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Macrophytes as bioindicators of heavy metal pollution in estuarine and coastal environments

D.R. Farias[a,*], C.L. Hurd[b], R.S. Eriksen[c,d], C.K. Macleod[a]

[a] Fisheries, Aquaculture & Coasts, Institute for Marine & Antarctic Studies (IMAS – FAC), University of Tasmania, Nubeena Crescent, Taroona 7053, Tasmania, Australia
[b] Institute for Marine & Antarctic Studies (IMAS), University of Tasmania, 20 Castray Esplanade, Battery Point, Hobart 7004, Tasmania, Australia
[c] Antarctic Climate & Ecosystem CRC Private Bag 80, UTAS, Hobart, 7001, Australia
[d] CSIRO Oceans & Atmosphere, Castray Esplanade Battery Point, Hobart 7004, Australia

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ABSTRACT

The Derwent estuary, in Tasmania (Australia), is highly contaminated with heavy metals with significant levels in both sediments and benthic fauna. However, little is known about metal content in benthic primary producers. We characterized metal content (Arsenic, Cadmium, Copper, Lead, Selenium and Zinc) in twelve species of macrophyte, including red, green, and brown algae, and seagrasses, from the Derwent. The metals, arsenic, copper, lead, and Zinc were detected in all of the macrophytes assessed, but the levels differed between species. Seagrasses accumulated the highest concentrations of all metals; with Zn levels being particularly high in the seagrass *Ruppia megacarpa* (from the upper Estuary) and Pb was detected in *Zostera muelleri* (from the middle estuary). *Ulva australis* was ubiquitous throughout the middle-lower estuary and accumulated Zn in relatively high concentrations. The findings suggest that analysis of multiple species may be necessary for a comprehensive understanding of estuary-wide metal pollution.

1. Introduction

Biological indicators can provide information on the long-term effects of metal contamination as well as an indication of the potential for impacts at higher levels as a result of trophic interactions. Organisms that accumulate metals in tissue can be particularly informative with species that are consumed by humans (e.g. mussels, fish, and oysters) providing an important public health understanding of the potential for impacts further up the food chain (Rainbow and Phillips, 1993). Using individual organisms to evaluate contaminant loading is known as biomonitoring, and such organism is classed as ‘bioindicators’ (Zhou et al., 2008). Zhou et al. (2008) proposed five features that would make a species a suitable bioindicator: i) the selected organism should be able to accumulate high levels of pollutants; ii) they should be sessile or constrained to a particular location in order to reflect local pollution; iii) they should be relevant in the food chain; iv) they should be abundant and v) they should be widespread. In addition, practical considerations such as ease of sampling and easy identification will also help to make a species a good bioindicator (Rainbow and Phillips, 1993).

Molluscs, crustaceans and macrophytes have consistently been shown to be valuable cosmopolitan bioindicators (Rainbow, 1995; Rainbow and Phillips, 1993). Macrophytes, seaweed and seagrass, have been used in many studies as bioindicators of contamination. A number of studies have used green algae, particularly alga in the Order Ulvales as bioindicators of metal pollution in a number of studies (Ryan et al., 2012; Boubonari et al., 2008; Zbikowski et al., 2007; Brown et al., 1999; Ho, 1990). The cosmopolitan distribution and high metal accumulation capacity of *Ulva lactuca*, an extremely common annual green alga, has shown it to be a very valuable bioindicator with a high affinity for manganese (Mn), iron (Fe), copper (Cu), zinc (Zn) and lead (Pb), consequently, this species provides a very good warning of both domestic pollution and industrial contamination (Ho, 1990). Several brown seaweeds are also frequently used for biomonitoring. For instance, *Fucus vesiculosus* has been shown to be a popular bioindicator of heavy and trace metals in the north hemisphere (Ryan et al., 2012; Stengel et al., 2005; Guisti, 2001; Jayasekera and Rossbach, 1996; O'Leary and Breen, 1997), *Ascophyllum nodosum* and *Laminaria digitata* have been used to indicate temporal and intraspecific metal fluctuation in a coastal area (Stengel et al., 2005), *Lessonia trabeculata* and *Lessonia nigricens* were effective in identifying Cu mining pollution in Chilean coastal waters (Sáez et al., 2012; Leonardi and Vasquez, 1999; Contreras et al., 2009). Red seaweeds have also been shown to be effective in detecting different trace and heavy metals (Ryan et al., 2012;

* Corresponding author.
E-mail address: D.FariasAqueveque@utas.edu.au (D.R. Farias).

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Ródenas de la Rocha et al., 2009; dos Santos et al., 2014; Leal et al., 1997).

Seagrasses are perennial plants, substrate stabilisers and have been shown to be sensitive to pollution, and therefore are useful for biomonitoring and as bioindicators of pollution (EPA, 2014). They also play a number of important ecological roles; providing a food source, habitat, refuge for marine animals and improving seawater quality by absorbing nutrients through their roots (Papenbrock, 2012; Huang et al., 2006). In South Australia, the ecological importance of seagrass communities and the associated risk from coastal pollution has been formally recognized with seagrass being protected in legislation under the Native Vegetation Act (1992).

Some seagrasses are quite specific in their sensitivities to contamination, and their effectiveness as bioindicators of pollution has been clearly demonstrated (Ralph et al., 2006; Romero et al., 2006a; Tupan et al., 2014). For instance, *Cymodocea nodosa* has been used to assess environmental levels of Cd, Mn, Zn, Cu and nickel (Ni) (Llagostera et al., 2011; Nicolaidou and Nott, 1998) and *Zostera marina* has been shown to be a useful indicator of temporal variability in concentrations of Cd, Pb, Ni, Mn, Fe, Zn, and Cu (Riosmena-Rodríguez et al., 2010). The leaves of *Enhalus acoroides* have been shown to concentrate Cd (Suwandana et al., 2011) whilst *Posidonia oceanica* has been found to accumulate high levels of Zn in its leaves (Schlacher-Hoenlinger and Schlacher, 1998). In areas with cobalt (Co), chromium (Cr), Ni, Cd, and Pb contamination *P. oceanica* was actually found to be a better gauge of environmental condition than the previously-used popular bioindicator *Mytulis galloprovincialis*, which had previously been used as a key bioindicator (Lafabrie et al., 2007).

The Derwent estuary in southern Tasmania is affected by a broad range of contaminants such as sewage, stormwater, industry, agriculture, and aquaculture inputs (Whitehead et al., 2010) and has been proposed as the one of the most metal polluted systems in Australia (Bloom and Ayling, 1977; Whitehead et al., 2010; Wood et al., 1992), possibly even in the world (Jones et al., 2003). Bloom and Ayling (1977) were the first to identify that metallurgical waste from a local refinery was causing the accumulation of metals such as mercury (Hg), arsenic (As), Cd, Cu, Zn and Pb, in the system. The high levels of metals in the sediment are a result of prior industrial practices; Zn and Hg are of particular concern with levels in many parts of the estuary being up to 10 times higher than the Inter Sediment Quality Guidelines (ISQG) ANZECC guideline levels (Whitehead et al., 2010). The Derwent Estuary is an important area for recreational fishing and boating activity, as well as marine transport, and therefore the level of contamination presents a threat not only to ecological processes but also to human health.

Amongst the many sources of metal contamination aquaculture is one of the few modern sources (Dean et al., 2007), with fish- feed containing a range of micro-nutrients, including Zn (Richardson et al., 1985; Grahn et al., 2001), and antifouling paints used on nets having the potential to increase Cu and Zn loadings in adjacent water and sediments (Macleod and Eriksen, 2009). Although it is important to note that the salmon industry in Tasmania no longer uses metal-based antifouling paints. In Tasmania, salmon aquaculture is a significant and developing industry, with currently produced in the region of 35,000 tons per annum (AUS$ 408.0 million in 2011) (Skirtun et al., 2012). Several Atlantic salmon farming operations are situated in the D'Entrecasteux Channel, a connected body of water located to the immediate south of the Derwent estuary. In addition, farmed fish can be affected by local water and sediment quality, and so there are also some concerns that the elevated metals levels in the Derwent might adversely affect fish health.

Metal levels in the Derwent sediments, water column, fish and some invertebrates have been monitored for > 30 years (Bloom and Ayling, 1977; Ratkowsky et al., 1975; Higgins and Mackey, 1987; Dix et al., 1975; Whitehead et al., 2010) and levels of metals in the water column and surface sediments have been decreasing over recent years, due to improvements in management (Whitehead et al., 2010). However, we still understand very little about the concentration of metals in the biota and in particular in the primary producers within the estuary, or the effects of this on interactive species. Consequently, the aims of this research are: i) to determine baseline levels in macrophytes of the dominant metal contaminants in macrophytes within the estuary (As, Cd, Cu, Pb, Se and Zn) with samples collected along a spatial gradient of both salinity and contamination, ii) to identify macrophyte species with the potential to be used as bioindicators of heavy metal contamination in the Derwent estuary.

2. Methods

2.1. Study area

Thirteen study sites were selected in the Derwent estuary, Hobart, Tasmania (42°52′ S: 147°19′ E). The sites were chosen to provide a gradient of both heavy metal impacts and environmental conditions (i.e. poor water quality, industrial discharges, sewage treatment plants, the presence of aquaculture or a recorded history of heavy metals). In addition, less-polluted areas were also sampled as reference sites. Study sites were sampled throughout the Derwent estuary, from Bridgewater in the upper estuary to Sheppards Point at the mouth of North West Bay in the lower estuary, and with samples collected from both sides of the estuary (Fig.1). The estuary was divided into three regions according to shoreline morphology, salinity, and bathymetry as previously described by (Jordan et al., 2001).

2.2. Macrophyte samples

Nine species of algae comprising red (*Gracillaria* sp., *Pyropia columbina* (formerly *Porphyra columbina*), *Porphyra lucassi* and *Grateloupia turuturu)*, brown (*Scytopsiphon lomentaria*, *Ecklonia radiata* and *Undaria pinnatifida)* and green seaweeds (*Ulva australis* and *Ulva compressa)* were sampled. Three species of seagrasses (*Zostera muelleri*, *Zostera nigricaulis (formerly Heterozostera tasmanica)* and *Ruppia megacarpa* were collected (Fig.1).

Sampling was carried out in October 2013. Fresh plant material was collected from the intertidal areas at low tide ($n = 3$), with the exception of *Z. nigricaulis*, which was collected by snorkelling and samples of *U. australis* and *G. tururu* from the infrastructure around the salmon cages at 2 m depth, which were collected by divers. All samples were transported to the laboratory in resealable plastic bags, and rinsed to remove epiphytes and sand following the methods of Gledhill et al. (1998). Plants of the same species from each study site were combined to provide a composite sample of approximately 100 g wet weight (WW), seagrasses samples were compounded by leaves and roots. These samples were weighed and dried in an oven at 105 °C for 24 h to remove all moisture, before being re-weighed to establish a dry weight (DW). Dried material was sent to a certified laboratory, Analytical Services Tasmania (AST) a NATA (National Association of Testing Authorities, Australia) certified laboratory, for digestion and metal analysis.

2.3. Digestion and metal detection

Dried samples were ground with a mortar and pestle to obtain a particle size of < 2 mm. Each 1 g samples was added to a 50 mL digestion tube to which 10 mL concentrated nitric acid (HNO_3 65%) and 10 mL concentrated hydrochloric acid (HCl 30%) were added. Following a 12 h digestion, the samples were heated to 112.5 °C for 120 min using an Environmental Express™ Hot-block. Upon cooling to room temperature, samples were made up to 50 mL with Milli-Q® water (18 MΩ), filtered using a 10 mL disposable needleless syringe (0.45 μm) before being analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to determine As, Cd, Cu, Pb, Se and Zn levels. Laboratory certified reference material (CRM), dogfish