuary (tidal range < 1 m) that covers ~130 km² and is located in south-western Australia (Fig. 2). It comprises two large, shallow basins (<2 m deep), namely the Peel Inlet and the elongate Harvey Estuary, and the tidal reaches of the Murray, Serpentine and Harvey rivers. Two short and narrow entrance channels connect the estuary to the ocean, namely the natural Mandurah Channel at the northern end of Peel Inlet and the human-made Dawesville Channel (or ‘Cut’) at the northern end of the Harvey Estuary (Fig. 2). The estuary supports significant ecological and human use values, as reflected by its Ramsar listing, valuable commercial and recreational fisheries, extensive marinas and high-value residential areas. Yet, the Peel–Harvey is also vulnerable to a wide range of natural and anthropogenic stressors. The system has experienced widespread catchment clearance and a long history of cultural eutrophication since 1900, the effects of which were especially prominent from the 1960s to mid-1990s when the system suffered from massive macro- and/or micro-algal blooms.⁴⁵ Major declines in rainfall since the 1970s have reduced river flushing and prolonged water residence times, exacerbating various stressors such as

hypoxia and nutrient accumulation.⁴⁴ A major engineering intervention, in the form of an artificial second channel (the Cut), was implemented in the mid-1990s to increase tidal flushing and alleviate these symptoms of eutrophication. Despite these pressures and manifestations of impacted condition, the last spatially extensive studies of sediments throughout the system were conducted in the late 1990s.⁴⁴

2.2. Sample collection

A wide-scale sediment collection program was undertaken across the estuary during November–December 2016. A total of 97 sites were surveyed throughout the two main estuarine basins (Peel Inlet and Harvey Estuary) and the estuarine reaches of the Serpentine and Murray rivers (Fig. 2), comprising 62 basin sites and 35 river sites.

We collected two replicate, intact sediment cores from within a localised area at each site, using a UWITECH corer (Mondsee, Austria) that comprised a 600 mm-long transparent PVC tube with an internal diameter of 59.5 mm. The corer was lowered to the sediment surface *via* a telescopic extension pole and pushed in until it met with increased resistance, which typically indicated the presence of a firm layer of clay (minimum core depth of 10 cm, ranging up to ~30 cm in softer sediments). The corer was then retrieved and bungs inserted into both ends of the tube to retain the structural integrity of the core, which was stored in the dark until processed (<90 min). The depth (m) of the water column was also recorded at each site.

At ~10% of sites, an additional pair of replicate cores was collected to provide a field duplicate sample for quality assurance. The duplicate cores were subjected to the same procedures as the sample cores (as outlined in Sections 2.3 and 2.4), and the resulting data used to calculate the relative percent difference between samples and their duplicates (*i.e.* the absolute difference in sediment values obtained from the original and field duplicate samples, divided by their mean and multiplied by 100).

2.3. Rapid assessment of qualitative sediment condition characteristics

Firstly, we recorded contextual information for each undisturbed core, including the depth (cm) of sediment and the

depth (cm) of the aRPD if present (indicated by a change in colour from yellow/brown surface sediments to underlying grey/black).⁴⁶ A rapid, semiquantitative assessment of sediment condition was then undertaken on each replicate core, based on sediment colour, texture and odour. Each of these characteristics was scored on an ordinal scale ranging from 0–5 (Table 1), reflecting poor to good sediment condition as outlined in the above conceptual model (Fig. 1). The scores for the three RAP variables were also summed to provide a total RAP score (0–15) for each core. Scores for replicate cores were then averaged to generate site-level RAP scores for use in subsequent data analyses.

2.4. Quantitative assessment of sediment parameters

2.4.1 Sample pooling in the field. Subsamples of sediment from pairs of replicate cores at each site were pooled in the field for subsequent laboratory analyses of quantitative sediment parameters. A pooled subsample of sediment from 0–2 cm depth was placed in a 30 ml polyethylene vial and frozen at –18 °C for analysis of % TC, % OC and % TN, and pooled sediment from 0–5 cm depth was placed in polyethylene ziplock bags and stored at –18 °C for characterisation of particle size.

2.4.2 Laboratory analyses. Particle size distribution was determined on air-dried samples using a hydrometer (Environmental Analysis Laboratory, Southern Cross University). Briefly, a known mass of air-dried sediment was mixed with deionised water and a 5% Calgon solution in an end-over-end shaker overnight, rinsed with deionised water, and hydrometric measurements taken after 30 s, 1 min, 6 min, 90 min, and 24 h.⁴⁷ The masses of each sample comprised of gravel (>2 mm), sand (50 µm–2 mm), silt (2–50 µm), and clay (<2 µm) were calculated and expressed as percentages. Data on the silt and clay fractions were then combined to produce a measure of the fine sediments at each site (% mud).

The content of TC and TN in sediments were determined from samples dried overnight at 60 °C. Sediments were ground using a ball mixer, weighed, folded into tin cups, then stored in a desiccator until analysis. To measure the OC content, an additional measure of each homogenised and ground sediment sample was weighed into a silver capsule and then acidified by

Table 1 Scoring of sediment condition characteristics under the Rapid Assessment Protocol (RAP), representing progressively poorer condition from left to right (high to low scores)

RAP variable	Scoring					
Colour	Qualitative assessment RAP score	Yellow/brown to depth of core 5	Yellow/brown overlying grey 4	Yellow/brown overlying black 3	Grey to depth of core 2	Black to depth of core 0
Texture	Qualitative assessment RAP score	Coarse grainy 5	Fine grainy 4		Smooth and silky 2	Oozy and slick/sticky 0
Odour	Qualitative assessment RAP score	No odour of hydrogen sulfide 5	Mild odour of hydrogen sulfide 4		Moderate odour of hydrogen sulfide 2	Strong odour of hydrogen sulfide 0

adding ~5 µL 10% HCl to remove inorganic C. After 30 min the acidified samples were re-dried at 60 °C, and the capsules crimped and stored in a desiccator. All samples were analysed using a Thermo Finnagin Flash EA 112 connected to an isotope ratio mass spectrometer (Thermo Delta V Plus) *via* a Thermo ConFlo III interface.⁴⁸ Standards containing known quantities of C and N were run every 10 samples to check for method drift. Standard materials were glucose (0% N, 40% C), urea (46.6% N, 20% C), cyclohexanone 2–4 DNPH (51.8% N, 20.1% C) and (NH₄)₂SO₄ (21% N, 0% C). The analytical coefficient of variation for both % TC and % TN was 1%. The method precision for sediment samples was 0.08% (C) and 0.006% (N).

2.5. Evaluating the efficacy of RAP scores as a proxy for sediment enrichment

All of the following analyses were undertaken using the PRIMER 7 multivariate statistics package with the PERMANOVA+ add-on module.^{49,50}

2.5.1 Data pre-treatment. Prior to analysis, the data for each of the above quantitative sediment variables and water depth were used to create pairwise scatterplots (draftsman plots) to visually determine any appropriate transformations required to ameliorate notable skew. % TC, % OC and water depth were square-root transformed and % TN and depth of oxic layer were fourth-root transformed. These data were then normalized to place them on a common measurement scale.⁴⁹

2.5.2 Defining a quantitative gradient of sediment enrichment. We subjected the pre-treated data for the three enrichment variables (% TC, % OC, % TN) to Principal Component Analysis (PCA) to define a quantitative gradient of observed enrichment across all study sites. This analysis sought to derive a linear function of the original variables (*i.e.* a single PC axis) which captured a large proportion (>70%) of the variation in enrichment among all sites.

2.5.3 Classifying sites based on sediment enrichment. The first principal component (PC1) scores for each site were then used as a basis for objectively classifying sites into three enrichment classes, denoted as 'Low', 'Medium' and 'High'. This was achieved by constructing a Euclidean distance matrix from the PC1 scores for all sites, then subjecting it to non-hierarchical *k*-*R* clustering *via* the CLUSTER routine, with *k* set to three.⁴⁹ This analysis grouped the sites into three sediment enrichment classes so as to maximise the value of the global *R* statistic, which ranges from 0–1 and measures (non-parametrically) the degree of overall separation of the three groups.⁵¹

2.5.4 Testing associations between RAP scores and sediment enrichment. The outputs from the above analyses were then used to evaluate the extent to which the RAP scores provide a robust proxy for the degree of sediment enrichment. Firstly, we determined how well the RAP scores differentiated among sites assigned to the three objectively-defined enrichment classes, *via* a canonical discriminant analysis (CDA) performed using the Canonical Analysis of Principal Coordinates (CAP) routine.⁵² A Euclidean distance matrix was calculated from the untreated colour, texture and odour RAP scores for all sites and

subjected to CDA, with the low, medium and high enrichment classes used as the grouping hypothesis. The number of principal coordinate axes used for this analysis (*m*) was set to three, given that we employed Euclidean distance and had many more observations than enrichment classes.⁵² A permutation test of the null hypothesis that the multivariate structure of RAP scores did not differ significantly among the three enrichment classes (*P* > 0.05) was included in the analysis, and employed Pillai's trace as the test statistic. Cross-validation outputs from the CAP, based on the misclassification error calculated for each class *via* a leave-one-out procedure,⁵⁰ were also used to quantify how well the RAP scores predicted and distinguished among the three enrichment classes.

2.5.5 Classifying and predicting sediment condition. To broaden the utility of the RAP approach beyond the current study, quantitative decision trees were developed for predicting the condition class of any new site in this system based solely on its colour, texture and odour scores. Separate analyses were undertaken for river and basin sites to account for any natural regional variation in sediment colour, texture and odour due to differences in hydrology, geology *etc.*

For each of the above regions, a Euclidean distance matrix was initially constructed from the site-level colour, texture and odour scores, then subjected to a similar clustering approach as described in Section 2.5.3, to objectively group sites into 'Good', 'Fair' and 'Poor' condition classes. Following a similar approach as Valesini *et al.*,⁵³ a model Euclidean response matrix was then created from the averaged colour, texture and odour scores in each condition class. This response matrix, together with the original site scores for each of these RAP characteristics as predictor variables, were then subjected to a multivariate regression tree approach (LINKTREE) and a concurrent Similarity Profiles test (SIMPROF).⁵⁴ This produced a binary decision tree with terminal nodes comprising the three condition classes, and branching nodes annotated with the RAP variable(s) and their score thresholds that were most tightly linked with the separation of those classes. Any new site can thus be allocated to its appropriate sediment condition class by comparing its colour, texture and/or odour scores to the thresholds at each branching node, and following the directed path until a terminal node is reached.

2.6. Quantifying and mapping key factors influencing sediment condition

Distance-based redundancy analysis (DISTLM⁵⁰) was used to quantify the proportions of the variation in sediment condition (*i.e.* RAP scores) that was attributable to water depth, % mud and enrichment (*i.e.* PC1 scores). Prior to analysis, these predictor variables were transformed where necessary, as described in Section 2.5.1, to improve the linear fit of the data.

Separate Euclidean distance matrices were calculated from the RAP scores for basin and river sites, given the potentially different influences at play in these hydrologically and geomorphologically different regions. The complementary pre-treated predictor variables were then fitted to these response matrices *via* a suite of models. Firstly, marginal tests quantified

the independent effects of each predictor. Then a series of sequential (conditional) tests partitioned the variation in sediment condition among samples that each predictor explains, having first accounted for the effects of the other predictors.⁵⁰ These sequential tests modelled all order combinations of the three predictor variables, *i.e.* including models that first fit water depth and % mud followed by enrichment, and *vice versa*. For each of the above models, the null hypothesis of no relationship between predictors and RAP scores was tested *via* permutation ($P = 0.05$), employing R^2 as the selection criterion, and non-significant predictors were excluded from inclusion in subsequent models.

Finally, spatially interpolated maps of sediment enrichment (% OC and % TN), water depth and % mud were produced to illustrate spatial differences in these potential influences on sediment condition throughout the estuary. The interpolation was undertaken in QGIS 2.18 using inverse distance weighting.⁵⁵ The interpolation raster was set to 20×20 m grid cells, and observed values of the variables were classified into quintiles (for % mud, % OC and % TN) or into five equal groups scaled between the minimum and maximum field values (for water depth), prior to interpolation.

3 Results

Sediment cores were collected from water depths of 0.1–3.4 m across the 97 sites. The relative percent difference in the quantified sediment parameters (% TC, % OC, % TN, % mud) between field duplicate samples was typically <10% and seldom exceeded 20% ($n = 3$ out of 48 duplicate pairs), indicating relatively minimal local variation in sediment parameters at a site. Among sites, sediment TC ranged from 0.07% to 7.85%, the vast majority of which typically comprised OC, whilst TN ranged from 0.01% to 0.90%. The mud content of sediments ranged from 1.3% to 85.8% among sites, with a mean of ~29%.

Duplicate cores typically returned identical RAP colour, texture and odour scores, or else varied by no more than one unit. RAP scores for colour, texture and odour all ranged from 0 to 5 among the surveyed sites, with mean scores of ~3.2 for colour and texture and 4.8 for odour.

3.1. Defining a quantitative gradient of sediment enrichment

Principal components analysis of the % TC, % OC and % TN data across all sites showed that the first axis (PC1) captured 96.6% of the variation in the enrichment data, with approximately equal contributions (eigenvectors) from each variable. This indicated that the PC1 scores provide an excellent composite proxy for the degree of enrichment across all studied sites.

3.2. Classifying sites based on sediment enrichment

The three enrichment classes, defined by clustering on the basis of their PC1 scores into low, medium and high enrichment groups, returned a global R value of 0.901, indicating a high degree of separation among these enrichment classes. Of the 97

sites surveyed, 59 and 34 belonged to the low and medium enrichment classes, respectively, with four sites comprising the high enrichment class. Sites in the low, medium and high enrichment classes exhibited consistent patterns across their TN, TC and OC values, with the median values of the high class being 10–15 times higher than those of the low class (Fig. 3).

3.3. Evaluating the efficacy of RAP scores as a proxy for sediment enrichment

The CAP analysis demonstrated a strong association between the RAP scores of sediment condition and the three quantitative enrichment classes, as reflected by the canonical correlation values for particularly the first CAP axis ($\delta_1 = 0.78$) and to a lesser extent the second axis ($\delta_2 = 0.62$). The RAP scores were also shown to differ significantly among the three enrichment classes (Pillai's trace = 0.997, $P = 0.0001$). Leave-one-out cross validation results confirmed that RAP scores provide a robust basis for differentiating sites among the objectively defined enrichment classes, with an overall allocation success of 83.5%. Only 16 of the 97 sites (16.5%) were misclassified into enrichment groups on the basis of their RAP condition scores; the misclassification error being lowest for sites in the low enrichment class (<12%) and similar for the medium and high enrichment classes (23.5–25%).

On the corresponding CAP plot, in which all sites are coded by their enrichment class, sites were distributed along two gradients (Fig. 4). One gradient, associated strongly with the RAP scores for sediment texture, colour and to a lesser extent odour (respective Pearson correlations with the first canonical axis of -0.91 , -0.82 and -0.78), separated sites in the low *vs.* medium/high enrichment classes, with RAP scores decreasing from low to high enrichment (*i.e.* from left to right along CAP1). The other gradient, most strongly associated with RAP scores for odour (Pearson correlation of -0.62 with CAP2), mainly separated sites in the high enrichment class from those in the other classes, with odour scores decreasing (reflecting increasing strength of odour) as enrichment increases.

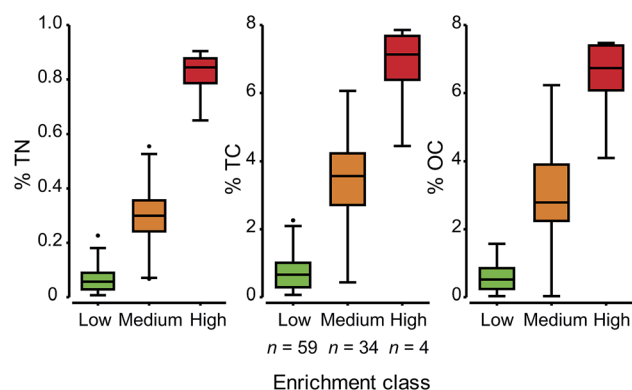


Fig. 3 Box and Whisker plots of % TN, % TC and % OC values across all sites classified as exhibiting low, medium and high enrichment based on their PC1 scores. Boxes are inter-quartile ranges; horizontal lines within boxes are medians; Whisker endpoints are high/low extremes, with outliers; n denotes numbers of sites within each enrichment class.

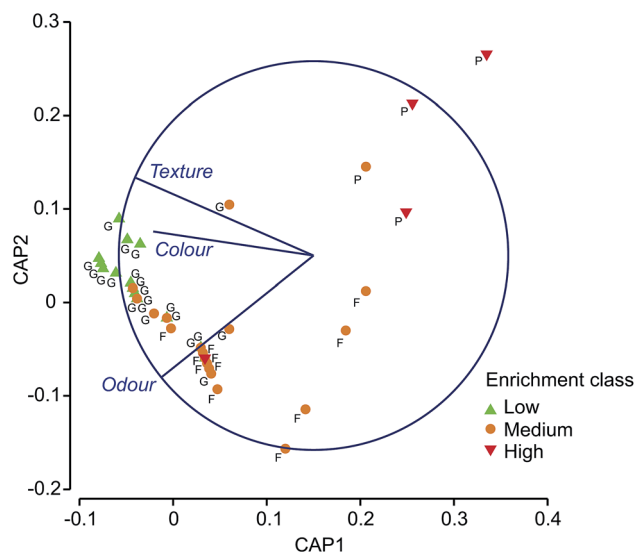


Fig. 4 Canonical analysis of principal coordinates (CAP) plot, with sites coded by symbols for their enrichment class and labelled with their Rapid Assessment Protocol (RAP) condition class (g – good, f – fair, p – poor). Plot contains overlapping points for many sites. Vectors denote the Pearson correlations of each RAP variable with the CAP axes.

Sediments in the low enrichment class generally had higher RAP scores for sediment colour and texture (median scores of 4 for both characteristics) than those in the medium (median colour = 3, median texture = 2) and particularly high (median colour = 0, median texture = 0.5) enrichment classes (Fig. 5). In contrast, both the low and medium enrichment classes exhibited comparably high median odour scores of 5, with low odour scores (*i.e.* moderate to strong odour of H_2S) being almost exclusively associated with sediments in the high enrichment class (median = 1.5). In combination, these patterns generated a clear trend of decreasing RAP total scores with increasing enrichment. Depth of the aRPD and mud content also differed across enrichment classes. Median aRPD depth decreased from 1.75 cm among low enrichment sites to zero at those in the high enrichment class. The median mud content among sites in the low enrichment class was only 6.7%, in comparison to 57–65% for medium to high enrichment sites (Fig. 5).

3.4. Classifying and predicting sediment condition

Clustering of sites into three sediment condition classes (good, fair and poor) on the basis of their RAP scores returned global R values of 0.98 for basin sites and 0.97 for riverine sites, indicating very clear differences in colour, texture and odour scores among condition classes (Fig. 6). Of the 62 basin sites surveyed,

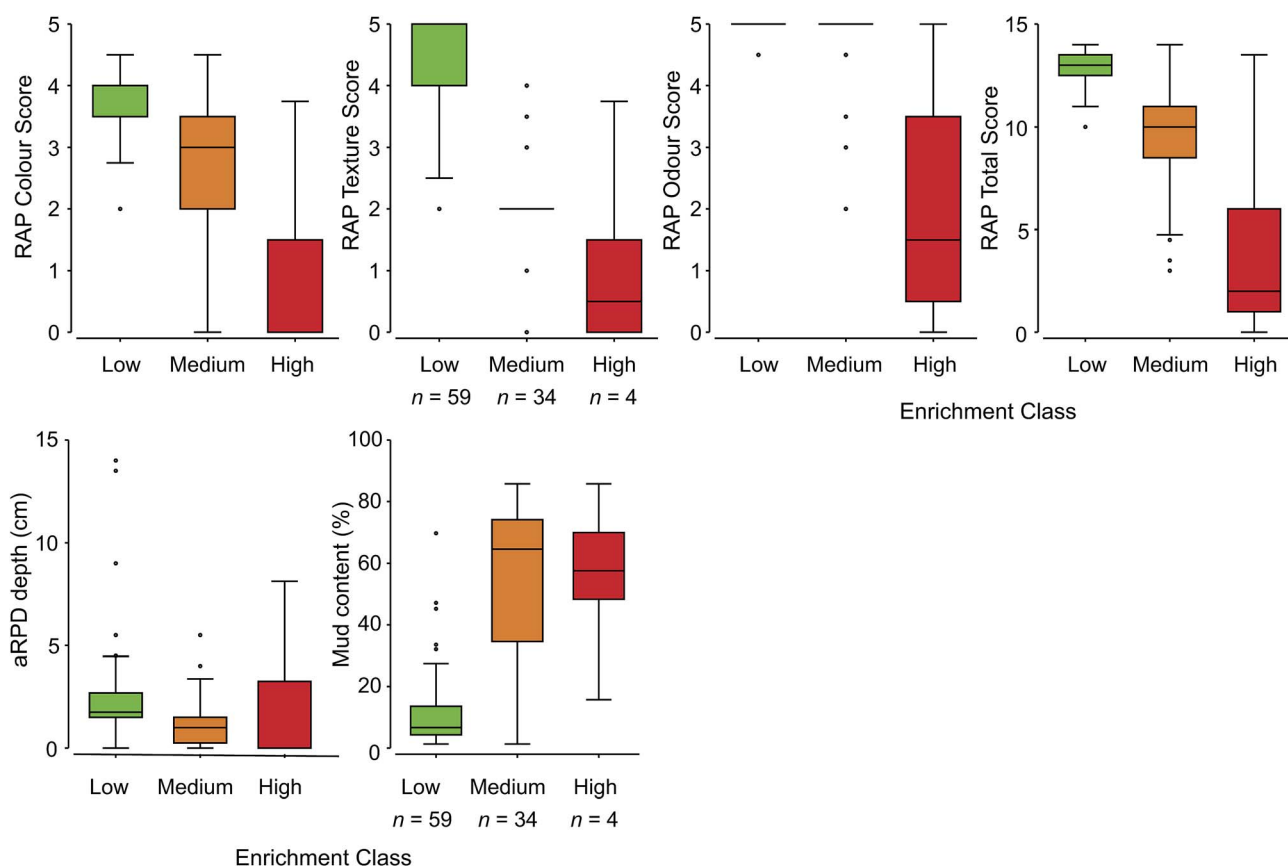


Fig. 5 Box and Whisker plots of sediment colour, texture, odour, and rapid assessment protocol (RAP) total scores, apparent redox potential discontinuity (aRPD) depth and mud content, across all sites classified as exhibiting low, medium and high enrichment based on their PC1 scores. Boxes are inter-quartile ranges; horizontal lines within boxes are medians; Whisker endpoints are high/low extremes, with outliers; n denotes numbers of sites within each enrichment class.

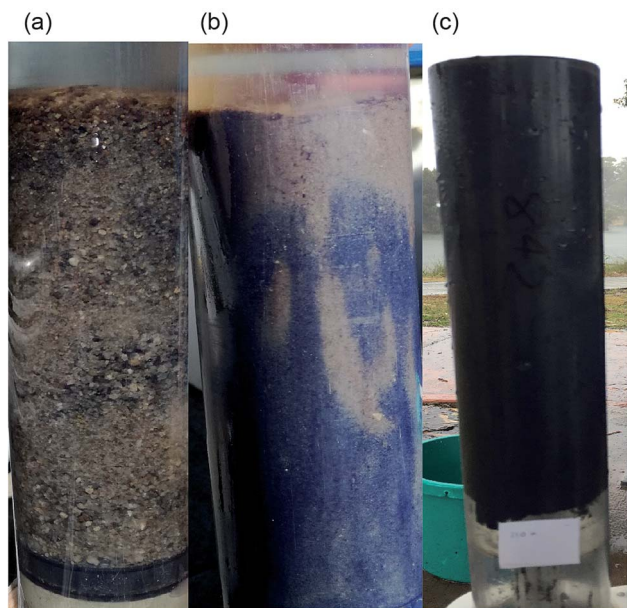


Fig. 6 Images of sediments classified as (a) good, (b) fair and (c) poor condition based on their rapid assessment protocol scores for sediment colour, texture and odour.

35, 25 and two were classed as in good, fair and poor condition, respectively. Among riverine sites, 27 were in good condition, six fair and two poor.

The patterns in RAP scores among condition classes differed slightly between basin and river sites. Among basin sites, colour and texture scores declined consistently from good (median scores of 4) through to poor condition (median scores of 0), as did total RAP scores (Fig. 7a). In contrast, riverine sites in fair and poor condition exhibited similarly low colour and texture scores (median ≤ 1) and total RAP scores (Fig. 7b). Low odour scores were largely restricted to basin and river sites classed as in poor condition, with respective median scores of 1 and 1.5.

The LINKTREE routine generated decision trees that enable the sediment condition class of any further basin and river sites to be predicted based solely on their observed RAP scores. The decision tree for basin sites indicated that poor sediment condition would be predicted for any future site with odour scores of ≤ 2 , or colour or texture scores of 0 (Fig. 8a). Any basin sites whose RAP scores did not meet any of these criteria would be assigned fair or good sediment condition, depending on whether their texture score was ≤ 2 or ≥ 3 , respectively. Among river sites, good sediment condition would be predicted for

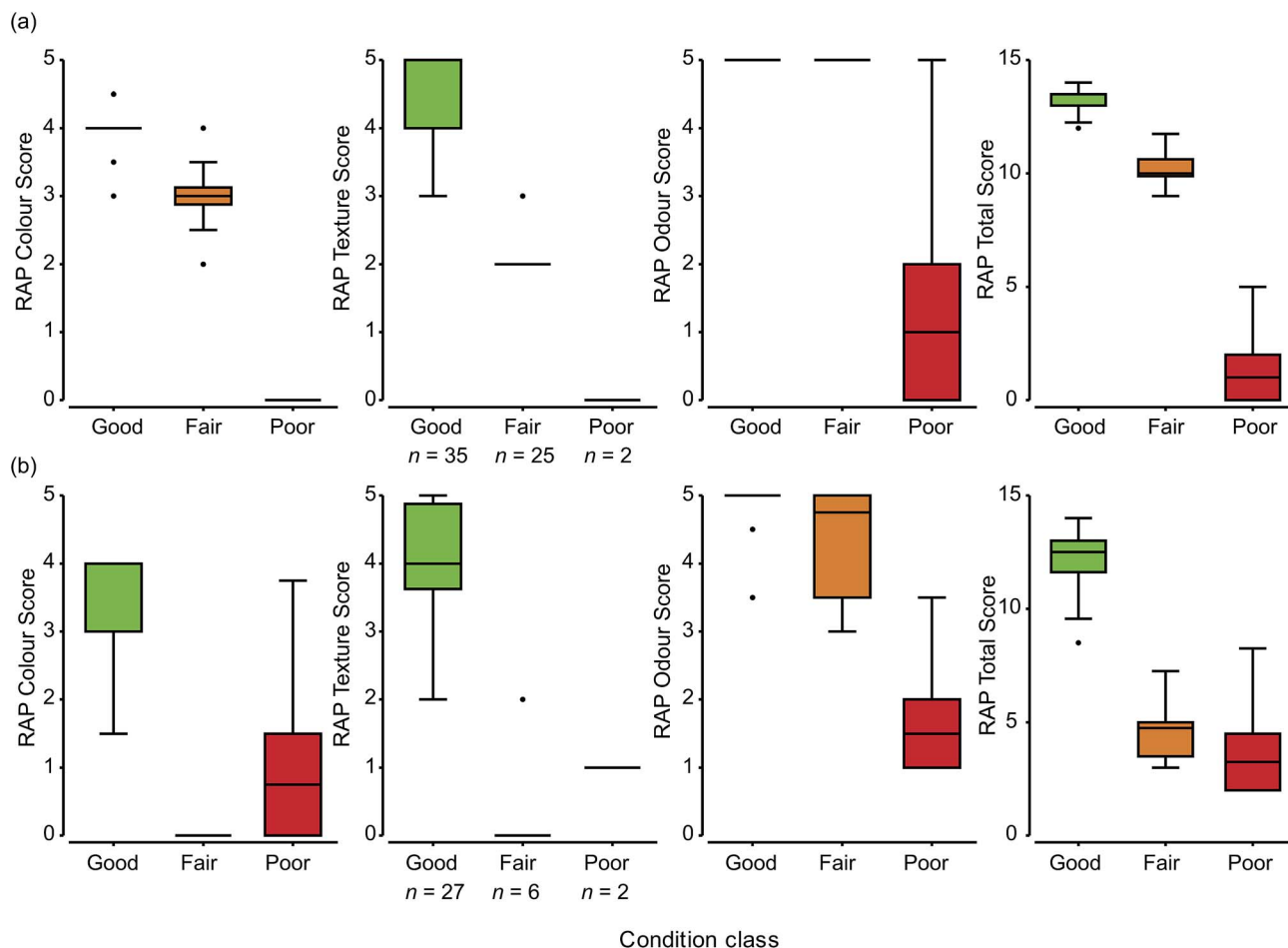


Fig. 7 Box and Whisker plots of sediment colour, texture, odour and total RAP scores among sites classified as being in good, fair and poor sediment condition, across (a) basins and (b) rivers. Boxes are inter-quartile ranges; horizontal lines within boxes are medians; Whisker endpoints are high/low extremes, with outliers; n denotes numbers of sites within each condition class.

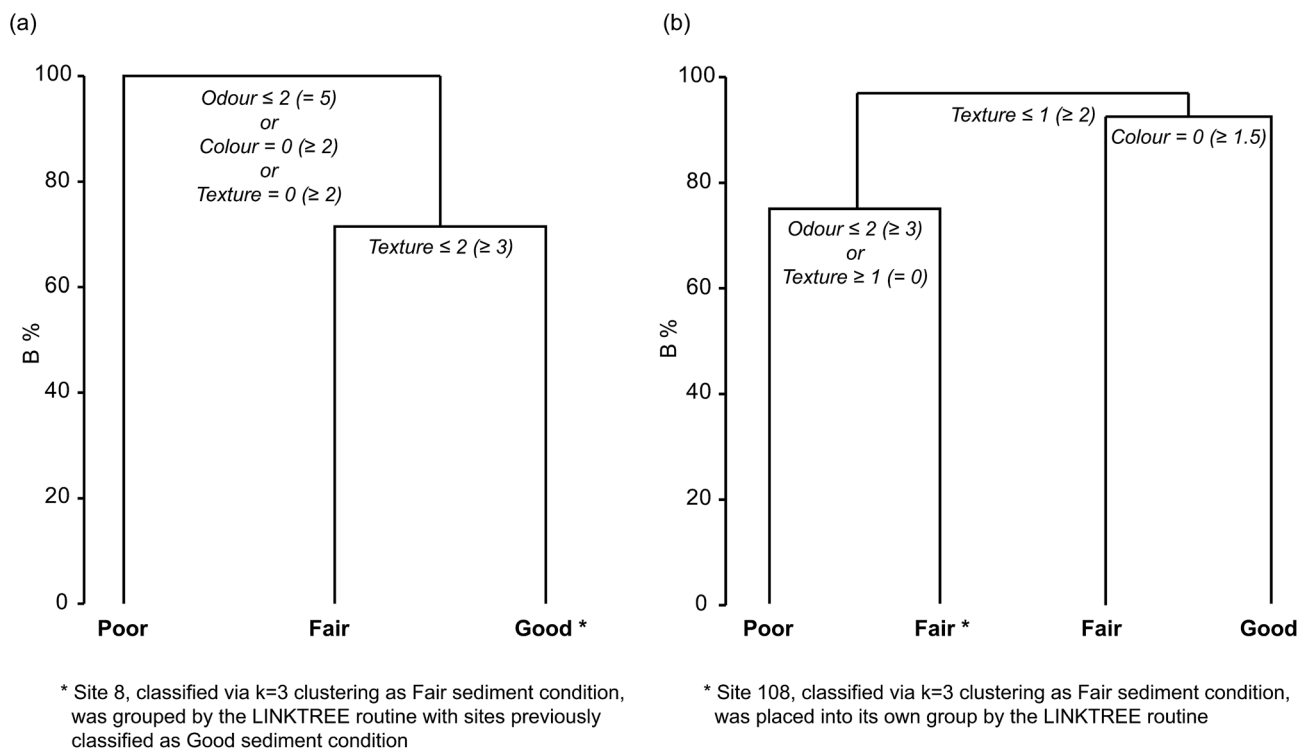


Fig. 8 Linkage trees and associated RAP score thresholds for assigning new (a) basin and (b) river sites in the Peel–Harvey Estuary to their appropriate sediment condition class (bold text at terminal nodes). Unbracketed and bracketed thresholds given at each branching node indicate that a left and right path, respectively, should be followed through the tree. B% reflects the extent of inter-class differences as a proportion of that between the most dissimilar condition classes.

those exhibiting texture scores of ≥ 2 and colour scores of ≥ 1.5 , and poor condition for sites with odour scores of ≤ 2 or texture scores of < 1 (Fig. 8b). In general, the structure of the linkage trees aligned well with the classification obtained by k -R clustering, with the exception of only one site in both the basins and rivers.

3.5. Quantifying and mapping key factors influencing sediment condition

Significant predictors together explained 61–62% and 52–54% of the respective total variability in RAP condition scores among basin and river sites (Table 2). Among basin sites, enrichment alone explained the largest proportion of the variability in RAP scores (57%), and a significant 16% of the variance even after the effects of water depth (21%) and mud (25%) were fitted. In contrast, mud explained 46% alone and only 4% after fitting enrichment, whilst water depth explained no significant additional variation after having first fitted enrichment and/or mud. Similarly, enrichment explained the largest proportion (52%) of variability in sediment condition among river sites, and 12% after fitting mud. Water depth was not a significant predictor of sediment condition among river sites, either alone or as a co-variate with other predictors (Table 2).

Interpolated maps illustrate the spatial relationships between water depth, % mud, enrichment and sediment condition throughout the Peel–Harvey Estuary. Deeper, central parts of the estuary basins generally exhibited fair sediment

condition, in contrast to the good condition of many sites on the shallower margins. These patterns generally reflected higher mud contents at the deeper basin sites, but particularly at those in the Harvey Estuary ($> 60\%$ mud; Fig. 9b), where levels of enrichment were also notably higher (Fig. 9c and d). Basin sites exhibiting poor condition occurred in localised areas of muddy sediments with the highest levels of enrichment, *e.g.* a navigation channel on the eastern side of the Peel Inlet and also in the south-eastern corner of that basin. Among river sites, fair to poor sediment condition typically coincided with higher levels of mud and particularly enrichment, and was most commonly observed in the upper reaches of the Serpentine and Murray rivers (Fig. 9c and d).

4 Discussion

The enrichment of sediments with inorganic nutrients and OM is a key anthropogenic stressor of estuarine ecosystems worldwide. Such enrichment impacts the broader condition or quality of sediments *via* various mechanisms, including changes to their redox status, biogeochemical processes and interactions with overlying water.^{23,56,57} These disruptions can have severe and wide-ranging effects on their biological communities and ecosystem service provision.^{27,58} Yet, estuary managers typically rely on intensive, costly and/or time-consuming approaches to quantify sediment condition (*e.g.* see Simpson *et al.*³³), thereby limiting the spatial and temporal scales over which condition is

Table 2 Proportions of the variation in rapid assessment protocol condition scores across all basin and river sites, explained by the predictors of water depth, % mud and enrichment (PC1 scores)^a

Test	Predictor	SS (trace)	Pseudo-F	Proportion explained	Cumulative proportion explained (R^2)	Res. SS	Res. df
Basin sites ($n = 62$; total SS = 184.55)							
Marginal	Water depth	38.76	15.95	0.21*			60
	Mud	84.05	50.18	0.46*			60
	Enrichment	105.74	80.50	0.57*			60
Sequential	Water depth	38.76	15.95	0.21*	0.21		60
	+Mud	46.46	27.59	0.25*	0.46		59
	+Enrichment	29.53	24.53	0.16*	0.62	69.80	58
Sequential	Mud	84.05	50.18	0.46*	0.46		60
	+Enrichment	29.50	24.52	0.16*	0.62	71.0	59
Sequential	Enrichment	105.74	80.50	0.57*	0.57		60
	+Mud	7.82	6.50	0.04*	0.62	70.99	59
River sites ($n = 35$; total SS = 212.59)							
Marginal	Water depth	13.17	2.18	0.06			33
	Mud	88.21	23.40	0.41*			33
	Enrichment	111.36	36.31	0.52*			33
Sequential	Mud	88.21	23.40	0.41*	0.41		33
	+Enrichment	26.25	8.56	0.12*	0.54	98.14	32
Sequential	Enrichment	111.36	36.31	0.52*	0.52	101.23	33

^a Marginal tests indicate the proportion of the variation the predictor accounts for alone, while sequential tests indicate the proportion added by the predictor to the cumulative proportion of explained variation. * Significant ($p < 0.05$); non-significant predictors were excluded from subsequent models. SS = sum of squares; df = degrees of freedom; Res. = residual.

characterized and compared. We therefore developed a Rapid Assessment Protocol (RAP) for assessing the condition of sediments based on their colour, texture and odour, and tested its utility for quantifying the degree and effects of sediment enrichment throughout the Peel–Harvey, a highly eutrophic estuary in south-western Australia.

The RAP provided a robust measure of the degree of sediment enrichment and its broader effects on sediment condition. This was demonstrated *via* a rigorous statistical testing framework utilizing quantitative enrichment data (% TC, % OC, % TN) from a broad-scale survey of 97 sites. RAP scores differed significantly between low, medium and high enrichment sites. More enriched sediments exhibited poorer condition, manifested as significantly lower RAP scores for sediment colour, texture and odour, particularly (but not only) if enrichment coincided with elevated mud content. The RAP approach has broad applicability for supporting cost-effective assessments of sediment condition, given its simple scoring system based on well-documented responses of sediment condition to enrichment, and the predictive framework we developed to classify the condition of any new site.

4.1. RAP scores as a proxy for sediment enrichment

The RAP provides an informative and robust proxy for the degree and effects of enrichment, with considerable potential for conducting rapid, broad-scale assessments of sediment condition at low cost. Patterns in the RAP scores differed markedly and significantly between the three enrichment classes (low, medium, high). Moreover, cross validation confirmed that RAP scores alone provide a robust basis for

differentiating sites among the objectively defined enrichment classes, correctly identifying the enrichment class to which 83.5% of sites had been assigned. The RAP was particularly successful (<12% misclassification rate) at identifying sites with low levels of enrichment, demonstrating its promise as a first-pass survey approach for identifying ‘least impacted’ reference or control sites to support impact assessments. The observed classification success rates compare favourably, for example, with those from studies of biotic indices of estuary health in the USA, in which classification efficiencies of >80% were considered high.^{59,60} Nonetheless, further characterisation of the responses of RAP scores across sites of medium to high enrichment would be desirable to obtain more robust condition classifications for more highly enriched sites in particular (see Section 4.3). The need for robust classification of the most impacted sites is particularly important, given the potential consequences and costs of failing to identifying such sites (*e.g.* adverse impacts on estuary ecology and/or water quality, and an inability to achieve future rehabilitation).

The generally high classification efficiencies reflect the very clear alignment between the groupings of sites under the independent enrichment and RAP condition classifications. The CAP analysis revealed that sites in the low enrichment class almost exclusively comprised coarse-grained sands with a clearly discernible oxic layer, *i.e.* a surface layer of yellow/brown sediments distinguished from underlying grey/black sediments by an aRPD, and little to no odour of H₂S. The low enrichment sites were almost always classified as exhibiting good condition, aside from a few sites that were classed as fair condition based on their lower texture scores (which in turn reflected their higher mud contents). Sites in the medium

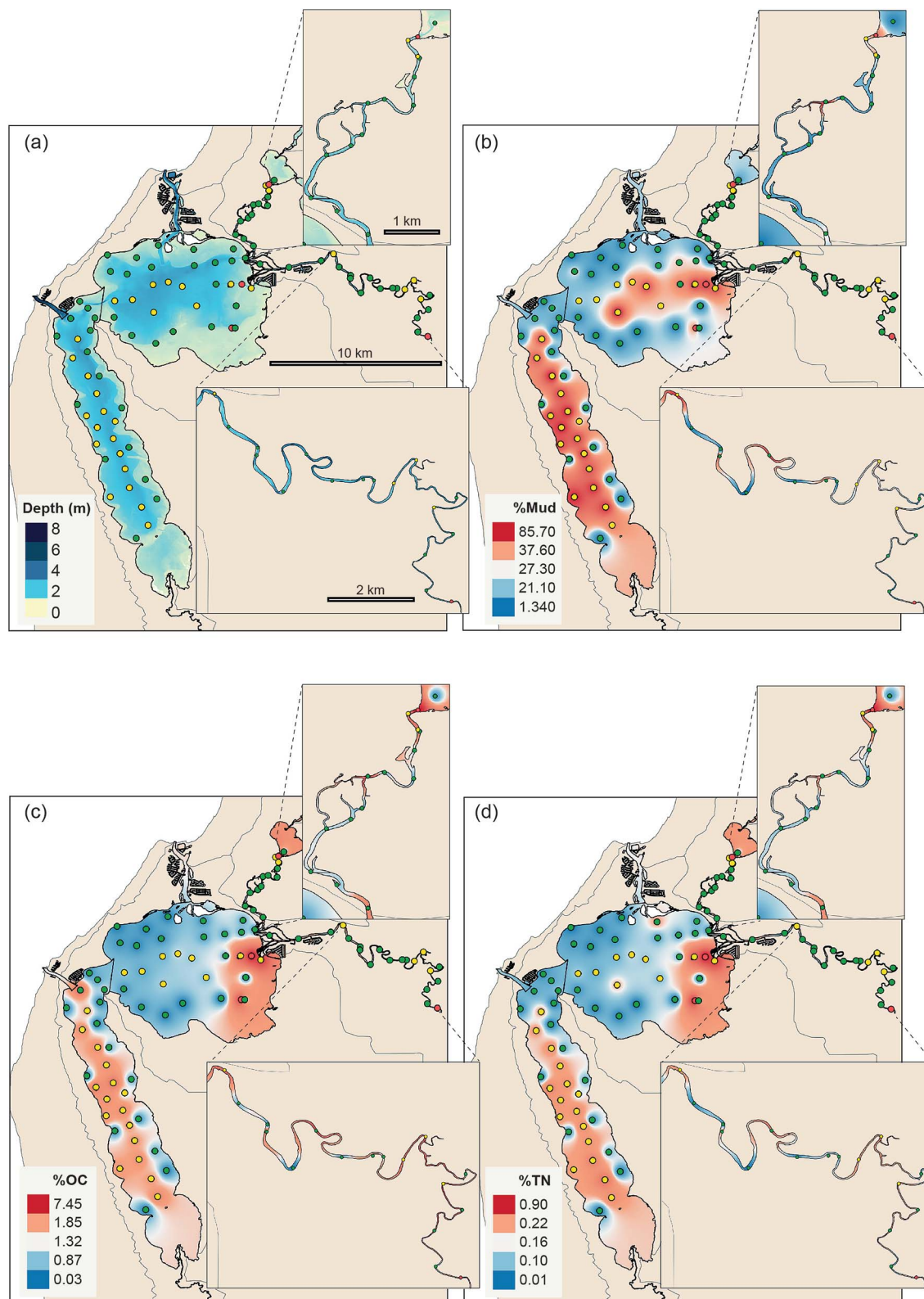


Fig. 9 Spatially interpolated maps of (a) water depth, (b) % mud, (c) % OC, (d) % TN. Circles denote locations of sampled sites, colour coded according to their sediment condition class (green, good; yellow, fair; red, poor). Insets provide higher resolution views of patterns in the rivers.

enrichment class ranged from good to fair condition, being far more variable in terms of their sediment colour and texture, yet very few of these sediments exhibited a discernible sulfidic

odour. In contrast, high enrichment sites (most of which were classified as poor condition) were typically oozy, grey/black muds with little to no surficial oxic layer and a moderate to

strong sulfidic odour. The one exception was a high enrichment site that, despite having an OC content of 6% and comprising 65% mud, exhibited no odour and a 6.5 cm-deep oxic layer and was therefore classed as fair condition. This likely reflects the location of this site in shallow waters (~0.7 m) on the eastern side of the wide Peel Inlet, which would encourage advective oxygenation of surface sediments through wave-induced pumping,⁶¹ driven by frequent and strong westerly winds.⁶²

The RAP approach is underpinned by a conceptual model of the effects of enrichment on sediment condition, modulated by the influence of fine sediments. According to this model, enhanced delivery of allochthonous and/or autochthonous OM, often in conjunction with increased fine particles (mud), alters the physical and biogeochemical properties of sediments, including their porosity, redox status and nutrient cycling processes (Fig. 1).^{23,56,63} These effects manifest as changes in sediment texture, colour and odour,^{15,20,21} which the RAP aims to summarise *via* a semi-quantitative scoring system. We acknowledge that the relationships between sediment enrichment, grain size and ecological condition are more complex than conceptually modelled here. For example, redox state is far more spatially and temporally heterogeneous than the simple characterization based on sediment colour,^{18,64} particularly at microscopic scales and when the influences of bioturbating fauna are considered.^{65,66} Nonetheless, the strong, statistically significant relationships between RAP scores and quantitative enrichment parameters demonstrated in our study provide clear evidence of the RAPs capacity as a robust and cost-effective proxy for quantifying the impacts of eutrophication on sediments across a system.

A high degree of correspondence was also evident between the individual RAP scores for sediment texture, colour and odour and the quantitative measures of sediment enrichment, grain size and aRPD depth. The RAP thus provides a useful and informative measure of not only the degree of enrichment, but also the impacts of enrichment on sediment condition more broadly. RAP texture scores effectively reflected the mud content of sediments throughout the estuary, and thus represent a highly cost-effective alternative to time-consuming, laboratory analyses of grain size. Moreover, as muddy sediments tend to contain more organic C and N, reflecting higher rates of OM retention and preservation,⁶⁷ texture scores alone are also broadly indicative of sediment enrichment (*e.g.* Fig. 4). Given these findings, we expect that texture scores could also provide a broad proxy for other nutrients and pollutants that, although not measured in our study, are known to be associated with fine sediments.^{32,68} For example, phosphorus binds to fine-grained particles and its accumulation is a major cause of the eutrophication of estuaries in south-western Australia and elsewhere,^{17,69,70} particularly due to its role in stimulating algal blooms.³⁰ Likewise, many heavy metals, chlorinated hydrocarbons and other pollutants sorb to fine particles and OM and therefore accumulate in enriched, muddy sediments.^{71,72}

Importantly, our RAP approach also provides an informative proxy for sulfur metabolism, an important aspect of sediment condition that is negatively impacted by enrichment.²⁴ Although we did not quantify the sulfide content of sediments

in this study, the CAP results indicate strong agreement between RAP odour scores and enrichment class. The most highly enriched, poorest condition sediments were not only characterised by low scores for both texture (fine-grained) and colour (black), but importantly were separated from all other sites by their very low odour scores, indicating the accumulation of hydrogen sulphide as a toxic by-product of anaerobic metabolism of OM.²⁸ Given the expense of quantifying sulphide content in the field, our evidence indicates RAP odour scores can provide a useful, rapid and low-cost alternative for identifying highly sulfidic sediments.

4.2. Key factors influencing sediment condition in estuaries

Estuaries naturally receive and often accumulate OM, inorganic nutrients and fine sediments from their catchments and *via in situ* processes. Yet, the rate of accumulation of these sediment constituents depends on both anthropogenic factors such as catchment clearing, urbanisation and agricultural practices that enhance delivery,^{8,9} and more natural characteristics such as estuary geomorphology and hydrology that influence deposition.⁷³ Crucially, the proportion of mud, which varies naturally with water depth,¹⁹ influences sediment enrichment as nutrients and OM bind to fine sediment particles and are remineralised less rapidly.^{14,74} Deeper waters therefore tend to harbour muddier and more enriched sediments, particularly in microtidal systems whose natural characteristics predispose them to limited flushing and extended water residence times.¹³

The Peel–Harvey Estuary exemplifies the synergistic effects of anthropogenic and more natural influences on sediment dynamics in microtidal systems, and the resulting vulnerability of these estuaries to enrichment. Like many other microtidal systems, the Peel–Harvey's once densely vegetated catchment has been extensively cleared and converted to drained and irrigated land for dairy pasture and horticulture, enhancing the delivery of fine sediments, inorganic nutrients and OM to the estuary's tributary rivers and wide receiving basins.⁴⁴ The accumulation of these anthropogenic inputs is exacerbated by naturally low levels of tidal flushing due to the estuary's narrow connections to the microtidal marine environment, and also by declining freshwater flows under a drying climate,⁷⁵ which are reducing the degree of riverine flushing and leading to increased stratification and retention.⁴⁴

Importantly, enrichment explained 12–16% of the variability in sediment condition among river and basin sites even after fitting mud, whereas mud was an insignificant or at best minor (4%) predictor after fitting enrichment. Thus, enrichment was significantly associated with poorer sediment condition among river and basin sites, irrespective of their mud content. Nonetheless, our results also showed that anthropogenic and natural influences combine to influence sediment condition in the Peel–Harvey Estuary, confirming the critical role of mud as a key stressor of sediment condition, and particularly in microtidal estuaries.^{12,13} Enrichment and mud exhibited covarying effects on sediment condition in the rivers of the Peel–Harvey Estuary, with more enriched river sediments exhibiting poorer condition particularly if they were muddier. However, any such differences

in the sediment condition of river sites were unrelated to natural differences in their water depth, as indicated by the lack of a significant depth effect in any DISTLM model. Enriched sediments with low RAP scores thus occurred at all depths in the rivers of this system, but were generally more prevalent in the upper reaches of the study area.

In contrast, water depth and mud content both significantly influenced sediment condition in the estuary basins. Mud explained 25% of the variability in sediment condition among basin sites after fitting water depth (which explained 21%), whereas water depth was insignificant after first fitting mud. This indicates that water depth influences the condition of basin sites through its effects on the mud content of their sediments: basin sediments in deeper waters were more likely to be muddier and therefore more enriched than those in the shallows, and thus have lower RAP scores. This pattern is particularly evident in the Harvey Estuary (Fig. 9). Historical sediment surveys in 1978–89 also revealed higher concentrations of OM, TN and total phosphorus in the finer-grained sediments of the central Harvey Estuary than in the Peel Inlet,⁶⁹ highlighting the long-standing nature of this problem. The intensively fertilized Harvey catchment, with its particularly high density of artificial drains and sandy sediments with low nutrient binding capacity, has delivered large quantities of inorganic nutrients to the estuary over many decades.⁴⁵ Moreover, significant freshwater flows from the upper Harvey River have been artificially diverted to the ocean since the 1930s,⁷⁶ contributing to the Harvey Estuary experiencing far less flushing than the Peel Inlet, which receives flows from the Serpentine and much larger Murray rivers. Consequently, fine sediments, nutrients and OM from the Harvey catchment have tended to accumulate in its basin to a greater degree, with evident impacts on sediment enrichment and condition. This outcome has potentially important implications for the future management of water resources and downstream impacts in the Harvey Estuary, particularly under a drying climate that will see further reductions in flushing river flows.⁷⁵

The poorest sediment condition in the Peel–Harvey Estuary occurred at sites with both high enrichment and mud content, and particularly those in artificially deepened navigation channels where flushing is minimal and thick macroalgal mats are known to undergo rapid burial below layers of fine sediment.⁷⁷ Previous, intensive studies of these channel sites have revealed strongly reducing, monosulfidic sediments that can release ammonium and phosphates into the water column even under oxic conditions.⁷⁸ These findings have significant implications given the forecast expansion of marina developments and boating channels within the system in coming decades, and particularly the proposed dredging of a new, large channel to support a major marina development opposite the Dawesville Channel.

More broadly, our findings from the Peel–Harvey Estuary align with those of previous studies in this and other estuaries of south-western Australia,⁷⁹ and other eutrophic estuaries worldwide. Sediment OC content is typically <1% in estuaries that are relatively unimpacted by eutrophication and in deeper sediment layers deposited prior to the 1800s.^{80,81} Yet, in

eutrophic estuaries as diverse as Mediterranean coastal lagoons and Norwegian fjords, anthropogenic enrichment typically elevates sediment OC content to ~3–4%, and potentially to 10% and above in highly depositional areas.^{79–82} For example, among a data set compiled from >2300 sites in estuaries along the east coast of the United States, the OC content of sediments at the vast majority of sites was <4%, ranging to a maximum of 16% at a limited number of locations.⁸³

4.3. Significance, applications and future work

Eutrophication is a threat to the health of estuaries across Australia^{84,85} and worldwide,^{11,17} with potentially significant ecological and socio-economic costs.⁸⁶ The associated enrichment of estuarine sediments with OM and nutrients, often accompanied by increased fine particles, degrades sediment condition, inducing a shift towards hypoxic/anoxic conditions and anaerobic pathways that produce potentially toxic by-products such as H₂S and ammonia.^{17,56} Such shifts typically result in impoverished faunal communities with fewer bio-turbating infauna,^{24,29,87} further exacerbating the effects of these stressors and impacting ecosystem function.^{27,58,88} Given such widespread and serious impacts of eutrophication on estuarine sediments, any robust, cost-effective approach for assessing sediment condition will have potentially wide-ranging applications for estuary monitoring and management.

The RAP approach we have described is far quicker and cheaper to employ than most traditional methods for assessing sediment condition, and its outputs are very well correlated with those of more intensive, time-consuming quantitative measurements of enrichment. As such, it provides a robust and cost-effective means of reliably assessing sediment condition over meaningful spatial and temporal scales, with numerous potential applications. For example, if employed for periodic, broad-scale surveillance monitoring,⁵ the RAP could enable the sediment condition of the estuary and its component regions to be tracked over time and help to signal a need for management responses where pre-defined limits of acceptable change are exceeded. The RAP could also be used as a first-pass method for identifying the least and most impacted sites throughout the estuary. The former sites would have potential value as reference or control sites for future environmental impact assessments, while the latter could inform areas to target for environmental restoration or support risk assessments of future dredging activities. Finally, RAP results are informing the construction of a coupled hydrological-biogeochemical model for the Peel–Harvey Estuary and helping to define spatial stressor gradients throughout the system. These outputs in turn are providing a framework for quantifying the ecological responses of benthic macroinvertebrate communities and subsequently establishing a biotic index of estuarine condition.⁴⁴

This study has also derived quantitative decision rules by which to determine the condition class of any future basin or river site in this system, based solely on their observed RAP scores. By extension, this predictive framework should theoretically enable the RAP to be applied to other estuaries in which

enrichment is a significant stressor, subject to additional testing and multivariate analyses as described above. The capacity to apply the RAP quickly and generically across systems could facilitate assessments and comparisons of sediment condition among estuaries at various spatial scales (e.g. local to bioregional), greatly helping to direct management resources to achieve the most effective and pragmatic outcomes.

However, further work would be required to maximise the broader applicability of our approach. As a first step, this study should be replicated in multiple estuaries across the region, encompassing largely pristine systems through to other heavily modified estuaries with high reported levels of sediment enrichment, such as the Swan–Canning.⁷⁹ Pooling the resulting data would provide more robust information on the relationship between enrichment and condition and how this varies among different estuary basins and rivers, and would enable the decision rules for condition classification to be modified where necessary to encompass the characteristics of all potential estuary sites across the region. Specifically, data from diverse sites across different estuaries could resolve potential issues associated with the small sample sizes of highly enriched/poor condition sites in the current study. Expanding the data set in this manner would generate more reliable thresholds for assigning sites to condition classes based on their RAP scores, and also enable independent validation (as opposed to cross-validation) of the classification of sites into enrichment groups based on their RAP condition scores. Despite these outstanding questions, the outputs of this study help to highlight the potentially broad importance of RAPs for supporting cost-effective monitoring and management of estuaries.

By extension, the RAP could be applied and tested yet more broadly, across different estuary types from lagoons to fjords and different climate zones worldwide. Testing the RAP under diverse conditions (including, for example, both anthropogenically and naturally enriched habitats, sheltered vs. exposed locations, and different water depths) would help to define the potential range of variability in RAP responses, and enable the protocol to be modified accordingly, with e.g. different scoring rules for different types of estuary. We therefore encourage other researchers to trial and evaluate the approach described here across a range of estuaries affected by eutrophication and enrichment.

Conclusions

Rapid Assessment Protocols (RAPs) based on qualitative or semi-quantitative evaluations of ecosystem attributes are commonly used for assessing and tracking the health or condition of rivers and wetlands worldwide. However, such tools are rarely employed for assessing ecological condition in estuaries, where more intensive, expensive and time-consuming quantitative approaches predominate. Our findings indicate that RAPs hold considerable promise for quantifying the effects of key stressors associated with eutrophication, i.e. organic and inorganic enrichment, on the condition of estuarine sediments. Our RAP approach, founded upon a simplified conceptual model of physical and biogeochemical responses to one of the

most widespread anthropogenic pressures, is likely to be broadly applicable to many regions worldwide. The simplicity and rapidity of the RAP facilitate large numbers of repeated observations in space and over time, enabling natural resource managers to respectively map impacts and monitor trends in estuary sediment condition in a more cost-effective manner. We envisage that the RAP approach could be particularly useful in areas of the world in which technical and financial resources are limited.

Conflicts of interest

There are no conflicts to declare.

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