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Recommendations for sampling and analysis of Darwin Harbour sediment

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Introduction

Darwin Harbour

Darwin Harbour is a macro-tidal drowned river valley on the coast of the Northern Territory. During low tide large expanses of mudflats are exposed and the fringes of these mudflats support large stands of mangroves. Several waterways discharge to Darwin Harbour, the largest being Blackmore River and Elizabeth River. Sediments in the river catchments are predominantly fine-grained, mainly clay and silt. Creeks and rivers may transport coarser material into the estuary during the wet season, though much is trapped by coastal vegetation, both riparian and mangrove (McKinnon et al. 2006). The fine sediment delivered to the upper arms of the harbour settles out of suspension and is then eroded and re-deposited by tidal currents. Hard substrates generally occur in high current environments and soft substrates (mud) form in low current areas such as sub and intertidal flats and mangroves. Hydrodynamic modelling of the fate of suspended sediment plumes has shown that substantial sediment fluxes are directed up-estuary causing trapping of fine sediment and that the sediment fraction exported to the ocean is relatively small (Williams et al. 2006).

Sediment sampling and analysis

There is a substantial literature on sampling and analysis of marine and estuarine sediment. For example, the Australian Guidelines for Water Quality Monitoring and Reporting (ANZECC 2000a) contains guidelines and several references on the subject. Maher et al. (1994) published a general framework for designing sampling programs which outlines the many considerations that should precede a sampling program. This includes defining the study objectives, the boundaries and scale of the study, the indicators to be sampled for, site selection, timing of sampling, replication, quality assurance and documentation. The successful outcome, or otherwise, of any study will depend on appropriate decisions being made regarding all of these factors.

The recommendations contained in this document arose from a recent baseline study of intertidal and mangrove sediment from Darwin Harbour conducted by Aquatic Health Unit (Department of Land Resource Management) and CDU (Munksgaard et al. 2013). The intention is to promote a common sampling and analytical methodology for adoption by consultants, government, researchers and others to facilitate the comparison of data sets and their collation into a single Darwin Harbour data set. The methodologies can also be used in other coastal NT waters.

It should also be noted that in some circumstances there may be a legal requirement for adherence to certain standard methods for sampling, preservation and analysis (e.g. methods published by Standards Australia, ISO or DIN).

Field sampling

Study design

Study designs that measure change between sites and over time include the BACI (before–after-control–impact) group of designs (ANZECC 2000a, 2000b). These study designs compare the values of parameters measured at both undisturbed and disturbed sites and draw inferences from the differences. Inferences should not be based solely on changes over time or changes over space unless there are no valid control sites or pre-disturbance data.

Site selection:

Once the study objectives and design have been defined, planning of sampling sites can proceed. Commonly, sites are located systematically in some pattern around sources of the anticipated impacts that are the focus of the study. The appropriate selection and location of one or several control (reference) sites is a fundamental requirement of most studies. Practical consideration of accessibility and safety must also be taken into account; in Darwin Harbour tidal conditions are one of the main determinants of accessibility.

Sampling device

Hand or winch operated grab samplers provide relatively convenient and fast sampling of bottom sediment in relatively deep water (including all of Darwin Harbour). Several designs of grab samplers exist (e.g. Van-Venn grab, Fig 1) and each type has advantages and disadvantages with respect to operating in soft and hard sediment and the degree of disturbance of the sampled sediment. Most grab samplers will cause some disturbance to sediment strata and the penetration depth is uncertain but usually in the range 5-10 cm for a 10 kg hand operated grab. Samples collected by grab may in some cases be subject to loss of fine grained portions of the sample as water drains from the grab during retrieval.

Figure 1. Van Veen grab sampler (at left) and AMS core sampler with liner; multiple extension rods can be added to the corer for use in water depths up to several meters.

Quantitative sampling of bottom sediment from a known area and depth are better carried out by coring. The choice of coring depth depends on several factors, primarily the requirement to ensure representative sampling which is related to factors such as sediment grainsize and the depth of anoxia where metal concentrations may change. The amount of material needed for analysis of all required parameters will also constrain the choice of coring depth and diameter. Previous sampling of intertidal sediments in most parts of Darwin Harbour used a 60 mm diameter corer to 50 and 100 mm depth (Munksgaard et al. 2013). A number of hand operated coring devices are available for operation in shallow waters (Fig. 1). However, sediment coring at water depths in excess of a few meters commonly requires heavy equipment unsuitable for small vessels. Core sampling can also be undertaken for mangrove sediments accessible by foot.

Recommendation 1: Core sample collection is undertaken, in preference to grab samples, whenever possible. The top 5 or 10 cm is sampled for chemical analysis.

It is imperative that the procedures carried out during sampling (including any sub-sampling) ensure that the sample taken is representative of the sediment being investigated. For example, coarse sediment requires a larger sample than fine grained sediment. Generally, sand should be sampled in the kg range whereas silt and clay may be sampled in the 100 g range.

Sample preservation

The preservation of sediment samples aims to avoid biological, chemical and physical changes before the sample can be analysed. The method of preservation will depend on the analytes to be measured. For metal analysis samples are commonly collected in zip-lock plastic bags without addition of any chemical additives and stored dark and cold (<4^{o}C). However, for other types of analyses (e.g. hydrocarbons and other organics) contact with plastics should be avoided (glass containers are preferred). Some analytes require the addition of chemical preservatives for stabilisation.

Analytical methods

Parameters of interest

The choice of indicators to be measured depends on their relevance to the study objectives. These indicators can be driving factors (e.g. nitrate concentrations) or resultant factors (e.g. chlorophyll concentration). The capabilities of the analysing laboratory to obtain the required data and data quality should be established during project planning.

Sample preparation

Sieving of sediment samples are commonly undertaken to selectively analyse a portion of a sediment sample. The aim may be to avoid inclusion of large or extraneous objects (e.g. leaves / roots/ gravel) that would otherwise cause the processed sample to be unrepresentative of the sediment. For this reason sediment samples are commonly sieved to <2mm grainsize. The aim can also be to isolate a defined grainsize fraction in order to enhance detection of change in a parameter that is linked to that grainsize fraction (e.g.

metals adsorbed to clay and silt in the <63μm fraction). It is imperative to ensure that representativeness of the original sediment is maintained throughout sample preparation. Sieved sediment is commonly air dried at a temperature not exceeding 60^{o}C to prevent loss of volatile analytes.

Recommendation 2: Sediment samples for chemical analysis are sieved to <2 mm grain size and dried at <60 °C.

Numerous extraction and digestion methods are available to prepare sediment samples for instrumental analysis. The choice of methods depends on the study objectives and indicators. For example, analysis of metals in sediment can be carried out by extraction (digestion) in different acids under different conditions. Common methods include: 1) a 'weak' acid extraction to measure bio-accessible concentrations, 2) a 'strong' acid extraction to include most metals in mature sediment and 3) a 'total' acid digest to include all metals including those bound in mineral lattices (Table 1).

Table 1. Acid extraction methods for analysis of metals in sediment

Method	Fraction determined	References
1N HCl	Bio-accessible	ANZECC 2000a
HNO_3+$HClO_4$ (conc)	'Near total'*	Munksgaard and Parry (2002)
HF+HNO_3+$HClO_4$+HCl (conc)	Total**	ALS (2013)

*: Includes most metals in mature clay, silt and carbonate and dominated sediment
**: Includes detrital mineral-bound metals; some rare earth element may not be completely extracted

Instrumental methods

Usually there are several analytical methods by which the required parameters can be determined. The selection of the preferred method(s) depends on many factors, including the feasibility of measurement with acceptable detection limits, precision, accuracy and cost. The analytical laboratory should be consulted prior to sampling as particular analytical methods may require specific procedures to be carried out during sampling and preparation.

Quality Assurance

The aim of a quality assurance program is to identify, measure and control errors. Errors during the sampling-analysis process include erroneous (or misunderstood) operation of the sampling device, contamination of samples during and after collection, preparation and instrumental determination errors. These errors can be assessed by adopting a detailed quality control program to include analysis of replicate samples, replicate sample preparations, replicate analyses, process blanks, spiked sub-samples and certified reference materials. Quality accreditation by the analysing laboratory may be required in some studies.

Documentation of field procedures (e.g. site coordinates, time of sampling, environmental conditions), sample labelling, laboratory procedures (e.g. analytical output and data processing) and chain of custody documents are critical quality assurance procedures.

Data Processing and presentation

Concentrations of analytes of interest are commonly used to directly assess sediment quality by comparisons between impact and control sites or by comparison with guideline levels. However, there can be confounding factors to take into account before a direct comparison can be made. For example, the effect of grain size on the spatial distribution of metals has long been recognised (Loring and Rantala 1995, Birch 2003). This confounding factor can be reduced by either separating or analysing a uniform sediment grain size (usually the <63 µm fraction), or the total sample data can be normalized to a conservative element which acts as a proxy for fine grained material. The normalisation of concentration data may provide clearer information regarding spatial patterns of dispersion of metals from point sources.

Three methods of metal/metalloid normalisation may be considered: 1. Grainsize normalisation, 2. Aluminium normalisation and 3. Post-extraction normalisation (PEN) accounting for undissolved non-metal-bearing silicates (Birch 2003). The PEN method appears unsuitable where shell carbonate contents are significant as in Darwin Harbour. Shell carbonates are relatively metal poor, but acid soluble, which violates the underlying assumption of the PEN method that the metal poor portion is composed of insoluble silicates. Normalisation to the clay+silt content (<63 µm fraction) often produce similar results to Al-normalisation as there is a strong correlation between these two parameters. Aluminium normalisation may be preferable to grainsize normalisation, as relatively costly grainsize analysis can be avoided and comparisons can be made to data sets for which grainsize data is unavailable. Al-normalised metal concentrations can be calculated as the equivalent metal concentration at an Al concentration of 10,000 mg/kg (1% by weight).

Recommendation 3: Sediments analysed for metals should include analysis of Al, and expressed normalised for Al concentration (This is not intended to exclude the analysis for sediment particle size distribution, though this may not be necessary).

The choice of statistical analysis of a data set depends on the information required and as different statistical procedures has different data requirements; these decisions need to be made before data collection starts. The number of samples and replicates as well as the precision of measurements will determine the smallest difference or change that can be detected between areas or over time.

Comparison to sediment quality guidelines

The sediment quality guidelines used in Australia and New Zealand (ANZECC 2000a) are based on an effects database for contaminated sites, on laboratory toxicity testing and on predictions based on equilibrium partitioning of contaminants between sediment and pore water. The recommended guideline values have been labelled interim sediment quality guideline (ISQG) values and the low and high values correspond to the effects range-low and -median used in the NOAA listing (Long et al. 1995). The consideration of sediment

quality in the ANZECC (2000a) guidelines follows a decision-tree approach (Fig 2). If the lower sediment quality guideline, the trigger value, for a particular contaminant is not exceeded, it is unlikely that it will result in any biological disturbance for organisms inhabiting that sediment. If the trigger value is exceeded, either management (including remedial) action is taken, or additional site-specific studies are conducted to determine whether this exceedance poses a risk to the ecosystem.

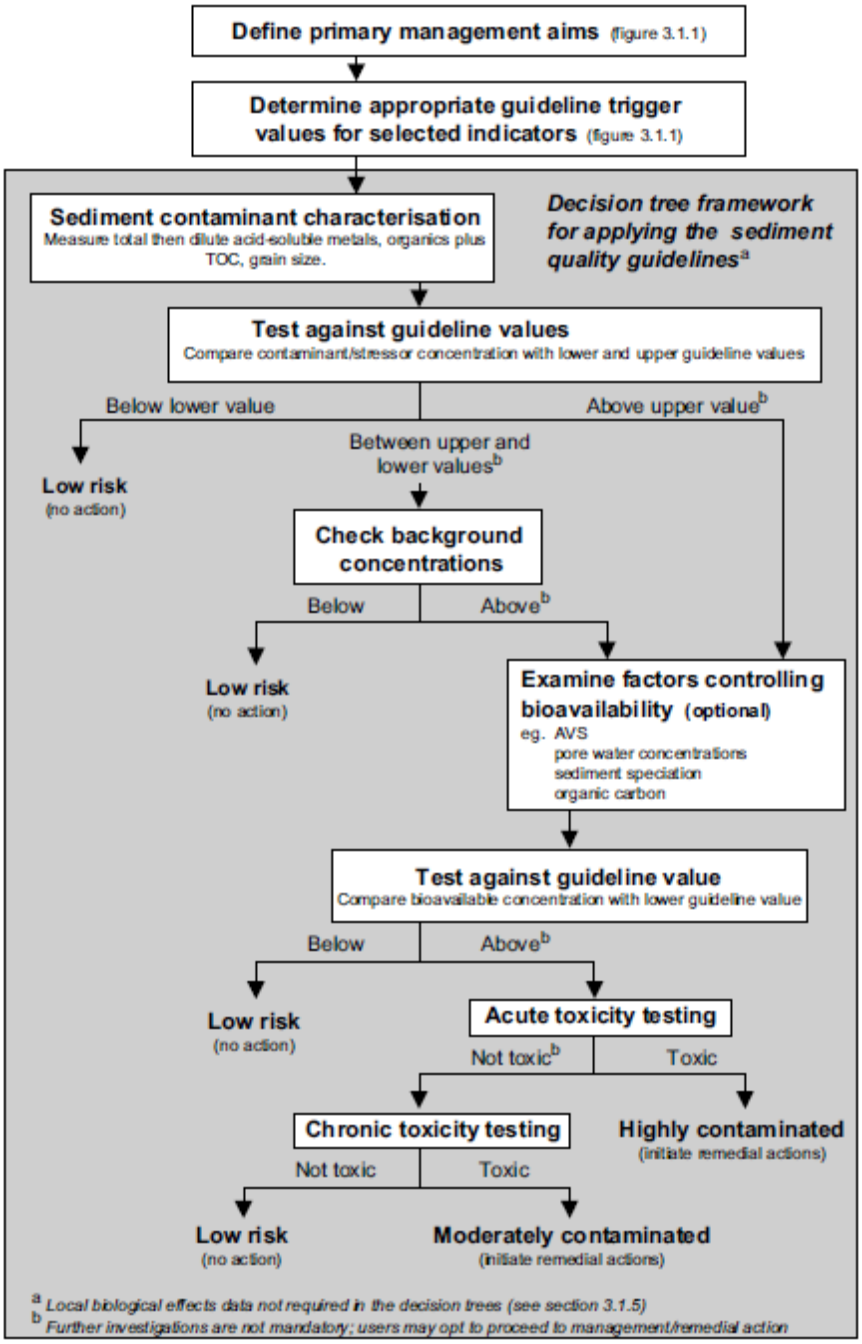

Figure 2. Decision tree for the assessment of contaminated sediments (copied from Figure 3.5.1, ANZECC 2000a).

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