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Guidelines for copper in sediments with varying properties

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ABSTRACT

A major weakness of sediment quality guidelines (SQGs) is their poor ability to predict how toxicity thresholds change for different sediment types. Using species sensitivity distributions (SSDs) of copper effects data, new guidelines were derived for copper in non-sulfidic marine sediments in which organic carbon (OC) and particle size strongly influence copper bioavailability. The derived SQGs varied in a predictable manner with changes in sediment particle size and organic carbon (OC), and were shown to offer a significant improvement on the existing 'single value' SQG. Adequate protection for all benthic organisms is expected to be achieved for a OC-normalised copper concentration of 3.5 mg Cu g^{-1} OC in the <63 μm sediment fraction. For short-term exposures, the equivalent acute guideline is 11 mg < 63 μm Cu g^{-1} OC. The new SQGs incorporate a high degree of conservatism owing to the use of copper-spiked sediments and laboratory-based bioassays that were expected to result in greater metal exposure of organisms to bioavailable copper than would be expected for field-contaminated sediments with similar total copper concentrations. SQGs that vary with sediment properties were prepared in an easily referenced tabular format.

1. Introduction

Sediment quality guidelines (SQGs) are a fundamental component of all sediment quality assessment frameworks (Batley et al., 2005; Chapman and Anderson, 2005; Bay et al., 2009; Choueri et al., 2010). However, while SQGs are generally useful for predicting when toxic effects due to a specific contaminant will not occur, their major weakness is their poor ability to predict how toxicity thresholds change for different sediment types and different test species (Batley et al., 2005; Di Toro et al., 2005; USEPA, 2005; Simpson and Batley, 2007; Strom et al., 2011). The toxicity of metal contaminants to benthic organisms is determined by the rate of metal uptake from both dissolved (via exposure to pore water, burrow water, or overlying water) and particulate sources (via ingestion of particles) (Simpson, 2005; Rainbow, 2007; Casado-Martinez et al., 2010) and by the sensitivity of the organism to these metal exposures (Simpson and King, 2005; Strom et al., 2011). The uptake rate is influenced by the chemistry and speciation of the metal in the sediments (Chapman et al., 1998; Besser et al., 2003; Simpson and Batley, 2007), and by the varying exposure pathways of different organisms (Luoma and Rainbow, 2008).

The most commonly used SQGs are empirical guidelines (Long et al., 1995) that were derived from matching sediment chemistry to the effects from laboratory or field exposures to contaminated sediments. While empirical SQGs are generally considered to provide a suitably conservative prediction of when toxic effects will not occur (Long et al., 2006; Simpson and Spadaro, 2011), they do not provide information on how effects are likely to change with changes in sediment properties (Batley et al., 2005). The prediction of metal bioavailability in sediments is considerably more difficult than for waters due to the greater range of metal interactions in sediments. For many metal contaminants, the influence of acid-volatile sulfides (AVS), particulate organic carbon (OC) and sediment particle size on metal bioavailability is now sufficiently well understood to allow mechanistic SQGs to be derived that improve the prediction of metal toxicity in sediments with widely varying properties (Di Toro et al., 2005; Strom et al., 2011).

As for waters, the toxic effects from copper in sediments are observed to occur over a very broad range of total particulate copper concentrations (Roper et al., 1995; Costa et al., 1996; Bat and Raffaelli, 1998; Marsden and Wong, 2001; Marsden, 2002; King et al., 2004; Simpson, 2005). However, the metal-binding properties of sediments influence the degrees of exposure and effects of metals more so than do variations in properties of waters. In sediments, the degree of partitioning between dissolved and particulate forms changes as well as the speciation in each of these phases. As copper in the dissolved phase will be more bioavailable than copper bound to sediment particles, understanding the partitioning of copper between these two phases is crucial to interpreting effects data (Simpson, 2005; Simpson and Batley, 2007).

For the majority of these studies that include naturally contaminated, field-collected and artificially contaminated, copper-spiked sediments using a range of benthic organisms, insufficient information has been provided on sediment properties and the partitioning of copper between the dissolved and particulate phases to

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allow interpretation of copper exposure routes. In a number of the past studies, very little time was allowed for the spiked copper to equilibrate with the sediments before tests were commenced, resulting in very high porewater and overlying water copper concentrations (e.g. >50 μg L^{-1}) compared to what is typically measured for field-contaminated sediments (i.e. <5 μg L^{-1}) with similar total copper concentrations (e.g. Bat and Raffaelli, 1998). Such abnormally high dissolved copper concentrations result in a misinterpretation of the sensitivity of organisms to sediment copper (Simpson, 2005).

Using copper-spiked fine sands pre-equilibrated for 24–48 h, Roper et al. (1995) observed that the bivalve, *Macomona liliana*, avoided sediments with 10 mg Cu kg^{-1} and did not bury in sediments having 25 mg Cu kg^{-1}. With no measurements of dissolved copper in either the pore water or overlying water, it was not possible to determine whether dissolved or particulate copper was the major cause of these effects. Using copper-spiked sediments with varying sediment particles sizes and organic carbon ranges, Costa et al. (1996) determined 10-d LC50 values for the amphipod *Gammarus locusta* of 6.8, 57 and >200 mg Cu kg^{-1} for sediments having fine fraction (%FF) to organic matter (by loss-on-ignition (LOI) ratios of 0.5%FF/0.9%LOI, 25%FF/1.9%LOI and 75%FF/7.1%LOI. The sediments had been spiked with copper and pre-equilibrated for only 24 h before toxicity testing and it is likely that most of the effects were due to dissolved copper that had not bound to the sediments. In tests with the amphipod, *Paracorphium excavatum*, a 10-d LC50 of 55 mg Cu kg^{-1} was observed with reduced recruitment of juveniles at 20 mg Cu kg^{-1} (Marsden, 2002; Marsden and Wong, 2001), however, the added copper was not pre-equilibrated with the sediment and dissolved copper concentrations were not measured. Bat and Raffaelli (1998) spiked silty sediment (<300 μm) with a mixture of Cd, Cu and Zn, and equilibrated for a few days (actual time not reported), before assessing survival of the amphipod *Corophium volutator*, with an LC50 of 37 mg Cu kg^{-1}. Dissolved Cd, Cu and Zn concentrations were abnormally high, exceeding 300, 400 and 100 μg L^{-1} respectively during the tests, indicative of inadequate pre-equilibration, and the effects were likely to be due to the dissolved metals. For metal-spiked muddy sediments, equilibrated for 9 d before testing, Hagopian-Schlekat et al. (2001) determined a 96-h LC50 of 282 mg Cu kg^{-1} for survival of the copepod *Amphiascus tenuiremis*. Dissolved metals measured in the pore water indicated that the effects were due to the exposure to the combined dissolved metals, with the LC50 for dissolved copper being 124 μg L^{-1}. For each of these studies, inadequate equilibration is evident as the dissolved concentrations greatly exceeded those observed for similarly contaminated field sediments. Simpson et al. (2004) demonstrated in laboratory studies that at least time of 20 d equilibration is required. The effects data are therefore of little use for guideline development.

It is widely recognised that for anoxic sediments with a molar excess of AVS over simultaneously extractable metals (SEM), the dissolved concentrations of Ag, Cd, Cu, Ni, Pb, and Zn in sediment porewaters should be negligible and acute or chronic effects should not result from these metals (Di Toro et al., 2005). The redox conditions in sediments are usually stratified and zones are frequently referred to as oxic, sub-oxic, and anoxic (Jorgensen and Revsbech, 1985; Kristensen, 2000). In the present study, we refer to oxic sediments as surface sediments penetrated by dissolved oxygen, sub-oxic sediments as those contain mixtures of dissolved Mn(II) and Fe(II) in equilibrium with iron(III) and manganese(IV) oxyhydroxide phases but containing negligible dissolved oxygen or sulfide, and anoxic sediments as those in which dissolved sulfide and AVS are dominant. While AVS phases may persist in surface sediments, having been formed under anoxic conditions or brought to the surface through bioturbation, they are eventually oxidised and the metals released to more bioavailable forms.

For oxic/sub-oxic sediments in which AVS does not significantly reduce the bioavailability of these metals, the porewater concentrations and sediment–water interface fluxes of metals are expected to be higher, but influenced considerably by OC and sediment particle size (Costa et al., 1996; Besser et al., 2003; Strom et al., 2011). Copper forms strong complexes with both dissolved and particulate OC and sediments having higher concentrations of OC and silt-sized particles provide a greater density of copper binding sites. For copper, Strom et al. (2011) described an approach that effectively predicted the acute toxicity to three benthic invertebrates based on the OC-normalised copper concentration of the <63 μm sediment fraction. For all three species, no effects were observed at dissolved copper (in pore water and overlying water) below 10 μg L^{-1} or below 12 mg Cu g^{-1} OC for < 63 μm sediment.

While water quality guidelines (WQGs) consider effects data for all aquatic organisms, guidelines for sediment pore waters should ideally consider only data for benthic organism life-stages that are in intimate contact with pore waters and not for organisms that do not reside in the sediments (e.g. fish), or life stages of benthic organisms that occur solely in the water column (e.g. planktonic/larval life stages of bivalves or crabs that live in the water column before settling on the sediment substrate). In the present study, the effects of dissolved copper on benthic marine organisms are reviewed and species sensitivity distributions (SSDs) are used to calculate acute and chronic guidelines for porewater copper. The porewater guidelines are compared with WQGs for copper (USEPA, 2003), and the differences in sensitivity to copper between organisms (e.g. amphipods, bivalves, copepods) and their location (e.g. North America, Europe, Australasia) are discussed.

For twelve benthic invertebrates, copper effects data from whole-sediment toxicity tests on copper-spiked oxic/sub-oxic silty sediments are used to derive an SSD-based SQG that is relevant to the specific properties of this sediment. Then utilising the approach of Strom et al. (2011), the relationships developed between acute toxicity and the OC-normalised copper concentration of the <63 μm sediment fraction are used to derive new SQGs that provide both adequate protection against toxicity and improve the prediction of effects of copper in sediments with varying properties.

2. Materials and methods

2.1. Toxicity tests to derive new copper effects data

The species were isolated for culturing or collected from relatively clean estuaries near Sydney, Australia. All organisms were kept in a temperature-controlled laboratory at 21 ± 2 °C in clean plastic holding trays containing sediment and overlying seawater (30 PSU). The amphipods, *Melita plumulosa* and *Hyale longicornis* were obtained from our laboratory cultures (Simpson and Spadaro, 2011), while *Corophium minor* was collected from the field. The snail, *Nassarius burchardi*, a dog whelk believed to be a carrion feeder and abundant in intertidal sandy and muddy habitats, and the crab, *Heloecius cordiformis*, a common semaphore crab that is primarily a deposit and detritus feeder were collected and handled as described previously for bivalves (King et al., 2010).

Clean seawater was collected from Port Hacking, Sydney, Australia, membrane filtered (0.45 μm), adjusted to salinity of 30 PSU with deionised water (18 MΩ cm^{-1}; Milli-Q Academic Water System) and acclimated to the room temperature of 21 ± 2 °C. The silty sub-oxic sediments were collected from Bonnet Bay, Woronora River estuary, New South Wales, Australia, and had low to moderate metal contamination and negligible concentrations of organic contaminants (King et al., 2004; Simpson et al., 2004).