

Antifouling paint particles in estuaries: Distribution, composition and biogeochemical effects

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Antifouling applications

Biocides:

TBT (1960s-1980s)

Cu(I) oxide, Cu(I) thiocyanate

Zn(II) oxide

Zn pyrithione, Diuron, Irgarol...(boosters)

Manufacturers:

International Paint, Blakes, EU-45...

Leaching rate in $\mu\text{g cm}^{-2} \text{d}^{-1}$



Direct and indirect effects of an antifouling biocide on benthic microalgae and meiofauna

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Abstract

When multitrophic, natural communities are exposed to a contaminant, indirect, food-web mediated effects may become as important as direct toxic effects. In this study the antifouling agent copper pyrithione (CPT) was used as a model toxicant to study toxic effects on microphytobenthos (MPB) and meiofauna, as well as on the interaction between them. The hypothesis was that exposure to CPT will decrease meiofaunal grazing pressure and that this effect would result in increased primary production and biomass of MPB. Two laboratory experiments (16 and 29 days long) were performed, using natural sediment that was exposed to both acute and repeated exposure of CPT (final dose 5 nmol CPT per g dry weight sediment). Variables measured included light utilization efficiency of MPB (PAM fluorometry), primary production (^{14}C -uptake), chl *a* content of the sediment, algal composition, meiofauna biomass and meiofaunal grazing pressure on MPB (^{14}C -incubations). Although CPT, added as a single dose or repeatedly, affected both MPB and meiofauna, no strong mechanistic evidence for a top-down control was found. The clearest direct CPT effects were seen for MPB function (light utilization efficiency and primary production), while algal biomass and composition were only marginally affected. MPB recovered rapidly from the toxicant exposure, a finding that verified the conclusion from previous experiments that the MPB community is highly resilient. The magnitude of the direct response of the microalgae depended on whether the total dose of CPT was added as one initial dose or divided between several additions; effects were larger after one initial dose. Although meiofauna biomass decreased at CPT exposure in both experiments, this decline was not reflected in decreased grazing pressure on MPB. Meiofauna grazed between 1 and 12% of the algal biomass per day. The lack

Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints

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Abstract

Two major antifouling biocides used worldwide, Irgarol 1051 and diuron, and their degradation products in Shoreham Harbour and Brighton Marina, UK were studied during 2003–2004. The highest concentrations of Irgarol 1051 were 136 and 102 ng L⁻¹ in water and 40 and 49 ng g⁻¹ dry weight in sediments for Shoreham Harbour and Brighton Marina, respectively. As the degradation product of Irgarol 1051, M1 was also widespread, with the highest concentration of 59 ng L⁻¹ in water and 23 ng g⁻¹ in sediments in Shoreham Harbour, and 37 ng L⁻¹ in water and 5.6 ng g⁻¹ in sediments in Brighton Marina. The target compounds showed enhanced concentrations during the boating season (May–July), when boats were being re-painted (January–February), and where the density of pleasure crafts was high. Overall, the concentration of Irgarol 1051 decreased following

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Antifouling pesticides in the coastal waters of Southern California ☆

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Antifouling biocides are used to prevent settlement and growth of organisms on the submerged surfaces of boats and ships. Organotins, particularly tributyltin (TBT) were the most widely used compounds in antifouling paints until the 1990s. After the United Nations International Maritime Organization passed legislation banning the use of harmful organotins (Konstantinou and Albanis, 2004), organic booster biocides were introduced as alternatives to organotin compounds in antifouling products. The antifouling agent Irgarol 1051 and other multi-use pesticides: diuron, chlorothalonil, dichlofluanid and TCMTB (2-(thio-yanatomethylthio)-1,3-benzothiazole) are among the most frequently used antifouling biocide ingredients in many countries (Thomas, 2001).

Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) is a triazine-based herbicide manufactured by Ciba Geigy Corp. Like other *s*-triazine herbicides, it is a photosystem-II inhibitor (Hall et al., 1999) and is highly toxic to non-target plant species at low ng/L concentrations (Konstantinou and Albanis, 2004). Irgarol degrades in seawater with half-life of about

from 4% to 7%. Diuron is more persistent than Irgarol in seawater and more toxic to fish (Okamura et al., 2002).

Irgarol and M1 have been widely detected in estuarine and coastal waters of European countries as well as in Japan and the USA. Although monitoring of Irgarol has been extensive worldwide (Konstantinou and Albanis, 2004), studies conducted in the USA only reported Irgarol concentrations in US waters along eastern coastal areas of South Florida (Gardinali et al., 2002, 2004; Zamora-Ley et al., 2006), Chesapeake Bay (Hall et al., 2004), North and South Carolina, Georgia and Florida (Hall et al., 2005).

This paper presents data on the occurrence of Irgarol in the surface waters of several marinas around San Diego, CA. To our knowledge, this is first study reporting Irgarol concentrations in western areas of the US, particularly in Southern California.

Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) standard was obtained from Ciba Specialty Chemicals Inc. (Tarrytown, NY, USA). 2-Methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (major

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Copper speciation survey from UK marinas, harbours and estuaries

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Abstract

The use of copper in antifouling paints has increased in the UK in the last 20 years as TBT and several other organic biocides have been phased out. To assess the probable impact of copper on estuarine systems a survey was undertaken to measure the different fractions of copper present in the water column at current usage. The different fractions measured were: labile copper, (LCu) considered as the free copper ions and inorganically bound copper, the total dissolved copper (TDCu) present, and the difference between them (the organically bound likely non-toxic copper fraction). The survey considered sites with different levels of boat use, namely marinas, harbours and estuaries, differing physical parameters of suspended and dissolved organic matter, different seasons of the year and different depths in the water column all of which control speciation behaviour. Suspended particulate matter (SPM) values were measured at all sites and increased from West to East coast locations (5.7–34.4 mg/l). Dissolved organic matter (DOM) values ranged from 0.58 to 2.2 mg/l C. The total dissolved copper concentrations ranged from 0.30 to 8 µg/l, with labile fraction ranging from 0.02 to 2.69 µg/l, and most labile copper concentrations below 1 µg/l. None of the yearly annual copper measurements exceeded the 76/464/EEC EQS of 5 µg/l. Of the 306 measurements, only one dissolved copper value in the season was above 5 µg/l.

This ratio of labile to total copper was between 10 and 30%. The results from this survey suggest that if toxicity of copper is due to the labile fraction then using the total dissolved copper concentrations as an indicator of impact overestimate the risk by a factor of four

The fate and effects of antifouling paint residues?



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Programme of Research

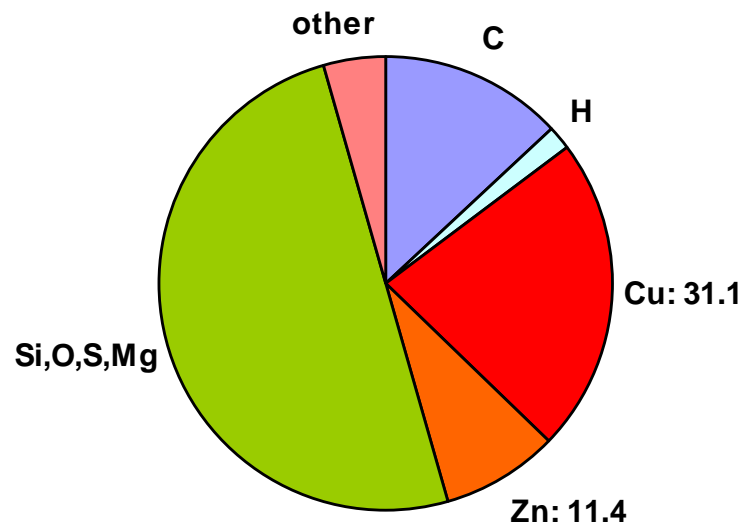
- Chemical composition of (leisure boat) paint fragments
- Solubility and bioaccessibility of chemical components
- Uptake of components by estuarine invertebrates

Ground paint composite



Elemental composition (%)

Pb	525 $\mu\text{g g}^{-1}$
Sn	550 $\mu\text{g g}^{-1}$
Cd	7.6 $\mu\text{g g}^{-1}$
Ni	150 $\mu\text{g g}^{-1}$
Ag	19 $\mu\text{g g}^{-1}$



Concentrations of metals in < 63 μm Plym estuarine sediment ($\mu\text{g g}^{-1}$)

	control	near boatyard	enrichment
Cu	98.5 ± 9.3	2230 ± 1900	22.6
Zn	129 ± 15	916 ± 600	7.1
Sn	8.2 ± 2.5	12.0 ± 1.0	1.5



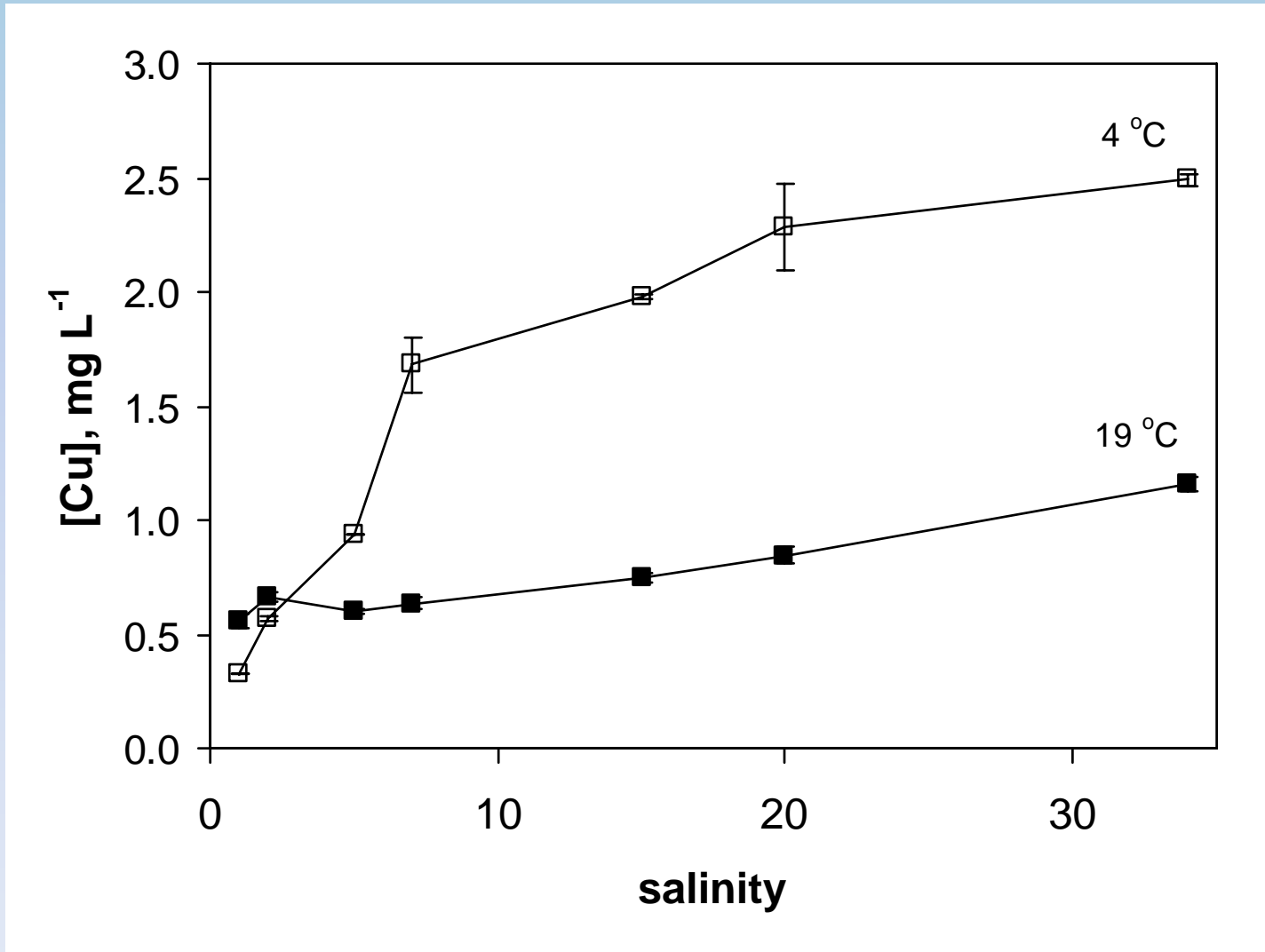
Organometallic fraction

Cu	$463 \pm 61 \mu\text{g g}^{-1}$	$0.15 \pm 0.02\%$
Zn	$1310 \pm 73 \mu\text{g g}^{-1}$	$1.15 \pm 0.11\%$
Sn	$16.4 \pm 2.6 \mu\text{g g}^{-1}$	$3.07 \pm 0.63\%$

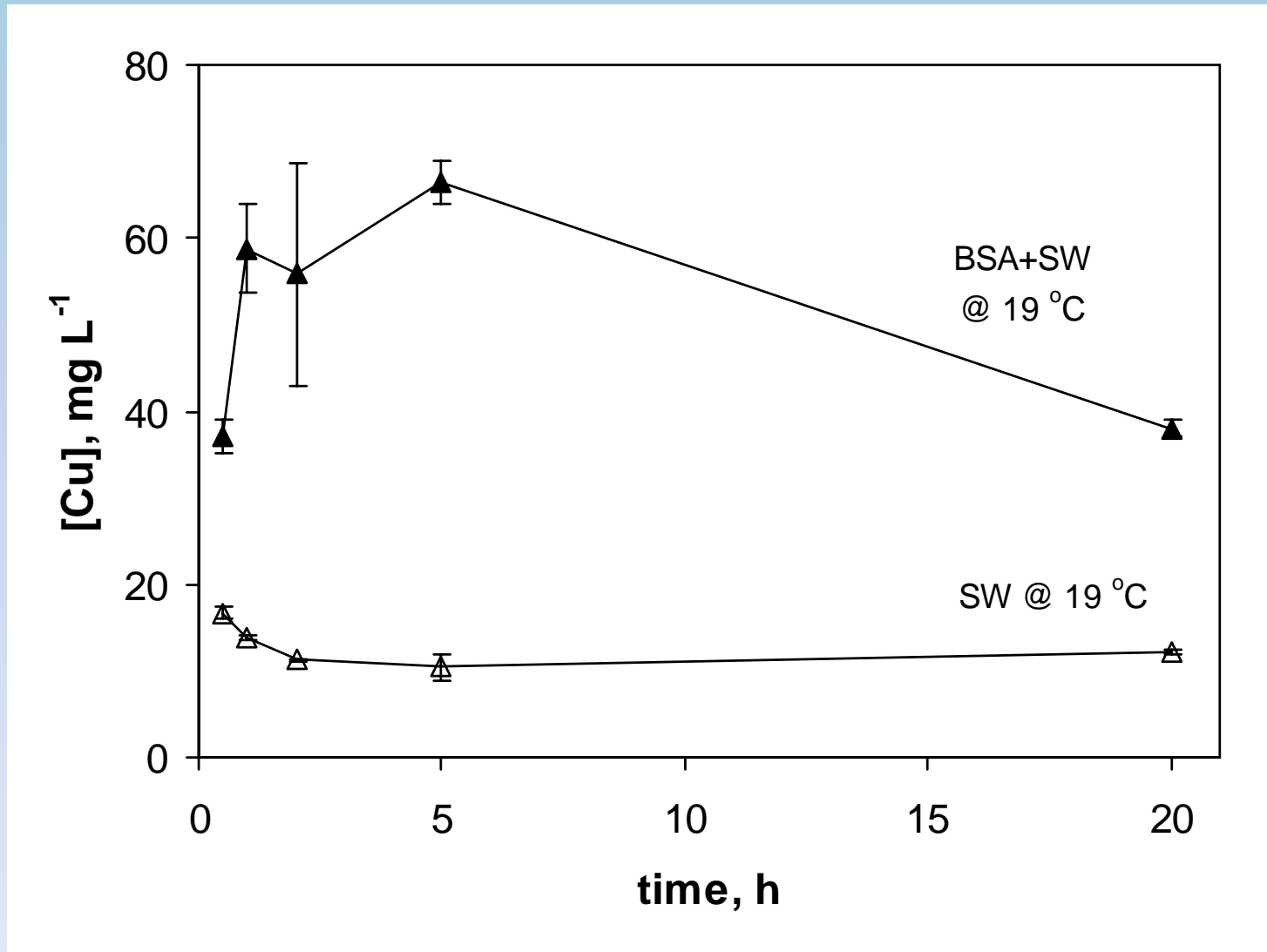
FTIR analysis:

- Zn-pyrithione @ 821.5 cm^{-1}
- Cu-pyrithione @ 831.5 cm^{-1}
- No Sn-C bond ($590 - 520 \text{ cm}^{-1}$) detected

120 h-leaching of Cu from 120 mg L⁻¹ of < 63 μm paint particles



Accessibility of a 1:10 paint to sediment mix to bovine serum albumin



Arenicola marina + 40 mg of < 1 mm paint particles

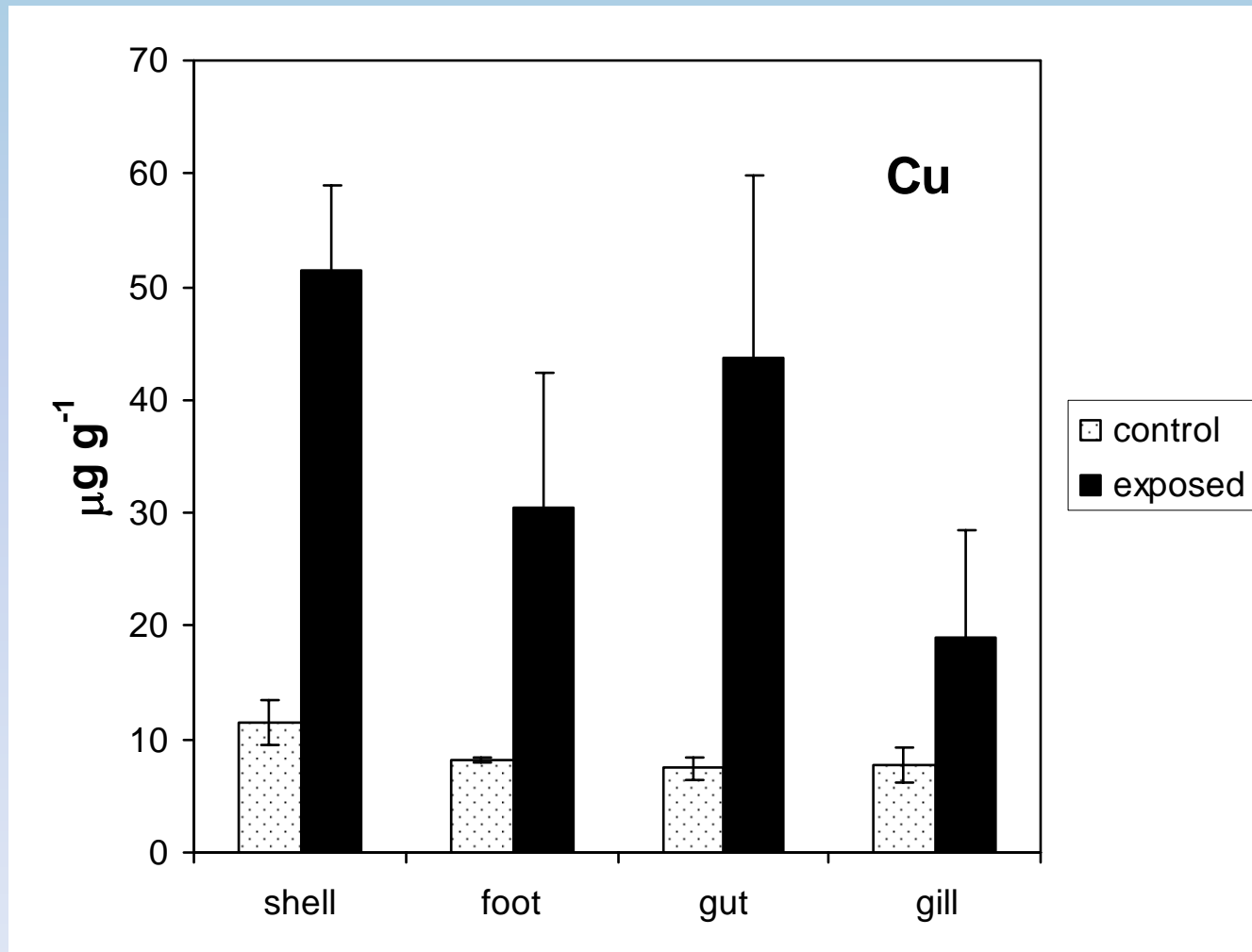


Cu in *A. marina*

Control $12.9 \pm 6.3 \mu\text{g g}^{-1}$ ($n=8$)

Exposed $26.5 \pm 3.5 \mu\text{g g}^{-1}$ ($n=3$)

Mytilus edulis + 80 mg L⁻¹ of a 1:5 paint to silt mix
(< 45 μm)



Conclusions

- Paint residues represent a significant source of contamination in estuaries impacted by boating
- Metallic components are highly soluble and bioaccessible
- Estuarine invertebrates cannot deselect paint particles and readily accumulate metallic biocidal constituents
- Stricter enforcement of codes of practice are required

Did the boater:

- a) Vacuum the dust and dispose of as hazardous waste
- b) Vacuum the dust and dispose of as domestic waste
- c) Sweep the dust into the sea?

