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Sediment quality guidelines for copper and zinc for filter-feeding estuarine oysters?

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A strong correlation between oyster tissue Cu and Zn concentrations and fine-fraction surficial sediment digested in 1 M HCl provided a sedimentary guideline which predicted tissue metal concentrations in oysters and established a level for protecting oysters from exceeding human consumption levels for these metals. The guidelines for fine surficial sediment developed in the present work accurately predicted oyster tissue concentrations in the field.

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ABSTRACT

Sediment quality guidelines (SQGs) assess the ability of bottom sediment to sustain healthy infauna and water quality guidelines (WQGs) provide protection for a designated percentage of aquatic species. Filter-feeding marine species, e.g. oysters and mussels, acquire food from particles in the water column and protection of these animals is not provided by SQGs or WQGs. The current work investigated the relationship between metal (Cu, Zn) concentrations in total and fine-fraction (<62.5 μm) surficial sediment digested in a range of acids and chelating agents and oyster tissue metal concentrations. A strong correlation between oyster tissue Cu and Zn concentrations and fine-fraction surficial sediment digested in 1 M HCl provided a sedimentary guideline which predicted tissue metal concentrations in oysters and established a level (<45 $\mu g\,g^{-1}$ and <1000 $\mu g\,g^{-1}$, respectively) for protecting oysters from exceeding human consumption levels (70 $\mu g\,g^{-1}$ and 1000 $\mu g\,g^{-1}$, respectively).

1. Introduction

Surficial sediments of coastal waterways in urbanised/industrialised regions of the world are frequently contaminated by a large range of chemicals (Hyland et al., 1999, 2000; Birch and Taylor, 1999, 2000; McCready et al., 2000). However, chemical data alone do not provide an effective basis to determine potential adverse effects on living resources. To establish biological significance of sediment-bound contaminants requires information on persistence, toxicity and bioaccumulation, whereas biodiversity and functionality of a biological community may be determined by measuring infauna structure and abundance. These measurements are, however time consuming, expensive and require a high level of expertise, hence sediment quality guidelines (SQG) are commonly used to make an initial assessment of sediment toxicity in the absence of biological effects data (Batley, 1987; DiToro et al., 1990; Chapman et al., 1992; Long et al., 1995). The concentration of contaminants with which toxicity and other adverse biological effects are associated has been determined using an empirical approach, which matches sediment chemistry and biological effects data. Numerical, effects-based SQG have emerged as an important management tool for initial screening of sediment chemical data and are used to identify and prioritise problem areas, as well as to determine contaminants of concern worldwide.

The effects-range guidelines developed by Long and colleagues (Long and Morgan, 1990; Long et al., 1995) are now the most widely used SQGs for estuarine and marine environments and are well established in many parts of the world, including the US, Canada, Australia, The Netherlands, and Hong Kong (Long and MacDonald, 1998). The scheme provides two values for each chemical, effects-range low (ERL) and effects-range median (ERM), which delineate three concentration ranges: concentrations below ERL values identify conditions where adverse biological effects are rarely observed; concentrations at or above ERM values represent a range above which adverse biological effects frequently occur; and concentrations equal to or greater than ERL, but below ERM represent a range within which biological effects occur occasionally. The SQGs adopted by Australia and New Zealand (ANZECC/ARMCANZ, 2000) are based on this scheme and provide Interim Sediment Quality Guidelines-Low (ISQG-L) and -High (ISQG-H)

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values, which are broadly equivalent to the ERL and ERM values, respectively (ANZECC/ARMCANZ, 2000).

Water Quality Guidelines (WQGs) (ANZECC/ARMCANZ, 2000) aim to protect animals in ambient waters from sustained (chronic toxicity) exposure to toxicants. Similar to SQGs, WQGs provide trigger values which are chemical-specific estimates, which are used directly or as part of a decision-making scheme to provide the protection required. Trigger values were derived for different protection levels (between 80% and 99% of species expected to be protected), however in most cases, the 95% protection level trigger level is applied to ecosystems that are slightly to moderately disturbed. Should the trigger value, as determined from management aims, be exceeded, then factors that modify toxicity and bioavailability are assessed, e.g. complexation (humic and fulvic acids), pH, organic carbon and hardness.

Bioaccumulation is a dynamic indicator of water quality and ecosystem integrity (Rainbow and Phillips, 1993; Verweij et al., 1992) and has gained universal acceptance as a measure of the bioavailable fraction of contaminants in the aquatic environment (Phillips, 1980). Bivalve molluscs, e.g. mussels and oysters, tolerate a wide range of temperatures, salinity, concentrations of suspended sediments and dissolved oxygen (Anderson, 2001). These animals are able to accumulate contaminants in tissue to high concentrations without lethal effects, these organisms are sedentary and easy to sample and therefore provide an attractive biomonitoring tool worldwide (Phillips, 1980). The Sydney Rock Oyster (*Saccostrea commercialis*) is commonly used in New South Wales (NSW), Australia as a biomonitoring species because it is ubiquitous on the east coast, it survives transplantation and exposure to contaminants, accumulates contaminants to concentrations proportional to ambient waters and is readily available from commercial growers (Brown and McPherson, 1992; Scanes, 1996; Scanes and Roach, 1999; Spooner et al., 2003).

Although SQGs are useful and widely adopted globally, they are specific to benthic populations and were not applicable to animals living in the water column. Attempts to relate tissue burden of filter-feeding molluscs to sediment chemistry (Scanes and Roach, 1999) and to SQGs (Spooner et al., 2003) have understandably failed as these measures involve analyses of total bottom sediment chemistry, i.e. materials with which these animals are not in contact. Filter-feeding animals remove particles from the water column and do not consume food directly from the substrate. Suspended material in the water column comprises sediment and organic material resuspended from the estuary floor and biological particles (e.g., phytoplankton) produced in the water column. Tissue of animals filtering material from the water column should therefore be more closely related to the fine, resuspendable fraction of bottom sediment than to total sediment chemistry when metals are mainly present in sediment and not in the dissolved phase of water. The objective of the current investigation was to determine the relationship between oyster metal (Cu and Zn) tissue burden and surficial sediment metal concentrations over a wide range of environmental and geographic conditions and to test the utility of setting SQGs based on fine-sediment metal chemistry for filter-feeding estuarine species using the Sydney Rock Oyster (*Saccostrea commercialis*).

2. Methods

2.1. Study sites

Four estuaries on the NSW coast were selected to represent a wide range of sedimentary types, environmental conditions and geographic locations (Hogg, 2007). One estuary (Fig. 1A) was selected from each of the four categories identified in the recent condition assessment of all 979 Australian estuaries (National Land and Water Resources Audit) (NLWRA, 2002), i.e. 'near-pristine' (Saltwater Creek), 'largely unmodified' (Port Stephens), 'modified' (Pittwater) and 'extensively modified' (Brisbane Waters). Four sample locations were selected in each estuary, except Pittwater where 8 sites were used to define a strong contaminant gradient.

Oysters were sampled randomly in lower Saltwater Creek, an estuary with a largely rural catchment. In Port Stephens, oysters were taken in two large marinas in the partly urbanised seaward basin and in two areas in the undeveloped upper basin (Fig. 1C). Sample locations were chosen along the highly-urbanised east coast in Pittwater to characterise the strong southerly increasing metals gradient (Birch et al., 1998; Judge, 1993) (Fig. 1D). Oyster samples were taken in the urbanised northern, muddy part of Brisbane Water (Fig. 1B), as well as in the largely residential, high-energy, sandy southern section of the waterway.

2.2. Sediment analysis

Five sediment samples were taken at each sampling location and approximately 15 Sydney Rock oysters were collected to facilitate meaningful statistical analyses. Sediment samples were taken in March 2007 with a stainless-steel boxcore and the oxic, upper 1 cm of sediment was taken to ensure only the most recent and most resuspendable sediment was collected. Samples were stored on ice until being returned to the laboratory. A two-litre water sample was collected at each location to determine suspended sediment load.

All glassware and plastic vessels were soaked in hot water and detergent for a minimum of 4 h before being scrubbed and placed in a nitric acid (HNO_3) bath for approximately 12 h. Prior to use, each vessel was rinsed with distilled water and dried.

Total and fine-fraction sediment (wet sieved at <62.5 μm) were digested in *aqua regia* (1:1 HNO_3:HCl) (US EPA method 200.8). A blank, duplicate and replicate International Reference Material (AGAL-10) were included in each digestion block ($n = 22$). Samples were heated at 120 °C for 2 h and made up to 30 mL with ultra pure water.

The bioavailability of metals in total sediment was estimated using Ethylenediaminetetraacetate (EDTA) and HCl digests (Batley, 1987; Ying et al., 1992). Approximately 5 g of sediment was placed into centrifuge tubes and 25 mL of 1 M HCl added. This procedure was repeated with 25 mL of 0.05 M EDTA. A blank was included in each batch of EDTA and HCl samples. Samples were shaken for 2 h and placed in a centrifuge for 10 min at 3200 revs/min.

2.3. Oysters tissue analyses

Five individual oysters of equal size (approximately 6×4 cm) from each site were measured for length, width and breadth before being shucked. The wet weight of oyster tissue and shell weight were recorded. Five oysters from each site were selected at random and remaining tissue was pooled. Individual oysters and homogenates were freeze dried and dry weights recorded. Pooled samples were homogenized with a blender after freeze drying.

Approximately 0.3 g of oyster tissue was weighed inside a teflon digestion tube and 5 mL of HNO_3 was added. Samples were digested in a closed-vessel, pressure-controlled microwave in a modified version of US EPA method 3052 (Baldwin et al., 1994; Walter et al., 1996; Maher et al., 2001). A blank and a replicate sample of Standard Reference Material (SRM 1566b) were included in each digestion block of 22 microwave tubes. Five replicate digestions were performed on each homogenate in the same manner as individual oysters.

2.4. Water samples

Two-litre water samples were filtered through a dried and pre-weighed 0.45 μm filter paper. Once filtered, papers were stored in a desiccator until dry. The dry weight of filter papers was recorded and the weight of total suspended sediment (TSS) was calculated. Filter papers were digested in *aqua regia* and 10 mL ultra pure water at 120 °C for 2 h. One blank and one replicate AGAL-10 sample was included in each digestion block.

2.5. Elemental analysis and data quality

Analyses were by Inductively Coupled Plasma Atomic Emission Spectra (vista AX CCD Simultaneous ICP-AES) for the main bioaccumulated metals, i.e. Cu and Zn. Detection limits, precision and accuracy for sediment and tissue analyses are give in Table 1.

2.6. Statistical methods

Linear regression was utilised to examine relationships between sediment metal concentrations (fine fraction, total sediment and bioavailable fractions) and oyster (single and blended) tissue metal concentrations using the statistical package SPSS™ (Seber and Lee, 2003). One way ANOVA was performed using SPSS™ to test for differences in mean metal concentrations in sediments and oysters between sites in each estuary (R^2) (Underwood, 1997). Data were ln (x) transformed to conform to Cochran's homogeneity of variance test. A Student–Newman–Keuls (SNK) test was performed on each analysis to rank sites based on metal concentrations (Underwood, 1997).

A significant relationship (detected by regression, ANOVA or t-test) is defined as one where the result is unlikely to have occurred by chance alone, i.e. the critical