



# Mobilisation and bioaccessibility of lead in paint from abandoned boats



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## ABSTRACT

Fragments of leaded paint sampled from abandoned boats have been ground as a composite and added in different quantities to aliquots of clean estuarine sediment in order to examine the mobility and bioaccessibility of Pb. Concentrations of Pb mobilised by sea water increased with increasing quantity of paint present, but the percentage of total Pb mobilised was greatest from paint-free sediment. Lead mobilisation was enhanced in the presence of the protein, bovine serum albumin, a surrogate for the digestive fluids of deposit-feeding invertebrates, but, likewise, the percentage of Pb mobilised was greatest from paint-free sediment. Lower percentage mobility and bioaccessibility in contaminated sediment than in paint-free sediment is attributed to the relatively low solubility and amenability of Pb compounds in the paint matrix. Despite the low mobility of Pb, however, sediment contaminated by as little as 0.2% paint is predicted to result in dissolved concentrations that exceed available water quality standards.

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## 1. Introduction

Abandoned boats in various states of disrepair are a common sight along the foreshores of the coastal zone. As well as posing a navigational hazard, abandoned boats represent a localised source of various toxic contaminants associated with residual fuels, oils and paints. Despite many of these chemicals being banned or restricted since their original use or application, contamination arising from boat abandonment has been largely overlooked, presumably because there appears to be no direct or enforceable regulation regarding boat disposal (Stevenson, undated; Lord-Boring and Zelo, 2006).

In a recent study, paint fragments from different structural components (e.g. hull, transom, nameboard, deck, cabin) of various wooden boats abandoned on the mudflats of two estuaries in eastern England were analysed for their elemental content by field portable-X-ray fluorescence spectrometry (Rees et al., 2014). Copper, barium and zinc were present in many samples at concentrations exceeding 1% by weight, but the metal of greatest concern in respect of both risks to human health and potential impacts on the local environment was lead. Thus, the metal was detected in all samples analysed with maximum concentrations in paints from several boats exceeding 20%. Lead compounds were added to marine paints to provide corrosion resistance and enhance drying as well as to provide colour and opacity (Booher, 1988; Lambouere, 2000). However, the well-documented health impacts arising from

Pb have since resulted in restrictions in the use of such compounds in many countries in both consumer and commercial formulations (Lamphear et al., 2003; Schwab et al., 2006).

In the present study, the potential impacts of leaded paint from abandoned boats in the benthic and intertidal communities are evaluated in the laboratory. Specifically, a composite of paints collected from the boats referred to above has been mixed in different proportions with clean estuarine sediment, and the mobilisation of Pb in coastal sea water and its bioaccessibility to deposit-feeding invertebrates have been determined in a series of timed experiments. Bioaccessibility is defined as the fraction of contaminant that is released in the digestive environment following ingestion, but is not necessarily equivalent to the quantity that enters the blood stream and systemic circulation (Lawrence et al., 1999). Here, bioaccessibility is evaluated using a solution of the commercial protein, bovine serum albumin (BSA), whose complexing capacity is equivalent to that of amino acids encountered in the near-neutral digestive tract of marine suspension-feeders and deposit-feeders (Chen and Mayer, 1998; Zhong and Wang, 2006).

## 2. Materials and methods

### 2.1. Materials

All plasticware and glassware used for sampling, sample processing or sample storage was pre-cleaned by soaking in a mixture of 0.5 M HNO<sub>3</sub> and 0.5 M HCl for at least 24 h before being rinsed three times with Millipore Milli-Q water (MQW). Reagents and standards were purchased from Fisher Scientific, CPI International

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and Sigma–Aldrich and were of analytical grade or equivalent. Coastal sea water (salinity = 33; pH 7.8) was piped directly to the laboratory from a fibreglass reservoir, having been collected in bulk from Plymouth Sound. Before being used, sea water was filtered through 0.45  $\mu\text{m}$  Whatman membranes using a polysulphone vacuum filtration unit into a series of 1 L high density polyethylene bottles that were stored at 4 °C and in the dark.

## 2.2. Sample collection and processing

About 1 L of surficial (<5 cm) sandy sediment was collected using a polyethylene trowel from the intertidal, marine reaches of the Erme, a small, protected estuary in south west England. The sample was wet sieved on site through a 1 mm Nylon mesh into a lidded, plastic bucket and transported in a cool box to the laboratory where it was stored frozen in a series of clear, zip-locked polyethylene bags.

Fragments of leaded paint had been collected from a variety of boats abandoned on the mudflats of several estuaries in eastern England as part of a separate research programme (Rees et al., 2014). Briefly, paint fragments were sampled from different structural components of barges, trawlers and houseboats using a pair of plastic tweezers and their elemental compositions subsequently ascertained by X-ray fluorescence spectrometry. In the present study, about 30 fragments known to contain appreciable concentrations (>1000  $\mu\text{g g}^{-1}$ ) of lead were ground using a granite pestle and mortar in a fume cupboard before the pooled contents were sieved through a 1 mm Nylon mesh and stored in a wide-necked 100 ml polyethylene bottle wrapped in aluminium foil.

## 2.3. Experimental

The general approach for the current study is based on protocols outlined in Turner et al. (2008) and Jones and Turner (2010) that were designed to examine the solubilities of Cu and Zn in sediment contaminated by antifouling paint waste. Thus, in experiment A, portions of about 25 g of defrosted sediment were accurately weighed into a series of five 250 mL wide-necked polyethylene bottles. Different quantities of the ground paint composite were accurately weighed into the bottles (0 mg and about 25 mg, 100 mg, 500 mg and 2.5 g) before 100 ml of filtered sea water was added to each preparation (hereafter referred to as A1–A5). The solid to fluid ratio in the experiment was about 180  $\text{g L}^{-1}$  and representative of the conditions encountered in the digestive environment of many marine deposit-feeding invertebrates while feeding (Lawrence et al., 1999). The contents were then wrapped in foil and agitated on a lateral shaker at 200 rpm at room temperature. At different time intervals up to 20 h (encompassing the gut passage time of most deposit-feeders; Mayer et al., 1997), subsamples of 15 mL were abstracted, transferred to polypropylene tubes and centrifuged at  $1600 \times g$  for 7 min. Supernatants were subsequently filtered through Whatman 0.45  $\mu\text{m}$  filters using a Millipore swinex syringe system and divided into triplicate 4 ml aliquots in a series of clean polypropylene tubes. Aliquots were then diluted to 20 ml with 2%  $\text{HNO}_3$  and stored in the dark awaiting analysis.

Experiment B (and the preparation of B1–B5) proceeded likewise but coastal sea water amended with bovine serum albumin (BSA, >96% fraction V), and prepared by dissolving 5 g of the protein in 1 L of sea water in a 1.5 L polyethylene bottle, was used as the extractant. Given the molecular mass of the protein (66,400  $\text{g mol}^{-1}$ ) and the number of component amino acids (AA = 583), working solutions were equivalent to an AA concentration of about 45 mM, or close to the median concentration encountered in the digestive environments of a range of temperate zone deposit-feeding organisms (Mayer et al., 1997).

## 2.4. Sediment and paint digestion

For the near-complete dissolution of Pb from the solids, triplicate 0.5 g portions of dried (at  $\sim 40^\circ\text{C}$ ) estuarine sediment and a reference material (LGC 6156 Harbour Sediment) and triplicate 0.1 g portions of the ground paint composite were accurately weighed into 50 mL borosilicate beakers to which 10 mL aliquots of aqua regia (1 part  $\text{HNO}_3$  to three parts HCl) were added. The contents were then covered with watch glasses and heated to 75 °C on a hot plate for 90 min. The cooled digests were subsequently filtered through 0.45  $\mu\text{m}$  and washed with MQW into 50 mL volumetric flasks. Procedural blanks were performed in triplicate likewise but in the absence of solids.

## 2.5. Analysis

Lead (as  $^{208}\text{Pb}$ ) was analysed in the diluted sea water- and BSA-extracts (arising from experiments A and B, respectively) by collision cell inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-Series ICP mass spectrometer (ThermoElemental, Winsford, UK) with a concentric glass nebuliser and conical spray chamber. The instrument was calibrated externally using six, matrix-matched standards in the range 1–250  $\mu\text{g L}^{-1}$  and three matrix-matched blanks, while internal calibration was achieved by the addition of 50  $\mu\text{g L}^{-1}$  of  $^{193}\text{Ir}$  to all standards, samples and blanks. RF power was set at 1400 W and coolant, auxiliary, nebuliser and collision cell gas flows rates were 13 L Ar  $\text{min}^{-1}$ , 0.70 L Ar  $\text{min}^{-1}$ , 0.75 L Ar  $\text{min}^{-1}$  and 3.5 mL 7%  $\text{H}_2$  in He  $\text{min}^{-1}$ , respectively. Data were acquired over a dwell period of 10 ms, with 50 sweeps per reading and three replicates.

Concentrations of Pb (and, for comparative purposes, Cu and Zn) were measured in aqua regia digests of sediment and paint by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 7400 analyser with a MiraMist PEEK nebuliser and cyclone spray chamber. Calibration was achieved using five, matrix-matched, mixed standards in the range 0.1–2  $\text{mg L}^{-1}$  for each metal, and three matrix-matched blanks. Instrument power was set at 1.2 KW, coolant, auxiliary and nebuliser flows were 12, 0.5 and 0.5 L Ar  $\text{min}^{-1}$ , respectively, and replicate ( $n = 3$ ) read time was 2 s. Analysis of digests of the reference material revealed recoveries of greater than 85% for Pb and Cu and greater than 90% for Zn.

## 3. Results

### 3.1. Concentrations of Pb in sediment, paint and mixtures thereof

The mean ( $\pm$ one standard deviation of) dry weight concentrations of Pb in the fractionated (<1 mm) estuarine sediment and paint composite were  $4.3 \pm 1.6 \mu\text{g g}^{-1}$  and  $48,700 \pm 5150 \mu\text{g g}^{-1}$ , respectively. By comparison, respective concentrations of Cu and Zn were  $15.9 \pm 6.3 \mu\text{g g}^{-1}$  and  $302 \pm 77 \mu\text{g g}^{-1}$  and  $25.9 \pm 4.6 \mu\text{g g}^{-1}$  and  $4440 \pm 405 \mu\text{g g}^{-1}$ . The average ratio of Pb:Cu:Zn in the paint of 161:1:15 is very different to that representative of paint waste collected from boatyards (1:593:217; Singh and Turner, 2009), reflecting the high content of Pb in old boat paints versus the high contents of biocidal Cu(I) and the pigment, ZnO, in contemporary antifouling formulations.

Table 1 shows the absolute and relative quantities of sediment and paint in the different preparations of the experiments. Note that the amount of sediment on a dry weight basis was derived from the weight loss incurred on drying (at  $\sim 40^\circ\text{C}$ ) triplicate, 1 g portions of thawed, wet sediment. Also shown in Table 1 are corresponding concentrations of Pb, and as derived from mean concentrations measured in the sediment and paint and the

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