



Incorporating bioavailability into management limits for copper in sediments contaminated by antifouling paint used in aquaculture



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HIGHLIGHTS

- Low bioavailability of copper in antifouling paints.
- Probability of chronic toxicity increases when bioavailable copper >65 mg kg⁻¹.
- Guidelines based on dilute acid-extractable copper most effective.
- Acid-volatile sulfide was ineffective as a SQG-modifying factor.
- Zinc from fish feed is more bioavailable, but much less toxic, than the copper.

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ABSTRACT

Although now well embedded within many risk-based sediment quality guideline (SQG) frameworks, contaminant bioavailability is still often overlooked in assessment and management of contaminated sediments. To optimise management limits for metal contaminated sediments, we assess the appropriateness of a range of methods for modifying SQGs based on bioavailability considerations. The impairment of reproduction of the amphipod, *Melita plumulosa*, and harpacticoid copepod, *Nitocra spinipes*, was assessed for sediments contaminated with copper from antifouling paint, located below aquaculture cages. The measurement of dilute acid-extractable copper (AE-Cu) was found to provide the most useful means for monitoring the risks posed by sediment copper and setting management limits. Acid-volatile sulfide was found to be ineffective as a SQG-modifying factor as these organisms live mostly at the more oxidised sediment water interface. SQGs normalised to %silt/organic carbon were effective, but the benefits gained were too small to justify this approach. The effectiveness of SQGs based on AE-Cu was attributed to a small portion of the total copper being present in potentially bioavailable forms (typically <10% of the total). Much of the non-bioavailable form of copper was likely present as paint flakes in the form of copper (I) oxide, the active ingredient of the antifoulant formulation. While the concentrations of paint-associated copper are very high in some sediments, as the transformation of this form of copper to AE-Cu appears slow, monitoring and management limits should assess the more bioavailable AE-Cu forms, and further efforts be made to limit the release of paint particles into the environment.

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1. Introduction

Antifouling paints are used on the hulls of boats and fish nets in the aquaculture industry to prevent biofouling, i.e. the growth and colonization of marine microorganisms (Yebrá et al., 2004; Braithwaite et al., 2007). Since the phasing out of the use of tributyltin (TBT)-based paint products due to well recognised environmental harm, paints that utilise copper as the biocidal component, mainly in the form of copper (I) oxide, now dominate the market. Zinc is also a component of many paint formulations, and usually present

as zinc oxide or pyrithione when used in antifouling paint formulations.

While the benefits to industries from reducing biofouling are considerable, elevated concentrations of copper frequently occur in confined waters such as marinas (Schiff et al., 2007), and in sediments due to the abrasion of painted surfaces (Dean et al., 2007; Turner, 2010; Takahashi et al., 2012; Simpson et al., 2012a). Fish aquaculture also introduces metals into the aquatic environment through input of fish feed (Burrige et al., 2010). Zinc is an important nutrient for fish and the major source of the zinc in the aquaculture sediments will originate from fish food formulations, rather than the paint. While the organic waste components of unconsumed feed and fish faeces that settle beneath aquaculture

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cages are degraded by microbes, the associated metals tend to accumulate. The enrichment of organic matter surrounding aquaculture cages may also enhance biofouling of nets (Dean et al., 2007). Frequent cleaning of aquaculture nets is often undertaken to remove biofouling, but less frequently for nets with antifoulants. This may occur *in situ*, but frequently the empty nets are lifted out of the water and dried before encrusted biofouling is removed by washing.

As the copper antifouling paints are intended to be toxic, the accumulation in aquatic environments has the potential to exert toxic effects on a range of non-target organisms (Gammon et al., 2009; Turner et al., 2009; Simpson et al., 2012a; Ward et al., 2013). In the sediments beneath aquaculture cages, the concentrations of copper and zinc are often in the 100–1000 mg kg⁻¹ range (Dean et al., 2007) and this results in considerable areas which exceed recommended sediment quality guidelines (SQGs) (ANZECC/ARMCANZ, 2000). Based on projected increases in aquaculture worldwide (Brugère and Ridler, 2004), improved management of water and sediment quality within and surrounding aquaculture leases is an ongoing challenge for the aquaculture industry. While there has been an industry trend towards using large and heavy circular cages that has increased use of antifouling paints due to the large effort required for on-shore cleaning, the industry also recognises the need for decreased use of antifoulants, particularly those containing non-biodegradable components such as copper.

The environmental risk posed of paint-derived metals in waters is strongly linked to the degree of flushing that can provide uncontaminated supplies of water (Schiff et al., 2007). Copper-based antifouling paints are intended to result in a slow, but continual release of the active copper (Yebra et al., 2004). However, once buried in sediments, the risk to the environment is influenced by a broad range of factors that alter the bioavailability and bioaccessibility of the metals (Simpson et al., 2002; Rainbow, 2007; Simpson and Batley, 2007; Jones and Turner, 2010; Maruya et al., 2010).

Within most assessment frameworks, the use of SQGs for common contaminants are a fundamental initial step in evaluating risk (Batley et al., 2005; Ahlf et al., 2009; Choueri et al., 2010). The exceedance of a SQG usually triggers additional assessment steps to determine whether there is indeed a risk posed by the contaminant. The toxicity of metals is strongly influenced by sediment properties, and increased amounts of silt, organic carbon, acid-volatile sulfide (AVS) will reduce the bioavailability and toxicity of copper and zinc (Di Toro et al., 2005; Strom et al., 2011). Therefore successive assessment steps usually involve assessing factors that influence contaminant bioavailability, and toxicity testing (USEPA, 2005; Mayor et al., 2008; Ahlf et al., 2009; Simpson et al., 2011).

This study evaluates approaches for incorporating metal bioavailability when setting SQGs for managing copper contamination of sediments arising from the use of antifouling paint in aquaculture. For a range of sediments from salmon aquaculture leases, the sublethal effects to reproduction of the amphipod, *Melita plumulosa*, and harpacticoid copepod, *Nitocra spinipes*, was assessed. The results were interpreted in relation to a range of possible SQGs, including those based on total or dilute acid-extractable metal concentrations, mean SQG quotients (Long et al., 2006), and the use of AVS (USEPA, 2005) or organic carbon and silt (Simpson et al., 2011) as metal bioavailability modifying factors.

2. Material and methods

2.1. General methods

All glass and plasticware for analyses were usually new and were cleaned by soaking in 10% (v/v) HNO₃ (BDH, Analytical Re-

agent grade) for a minimum of 24 h, followed by thorough rinsing with deionized water (Milli-Q, 18 MΩ cm). All chemicals were analytical reagent grade or equivalent analytical purity. Water pH, salinity, temperature and dissolved oxygen measurements were made with probes, each calibrated according to manufacturer instructions. Methods for sediment particle size (by wet sieving through 63 μm nylon sieves followed by gravimetry), total organic carbon (TOC, by high temperature TOC analyzer), porewater (PW) extraction under nitrogen (centrifugation at 800g for 5 min), and dissolved ammonia analyses are described in Spadaro et al. (2008). Total recoverable metals (TRM, by microwave assisted aqua regia digestion), acid-volatile sulfide (AVS) and the simultaneously extracted metal (SEM) measurements were made on subsamples of the same homogenized sediment according to the method described previously (Simpson, 2001; Simpson and Spadaro, 2011). The dilute acid-extractable metal (AEM) concentration is the same as the SEM concentration, i.e., determined by extraction of wet sediment sample in 1 M HCl for 60 min, but not necessarily extracted simultaneously with AVS. Dissolved metal concentrations in acid-digests of water and sediment samples were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 730-ES) and inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce). As part of the quality assurance, analyses of filter and acid-digest blanks, replicates for 20% of samples, analyte sample-spikes and the certified reference materials (CRMs) were made. Replicates were within 20% and recoveries for spikes and CRMs, and PACS-2 for sediment (National Research Council Canada, NRCC), were within 85–115% of expected values. The limits of reporting for the particulate metals analyses (AEM and TRM) were 0.1 mg kg⁻¹.

2.2. Test media

Clean seawater was collected from Port Hacking, Sydney, Australia, membrane filtered (0.45 μm), and acclimated to a room temperature of 21 ± 1 °C. Where necessary, the salinity of the filtered seawater was adjusted to the test salinity of 30 PSU using Milli-Q water. Clean sediments for use in culturing and controls were collected (0–3 cm depth) from a range of intertidal estuarine locations near Sydney, Australia. These sediments had previously been characterised and found to have low concentrations of contaminants of concern (Spadaro et al., 2008; Strom et al., 2011). Sediments contaminated with copper-based antifouling paint were collected from in and around fish farms within the Huon River Estuary, Tasmania, Australia. Based on existing survey data (unpublished), sediment sites were chosen to have copper concentrations towards the higher end of the contamination range, but to not have high concentrations of ammonia that is often high in unfallowed aquaculture sediments. A consequence of this process was that the sample range was not representative of the typical, and lesser, degree of copper contamination within the majority of the Tasmanian aquaculture leases. While some sediments exist within the leases with higher copper concentrations, typically most have considerably lower concentrations. All samples were stored refrigerated until use. The copper-based antifouling paint used on the aquaculture nets contained 13% copper (I) oxide and 4% zinc oxide Hempanet 7150A (Hempel, 2009). For all sediments, analyses were made of porewater metals, ammonia and sulphide, and AVS, TRM, AEM and TOC on the unmodified sediment, and TRM, AEM and TOC analyses of the <63 μm sediment fraction.

2.3. Organisms and bioassays

Sub-lethal whole-sediment toxicity tests for *Melita plumulosa* and *Nitocra spinipes* were based on rapid chronic (reproduction) tests initially described by Mann et al. (2009) and Perez-Landa

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