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Bioaccessibility and Bioavailability of Cu and Zn in Sediment Contaminated by Antifouling Paint Residues

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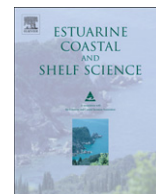


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Bioaccessibility and mobilisation of copper and zinc in estuarine sediment contaminated by antifouling paint particles

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ABSTRACT

Clean estuarine sediment amended with antifouling paint particles has been digested in biologically relevant reagents in order to evaluate the bioaccessibilities of Cu and Zn to deposit feeders in coastal environments where boat maintenance is important. Concentrations of Cu and Zn in the estuarine sediment of about 20 and 70 $\mu\text{g g}^{-1}$, respectively, increased to about 930 and 330 $\mu\text{g g}^{-1}$, respectively, on addition of 1.3% of a composite of fractionated paint particles collected from a boat repair facility. Seawater containing the vertebrate bile salt, sodium taurocholate, representative of surfactants in the digestive environment of deposit feeders, mobilised significantly greater quantities of metal (up to about 2 $\mu\text{g g}^{-1}$ of both Cu and Zn) than seawater alone, presumably through complexation and exchange reactions. Seawater solutions of the protein, bovine serum albumin (BSA), a surrogate for proteinaceous material and amino acids encountered in the digestive tract, mobilised even greater quantities of metal (up to about 80 and 40 $\mu\text{g g}^{-1}$ of Cu and Zn, respectively) via strong complexation, although addition of taurocholate reduced this capacity through interactions between the two reagents. Overall, and through feeding, burrowing and bioirrigation, infaunal invertebrates are predicted to greatly accelerate the rate of mobilisation and local dispersal of metals in sediment contaminated by antifouling paint particles.

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1. Introduction

Despite codes of practice or guidance regarding their safe disposal, fragments of antifouling paint are commonly observed on the hardstandings and slipways of boat repair facilities and marinas (Thomas et al., 2003; Tolhurst et al., 2007). Through runoff and wash down or as airborne dust, paint particulates enriched in a variety of toxins, including Cu and Zn and a variety of herbicides, enter the local marine environment (Page et al., 1996; Turner et al., 2008a). Consequently, accumulations of coloured paint particles have been reported in the benthic and intertidal environments of estuaries and coastal environments where shipping activities or boat repair is important (Pynaert and Speleers, 2005). From mass balance considerations, Singh and Turner (2009a) estimated that fine, surficial sediment from an estuarine creek in the locale of a leisure boat maintenance facility was contaminated by almost 1% (w/w) of antifouling paint particles.

The effects and fate of paint particulates interspersed within sediment are largely unknown. However, it is reasonable to hypothesise that leaching of toxins into poorly circulating pore waters results in elevated concentrations of the most persistent

biocides in interstitial waters and, consequently, in infaunal organisms. Burrowing, non-selective deposit feeders are predicted to be particularly significant to the location and kinetics of the leaching process through the vertical circulation of paint particles and their ingestion–digestion (Turner et al., 2008b). Mobilisation of particulate contaminants in the digestive environment is more rapid than in seawater because of strong complexation, ion exchange and hydrophobic effects incurred by a variety of hydrolytic enzymes, organic ligands and anionic surfactants (Mayer et al., 1997; Ahrens et al., 2001).

In this study, we examine the release of Cu and Zn from clean estuarine sediment amended with antifouling paint particles by seawater and by different solutions designed to mimic the digestive fluids of estuarine and coastal deposit-feeding invertebrates. Specifically, we employ solutions of the commercial protein, bovine serum albumin (BSA; molecular mass = 66,400 g mol^{-1}), and the vertebrate bile acid salt, sodium taurocholate ($\text{C}_{26}\text{H}_{44}\text{NO}_7\text{SNa}$; molecular mass = 537.7 g mol^{-1}). Appropriate concentrations of BSA approximate the complexing capacities of amino acids in the near-neutral digestive tract of suspension feeders and deposit feeders (Chen and Mayer, 1998; Zhong and Wang, 2006), while micellar concentrations of sodium taurocholate represent, at least structurally, anionic surfactants encountered in the digestive environment of deposit feeders (Smoot et al., 2003).

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2. Materials and methods

2.1. Materials

Before being used for sampling, sample processing or sample storage, all plastic- and glass-ware were soaked in 1 M HCl for at least 24 h and rinsed three times with Milli-Q distilled deionised water (MQW). Reagents were purchased from Fisher, Merck and Sigma–Aldrich and were of analytical or HPLC grade or equivalent. Seawater (salinity = 33; pH: 7.5) was piped directly to the laboratory from a fibreglass reservoir, having been collected in bulk from the English Channel.

2.2. Sample collection and processing

Approximately 6 L of surficial (<5 cm) sandy sediment was collected at low water from the marine reaches of a protected estuary (Erme, south west England). The sample was wet sieved on site through 1 mm Nylon mesh into a lidded plastic bucket. In the laboratory, subsamples of about 300 g were transferred to a series of zip-locked bags and stored frozen until required.

Fragments of antifouling paint were collected manually from the hardstandings of a commercial boat yard in Plymouth (C&C Marine Services) that caters for the maintenance and painting of pleasure craft. Fragments were cryogenically ground in a fume cupboard using a porcelain pestle and mortar and the resulting contents were sieved through Nylon mesh of pore size 1 mm. The fine fraction of the composite was stored in a 100 mL darkened plastic canister at room temperature.

2.3. Experimental

Solutions of bovine serum albumin (BSA, >96% fraction V) and sodium taurocholate (taurocholate acid sodium salt, 97%+) were prepared by dissolving an appropriate quantity of solid in 800 mL of filtered (<0.45 µm) seawater in a 1-L high density polyethylene beaker, a process assisted by magnetic stirring. Concentrations of BSA ranged from 1 to 8.5 g L⁻¹, equivalent to amino acid (AA) concentrations of about 10–75 mM and encompassing the range encountered in the digestive environments of a broad range of deposit feeders (Mayer et al., 1997). In order to prevent excessive foaming during subsequent phase separation, we used a concentration of sodium taurocholate of 4 g L⁻¹ (or about 7 mM), lower than that recommended by Voparil and Mayer (2004) but above the critical micelle concentration in artificial seawater reported by these authors (2.3 mM). The pH of seawater was not affected by addition of sodium taurocholate, but was reduced by up to one unit in the presence of BSA.

As required, a bag of sediment was defrosted and 40 g aliquots were weighed into six screw-capped 250 mL polyethylene bottles. (The dry weights of the samples were established from the weight losses incurred on drying separate aliquots.) To four bottles, 0.4 g of paint composite was also added. One hundred and sixty millilitres of filtered seawater were pipetted into one bottle containing sediment and one bottle containing sediment and paint, and to the remaining bottles 160 mL of a 1-g L⁻¹ solution of BSA in seawater was added. The solid to fluid ratio in the experiments was about 200 g L⁻¹, or close to that encountered in the digestive environment of many marine deposit-feeding invertebrates (Lawrence et al., 1999). The contents were then wrapped in foil and agitated on a rotary shaker at 150 rpm at room temperature. At different time intervals up to 5 h (encompassing the gut passage time of most deposit feeders; Mayer et al., 1995), subsamples of 15 mL were abstracted, transferred to polypropylene tubes and centrifuged at 1600×g for 7 min. Ten millilitres of the supernatants were

transferred to individual Sterilin tubes pending analysis. This approach was repeated using different concentrations of BSA solution, 4 g L⁻¹ of sodium taurocholate solution and different concentrations of BSA with 4 g L⁻¹ of the surfactant.

2.4. Sediment and paint digestion–extraction

For the near-complete dissolution of metals from the solids, triplicate 0.5 g portions of estuarine sediment, reference harbour sediment (LGC 6156) and paint composite were added to 50 mL borosilicate beakers to which 10 mL aliquots of aqua regia (1 part HNO₃ to three parts HCl) were added. The contents were heated to 75 °C on a hot plate for 2 h and the cooled digests were then filtered and washed with MQW into 50 mL volumetric flasks. Procedural blanks were performed likewise in the absence of solids.

Organometallics (or hydrophobic metal complexes) were extracted from the paint composite using dichloromethane (DCM). Thus, 0.1 g of paint particles were added to a test tube and 1 mL of DCM added. The contents were ultrasonicated for 20 min and subsequently centrifuged at 1700×g for 5 min. Five hundred microlitres of supernatant were then transferred to a 10 mL borosilicate beaker and blown down under high purity nitrogen. The residue was dissolved in 10 mL of 1 M HNO₃ and transferred to a 30 mL polypropylene bottle. Extraction was also performed on dried and filtered 0.1 g paint particle samples that had been incubated for 5 h with 40 mL solutions of BSA and surfactant.

2.5. Analysis

Barium, Cd, Cr, Cu, Fe, Ni, Pb, Sn and Zn were analysed in the supernatants arising from the experiments and in aqua regia digests and solvent–acid extracts by inductively coupled plasma–optical emission spectrometry (ICP-OES) using a Varian 725-ES (Mulgrave, Australia). The power was set at 1.4 KW, plasma, auxiliary and nebuliser flows were 15, 1.5 and 0.68 L min⁻¹, respectively, and replicate read time was 4 s. Calibration was achieved using mixed, matrix-matched standards prepared from plasma emission solutions, and 1 ppm of yttrium was added to all samples and standards for internal standardisation. Analysis of digests of the reference sediment revealed that accuracy was better than 90% for all metals analysed. The carbon, hydrogen and nitrogen contents of the sediment and paint composite were determined in triplicate by elemental analysis using a CE Instruments EA1110 CHNS with conductivity detector. The instrument was calibrated with cyclohexanone-2, 4-dinitrophenylhydrazine and accuracy, based on triplicate determinations of C in reference sediment (PACS 1 harbour sediment, National Research Council, Canada), was better than 95%.

3. Results and discussion

3.1. Chemical composition of the paint composite

Dry weight concentrations of all elemental constituents analysed in the estuarine sediment and paint composite are given in Table 1. High concentrations of Cu and Zn in the composite are consistent with their use in contemporary antifouling formulations as the principal biocidal pigment, Cu₂O, the weaker biocide and erosion facilitator, ZnO, and various organometallic co-biocides (e.g., Cu and Zn pyrithiones; Holmes and Turner, 2009). Other metals that are elevated in the composite compared with clean sediment (Ba, Cd, Pb, Sn) are components of coloured pigments, particle extenders, driers, corrosion inhibitors and curing catalysts

Table 1

Measured elemental concentrations in the estuarine sediment and paint composite and computed values in the sediment–paint mix. Errors represent one standard deviation about the mean of three determinations.

| | Sediment | Paint composite | Sediment–paint mix |
|--------------------------|-----------------|-------------------|--------------------|
| Ba, $\mu\text{g g}^{-1}$ | 13.4 ± 1.7 | 1030 ± 121 | 26.7 |
| Cd, $\mu\text{g g}^{-1}$ | 0.31 ± 0.05 | 8.49 ± 0.34 | 0.42 |
| Cr, $\mu\text{g g}^{-1}$ | 16.2 ± 0.44 | 14.2 ± 0.4 | 16.2 |
| Cu, $\mu\text{g g}^{-1}$ | 23.4 ± 10.2 | 69300 ± 11000 | 935 |
| Fe, $\mu\text{g g}^{-1}$ | 17000 ± 535 | 16300 ± 737 | 17000 |
| Ni, $\mu\text{g g}^{-1}$ | 22.6 ± 0.4 | 18.9 ± 1.8 | 22.5 |
| Pb, $\mu\text{g g}^{-1}$ | 24.8 ± 4.7 | 272 ± 3.3 | 28.0 |
| Sn, $\mu\text{g g}^{-1}$ | 1.77 ± 0.12 | 51.3 ± 6.9 | 2.42 |
| Zn, $\mu\text{g g}^{-1}$ | 72.5 ± 13.4 | 19800 ± 3080 | 332 |
| C, % | 4.18 ± 0.50 | 36.43 ± 2.29 | 4.60 |
| H, % | 0.22 ± 0.01 | 4.20 ± 0.29 | 0.27 |
| N, % | 0.11 ± 0.07 | 0.54 ± 0.18 | 0.12 |

(Lambourne, 1999). Also shown in Table 1 are elemental concentrations in the sediment–paint mixture, computed from concentrations in the component solids and a dry weight sediment to paint ratio of 75:1. Clearly, antifouling particulates represent a significant, heterogeneous source of a cocktail of metallic contaminants to estuarine and coastal environments. Hereafter, however, we focus on the metals whose concentrations are about an order of magnitude greater in the paint–sediment mix than in clean estuarine sediment; namely, Cu and Zn.

3.2. Cu and Zn mobilisation from estuarine sediment

Fig. 1 shows the time-dependence of Cu and Zn mobilisation (on a dry weight concentration basis) from clean, estuarine sediment by the different reagents. Seawater alone is able to mobilise small quantities of metals, presumably through desorption of cations loosely bound to the sediment surface (although metals in residual pore waters may also have been present). Addition of micellar concentrations of the anionic surfactant, sodium taurocholate, to seawater enhances mobilisation such that by end of the time-courses about 0.2% of total Cu and 0.1% of total Zn were released. Solutions of the protein, BSA, effected greater mobilisation than the surfactant, and at the highest BSA concentration employed (illustrated in Fig. 1) an order of magnitude more Cu and Zn was available to the protein than the surfactant after 5 h incubation.

The surfactant and protein are predicted to mobilise metals from sediment by two mechanisms. Firstly, since many

components of BSA are strong metal complexants (Kalman and Turner, 2007), there is competition for metal cations between adsorption sites on the sediment surface and binding sites of the protein; mobilisation likely involves the formation of a complex at the sediment surface which is subsequently released into bulk solution. The carboxylic groups of the surfactant are able to bind metals, albeit weakly but the surfactant is also able to undergo counter-ion exchange or, in micellar form, act as a competitive sorbent for metals in solution (Doong et al., 1998). Secondly, because of the amphiphilic nature of the surfactant and protein, both reagents are able to interact with particulate organic matter hydrophobically, an effect that results in the partial denudation of this phase and the dissolution of metals contained therein (Singh and Turner, 2009b).

Despite the ability of both reagents to mobilise Cu and Zn from sediment, BSA and sodium taurocholate do not act additively or cooperatively. Rather, there appears to be some interaction between the surfactant and protein (and/or sediment) such that net metal release is inhibited. Electrostatic and hydrophobic interactions between molecules (and micelles) in solution could reduce the overall complexing capacity or denuding potential of the reagents (Kelley and McClements, 2003), while partial adsorption of one reagent may reduce the surface area of sediment exposed to the other.

3.3. Cu and Zn mobilisation from the sediment–paint mix

Fig. 2 shows the mobilisation of Cu and Zn from estuarine sediment amended with paint particles. For Cu, an increase in concentration mobilised is observed throughout each time-course, with no evidence of equilibrium being attained. The greatest quantity of Cu mobilisation (about 9% of total Cu) occurs after 5 h incubation at the highest BSA concentration employed. However, the extent (or rate) of mobilisation does not vary proportionally with BSA concentration. Specifically, a BSA concentration of 1 g L^{-1} releases greater quantities of Cu than BSA concentrations of 2.5 and 5 g L^{-1} . Regarding Zn, the maximum quantity mobilised is also about 9% of total metal, but the extent of mobilisation varies in step with BSA concentration and, within experimental error, equilibrium appears to be attained in each case.

In these experiments, both greater concentrations of Cu and Zn were present and greater percentages of total metal were accessible than in equivalent experiments conducted in the absence of anti-fouling paint particles. In seawater, Cu and Zn are designed to leach

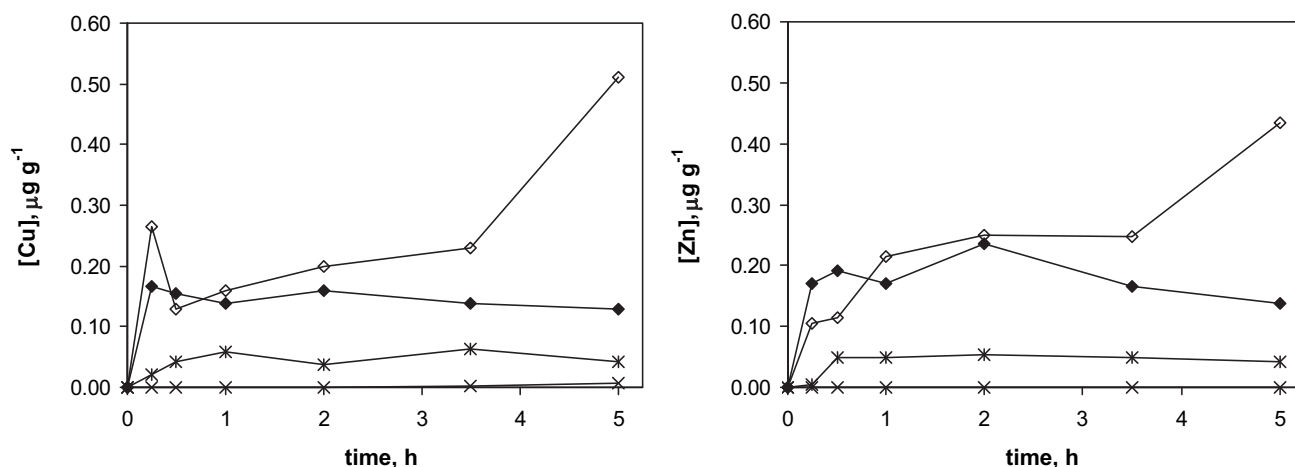


Fig. 1. Concentrations of Cu and Zn in the clean estuarine sediment sample available to seawater (x), 3.5 g L^{-1} sodium taurocholate in seawater (x), 8.5 g L^{-1} BSA in seawater (◇) and 4 g L^{-1} sodium taurocholate and 8.5 g L^{-1} BSA in seawater (◆) as a function of time.

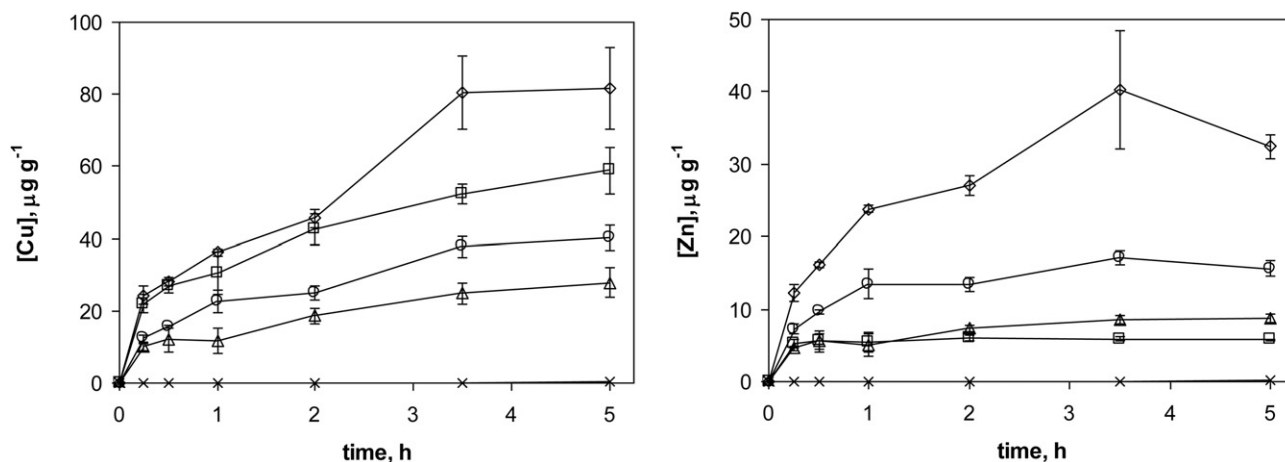
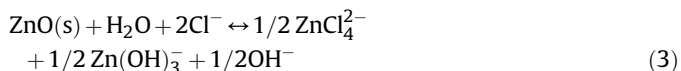
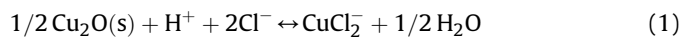


Fig. 2. Concentrations of Cu and Zn in the sediment–paint mix available to seawater (×) and different concentrations of BSA in seawater (□ = 1 g L⁻¹; Δ = 2.5 g L⁻¹; ○ = 5 g L⁻¹; ◇ = 8.5 g L⁻¹) as a function of time. Error bars represent one standard deviation about the mean of three independent experimental determinations.

readily but in a controlled fashion from a painted hull. In their most commonly employed, oxidic forms, Cu (I) and Zn (II) are released according to the following reactions (Omae, 2003; Yebra et al., 2007):



where, in the presence of dissolved oxygen, univalent copper is rapidly oxidised to Cu²⁺. Thus, the leaching of both Cu and Zn from their respective oxides is dependent on the square of the concentration of chloride. Reactions 1 and 3 proceed more rapidly when paint is in fine, particulate form because of the greater surface area of oxides exposed to the aqueous medium. In the presence of BSA, leaching is accelerated further, presumably because the component amino acids of the protein act as additional, strongly binding ligands.

Fig. 3 shows the results of equivalent experiments in which 4 g L⁻¹ of sodium taurocholate was present. Micellar

concentrations of the surfactant are able to mobilise significantly greater quantities of Cu and Zn from the sediment–paint mix than seawater. Although this is perhaps, in part, the result of a complexation or exchange effect (see above), since taurocholate is not a particularly strong complexant we suspect that the surfactant plays an additional role. For example, it is possible that, through peptisation, sodium taurocholate is able to disperse fine (and, consequently, filterable) colloidal grains of Cu(I) and Zn(II) oxide. It is also possible that any adsorption of paint-derived Cu and Zn ions to neighbouring sediment grains is suppressed in the presence of the amphiphile through the shielding or occupation of surface sites (Turner and Xu, 2008).

Addition of BSA to the taurocholate solution enhances metal mobilisation and results are, qualitatively, similar to those reported in the absence of the surfactant (Fig. 2). That is, Zn appears to approach equilibrium and release is largely dependent on BSA concentration, whereas Cu does not attain equilibrium over the time period of the experiments and release exhibits no clear dependence on BSA concentration. As in the experiments performed without paint particles, however, mobilisation of metal by BSA in the presence of sodium taurocholate is lower than mobilisation by the protein alone, presumably due to the solute–solute and solute–particle interactions described above.

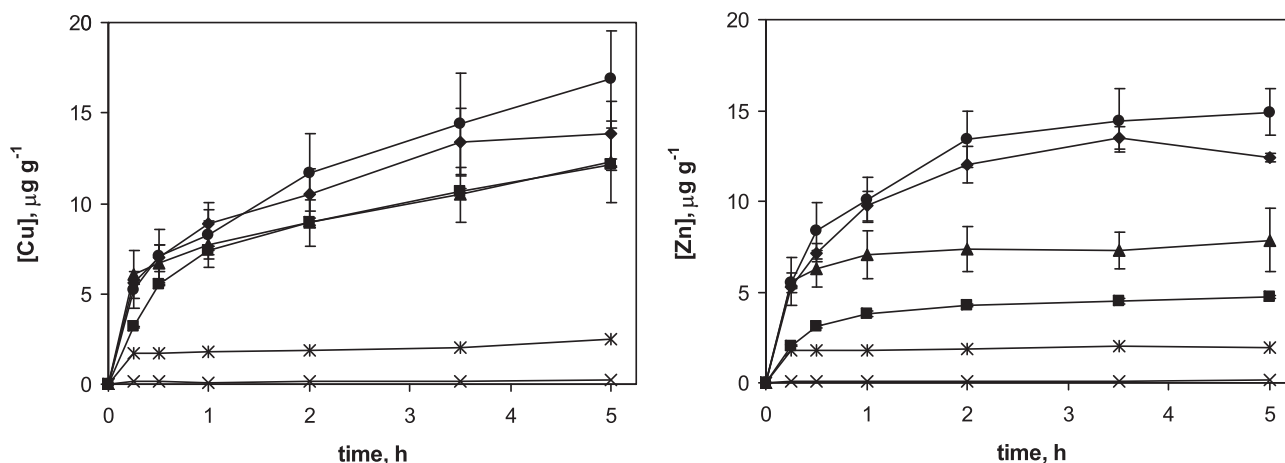


Fig. 3. Concentrations of Cu and Zn in the sediment–paint mix available to seawater (×) and different concentrations of BSA in seawater in the presence of 4 g L⁻¹ of sodium taurocholate (× = 0 g L⁻¹; ■ = 1 g L⁻¹; ▲ = 2.5 g L⁻¹; ● = 5 g L⁻¹; ◆ = 8.5 g L⁻¹) as a function of time. Error bars represent one standard deviation about the mean of three independent experimental determinations.

3.4. Forms of mobilised Cu and Zn

Although the results reported above are for total Cu and Zn, it is important to appreciate that different forms of these metals may be mobilised by seawater and the surrogate digestive reagents. Copper(I) released from a painted hull immersed in seawater (equations (1) and (2)) is rapidly oxidised to Cu(II) in the presence of dissolved oxygen. However, in discarded particulate form and in the presence of sediment and pore waters that are not fully oxygenated it is possible that Cu(I) is more persistent. Significantly, the stability of Cu(I) is enhanced in the presence of certain ligands, including thiolic compounds (Leal and van den Berg, 1998). Since this kind of ligand and other, sulphur-containing amino acids are abundant in both BSA and the digestive environments of non-selective, sediment-ingesting invertebrates (Lawrence et al., 1999; Fan and Wang, 2003), particle processing by such organisms may represent an important means of stabilising Cu(I) in marine interstitial waters.

Hydrophobic complexes of Cu and Zn (mainly pyrrhionones) are also commonly employed in many contemporary antifouling formulations as booster biocides (Turley et al., 2000). Although we were unable to discriminate hydrophilic (inorganic) and hydrophobic (organometallic) forms in the present experiments, a qualitative insight into their relative significance was gained by solvent-extraction of paint particles that were digested (without sediment) in solutions of BSA and sodium taurocholate (see Fig. 4). Thus, concentrations of solvent-extractable (organo-) Cu and Zn in the composite were about 600 and 500 $\mu\text{g g}^{-1}$, respectively, or about 1 and 2.5% of the respective total concentrations. After exposure to seawater, the concentrations of organo-Cu and Zn were reduced, suggesting that hydrophobic forms are released more readily than hydrophilic (oxidic) forms. This assertion is consistent with results of leaching experiments in which hydrophobic and hydrophilic forms released to the aqueous phase from an antifouling paint composite were discriminated by solid phase extraction (Holmes and Turner, 2009). Digestion in seawater solutions of increasing BSA concentration yielded progressively higher concentrations of organometals in the resulting composite, suggesting that hydrophilic forms are preferentially mobilised by the protein, presumably through complexation reactions. In the presence of surfactant under otherwise identical conditions, a similar trend was observed but organometallic concentrations were lower. This

suggests that the solubilities of organo-Cu and Zn are enhanced by taurocholate, presumably through hydrophobic interactions between organometals and the hydrophobic domain of the surfactant.

3.5. Environmental implications

The results of this study provide estimates of the bio-accessibility of Cu and Zn in paint-contaminated sediments under a variety of simulated digestive conditions. Accordingly, maximum accessibility of about 9% of total Cu and Zn is effected by the highest concentration of the protein after 5 h incubation; about 2% of total Cu and 4% of total Zn are released under identical conditions but in the presence of the surfactant. Bio-accessibility of Cu in the digestive environment of marine deposit feeders is predicted to be dependent on, but not proportional to, the concentration of AA, surfactancy and gut residence time. Bioaccessibility of Zn is predicted to increase with increasing AA concentration and a reduction in surfactancy but is less sensitive to gut passage time. Under all simulated conditions, however, accessibility is considerably greater than the percentages of metal mobilised by seawater alone due to complexation reactions and additional interactions incurred by the surfactant, protein and sediment.

The bioaccessible fraction of metal is not necessarily equivalent to the fraction that enters the blood and systemic circulation. Results of microcosm experiments have shown that a small percentage of accessible Cu is accumulated by invertebrates exposed to antifouling paint particles, and that Zn is, at least partly, regulated (Turner et al., 2008b; Gammon et al., 2009). Clearly, therefore, a large proportion of paint-bound metal that is mobilised under digestive conditions is egested into the interstitial environment. Animals that also irrigate their burrows during feeding are likely to accelerate the mobilisation of metals to the overlying water column. Given the abundance of sediment-ingesting macro-invertebrates in shallow coastal environments (Riisgård and Banta, 1998; Volkenborn et al., 2007; Granberg et al., 2008), non-selective feeding and bioirrigation are likely to be highly significant in the mobilisation, translocation and dispersion of metals from sediment contaminated by antifouling paint residues. Clearly, these effects require consideration in risk assessments and contaminant fate models in environments impacted by boat maintenance or shipping activities.

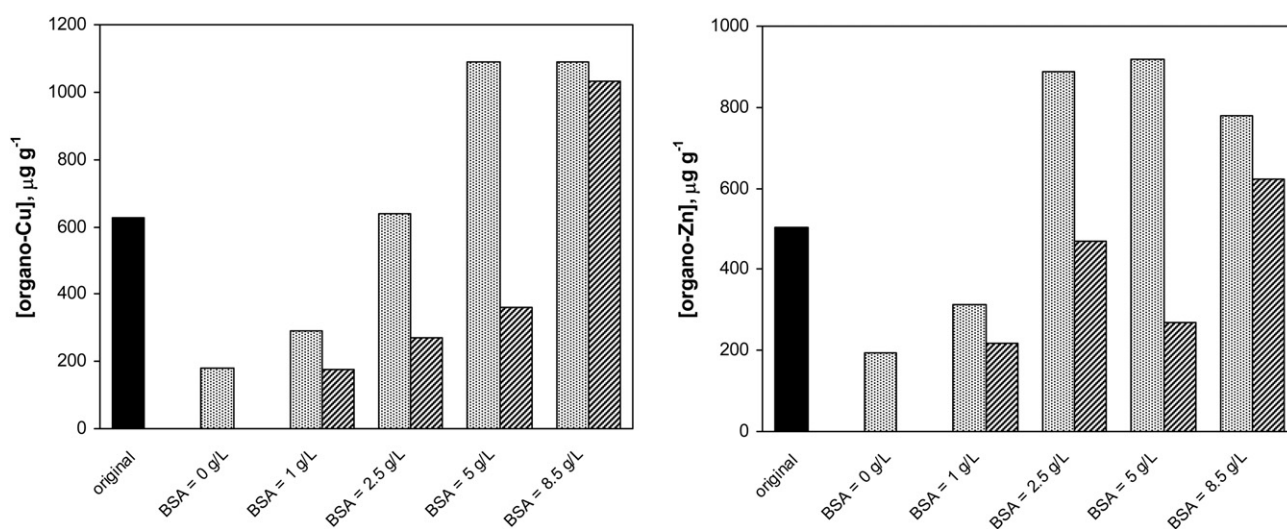


Fig. 4. Concentrations of organo-Cu and organo-Zn in the original paint particle composite and in the composite after 5 h digestion in different concentrations of BSA in seawater, with and without 4 g L⁻¹ of sodium taurocholate (hatched and stippled bars, respectively).

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