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Determining riverine sediment storage mechanisms of biologically reactive phosphorus in situ using DGT

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Metal contamination of sediment by peeling paint on abandoned boats, with particular reference to lead

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Abstract

Fragments of boat paint have been sampled from eighteen boats (including sailing barges, houseboats, a trawler and a ferry) abandoned on the intertidal mudflats of two estuaries in eastern England. The surfaces of each sample were analysed for Cu, Pb and Zn by field portable X-ray fluorescence (XRF) spectroscopy while total metals were determined in fragments by inductively coupled plasma-mass spectrometry (ICP-MS) following acid digestion. Lead was detected by XRF in all cases (430 analyses of 155 fragments) and median concentrations on each boat ranged from about 350 to 35,000 μg g^{-1}, with individual concentrations exceeding 20% in several cases. Zinc was detected in most samples with median concentrations ranging from about 50 to 10,000 μg g^{-1} and a maximum individual concentration of 24%. Copper was detected in fewest (277) cases and mainly on samples taken from the outer hulls, with median concentrations on each boat ranging from about 50 to 1900 μg g^{-1} and an individual maximum concentration of 17%. For all metals, multiple, surficial XRF analyses of each fragment were correlated significantly with single, total analyses conducted by ICP.

The relatively high abundance and persistence of Pb in the paints resulted in greatest contamination of local sediment by this metal, with concentrations exceeding quality guidelines (of 112 μg g^{-1}) in several instances. Among the metals considered, therefore, Pb is of greatest concern from both environmental and human health perspectives. Contamination arising from peeling paint on abandoned craft is likely to be a general, albeit localised problem, whose significance depends on the size, age, condition and nature of the boat. Although further research into the problem is required, including an assessment of the aquatic toxicities of metals in old paints,

immediate recommendations are clear legislation preventing the abandonment of boats and the creation of facilities designed to assist boat owners with the disposal of end-of-life vessels.

Keywords: *abandoned boats; paint; antifouling; hull; metals; contamination; sediment*

1. Introduction

The abandonment of boats appears to be either a practice that is exempt from any clear or direct legislation or an illegal activity that is essentially unenforceable (Lord-Boring et al., 2004; Lord-Boring and Zelo, 2006; National Association of State Boating Law Administrators, 2009; Washington State Department of Natural Resources, 2013; Stevenson, undated). Consequently, abandoned boats in various states of disrepair are commonly observed on the foreshores, intertidal flats, reefs and mangroves of the coastal zone. As well as an eye sore, and depending on their size, location and state of dereliction, abandoned boats can present both a physical and navigational hazard. From an environmental perspective, they are also responsible for a loss of habitat, pose an entrapment risk to wildlife and can act as a local source of contamination. With respect to the latter, leaking oil presents an immediate, albeit significant threat (Lord-Boring and Zelo, 2006), while deteriorating and flaking paint potentially represents a longer-term environmental problem (Turner, 2010).

Studies conducted in the vicinity of shipyards and boatyards have revealed that local sediment is often considerably contaminated by antifouling paint waste containing biocidal components, including Cu(I) and various organic compounds, that are toxic to marine life (Takahashi et al., 2012; Turner, 2013). Regarding abandoned boats, an additional concern is that old, peeling paint from the hulls and other structural components may contain substances that are currently restricted in use or that have been banned since their original application. In a recent study, for instance, high concentrations of Sn, presumably as organotin (e.g. tributyltin), and Pb (as various inorganic pigments and, possibly, organolead biocides) were measured in various paint fragments sampled from boats abandoned on sediment flats of UK estuaries (Turner et al., 2014).

In the present study, we measure metals in paint fragments sampled directly from boats abandoned on the intertidal mudflats of two estuaries in eastern England. Specifically, we have targeted locations where there are clusters of a variety of decaying wooden vessels, many of which are more than a hundred years old, and use both non-destructive surface mapping and total analysis following acid digestion to determine the distributions and concentrations of metals in paint fragments collected from various regions of each boat. We also measure metals in surficial sediment samples surrounding each boat or cluster of boats and compare concentrations with those in local control sites in order to ascertain the degree and significance of contamination arising from peeling paint on abandoned vessels.

2. Materials and methods

2.1. Sampling and sample locations

Sampling was conducted during December 2012 on the intertidal mudflats of two estuaries in eastern England (Orwell and Blackwater; Figure 1a) at locations where a variety of abandoned boats were known to be present (and have been for many years) and where there were no obvious confounding sources of contamination (for example, from slipways or boatyards). The Orwell is a mesotidal, coastal plain estuary of 20 km in length and with a shoreline of about 50 km. Here, sampling was undertaken near the community of Pin Mill (PM), located about half way along the southern shores of the estuary (Figure 1b). The Blackwater is a macrotidal, coastal plain estuary of 21.3 km in length and with a shoreline length of about 110 km. Here, sampling was undertaken in Heybridge Creek (HC) and Heybridge basin (HB), towards the head of the estuary (Figure 1c), and in Tollesbury Fleet (TF), a managed realignment area on the north bank towards the mouth of the estuary (Figure 1d).

At each location, paint was sampled from different regions of accessible boats, as defined and coded in Table 1 and exemplified photographically in Figure 2, using a pair of plastic tweezers. Samples were carefully cleared of any visible extraneous material (algae, shell debris, grit) before being stored in individual zip-lock bags and in the dark until required for analysis. The name and type of boat, year of commissioning and port of registration were ascertained by visual inspection and/or consultation with the appropriate literature (e.g. The Society for Sailing Barge Research, 2012). The approximate year of boat abandonment was established from the literature or by using the time slider facility in Google Earth.

Sediment was sampled at three locations within a few metres of each boat or, where boats were close and/or access limited, at locations between pairs of boats (PM2/PM3 and HC2/HC3). Control samples were collected in triplicate from each environment at locations a few hundred metres away from the abandoned boats. In each case, about 100 ml of surface, oxic mud was scraped into a zip-lock bag with the aid of a plastic spatula and the contents were transported to the laboratory in Plymouth in a cool box before being stored frozen pending digestion and analysis.

2.2. XRF analysis

The surfaces of the paint fragments were analysed for a variety of metals, of which Cu, Pb and Zn are the focus of the present study, by energy dispersive X-ray fluorescence (XRF) spectrometry using a Thermo Scientific Niton hand-held XRF analyser (model XL3t 950 He GOLDD+). The instrument is fitted with an X-ray tube with Ag anode target excitation source and a geometrically optimised large area drift detector, and data are transferred using Thermo Scientific Niton data transfer (NDT) PC software. In the present study, the instrument was operated in the laboratory in an accessory stand. Each paint fragment was carefully placed in the centre of a 6 μm polypropylene slide, outer face downwards, and the slide was then placed over a 3 mm small-spot collimator above the detector. Overall measurement time was between 120 and 150 seconds and spectra up to 30 keV were quantified by standardless analysis in ‘plastics’ mode. Where possible, measurements were repeated after repositioning the fragment with respect to the collimator and after the inversion of the fragment to expose the inner face to the detector (the total number of analyses undertaken depended on the size and apparent heterogeneity of the sample).

Metal concentrations were reported in parts per million ($\mu g\ g^{-1}$) with an error of 2σ (95% confidence). Instrumental detection limits, supplied by the manufacturer and for a SiO_2 matrix analysed using the optimum ('mining') mode and for a period of 60 seconds, were 12, 4 and 6 μg g^{-1} for Cu, Pb and Zn, respectively. Triplicate measurements of a polyethylene reference material (Niton PN 180-554) containing 1002 μg g^{-1} of Pb returned a mean (± one sd) concentration of 922 (± 3) μg g^{-1} (Note that the reference plastic had not been amended with Cu and Zn.)

2.3. Paint fragment and sediment digestion

For comparative purposes, the total concentrations of metals in selected paint fragments (n = 27) were also measured by inductively coupled plasma-mass spectrometry (ICP-MS) after acid digestion. Thus, whole fragments or pieces thereof weighing up to 0.1 g were accurately weighed into individual 25 ml Pyrex beakers to which 5 ml of aqua regia (3:1 HCl:HNO_3; both Fisher Scientific TraceMetal grade) were added. The contents of the beakers were gently boiled under watch glasses for about an hour before being allowed to cool. Digests were then transferred to individual 100 ml Pyrex volumetric flasks and diluted to mark with Millipore Milli-Q water (> 18 MΩ cm).

One g aliquots of freeze-dried sediment samples and triplicate 1 g aliquots of a reference material certified for metal concentrations available to aqua regia (Harbour Sediment, LGC6156) were accurately weighed into Pyrex beakers to which 8 ml of aqua regia were added. The contents were digested as above before being transferred to individual 50 ml volumetric flasks and diluted with Milli-Q water. Procedural controls were performed in triplicate likewise but in the absence of paint fragments or sediment.

2.4. ICP analysis

Digests and, as necessary, dilutions thereof, were analysed for ^{65}Cu, ^{208}Pb and ^{66}Zn by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-Series ICP mass spectrometer with collision cell (ThermoElemental, Winsford, UK). Samples were introduced via a concentric glass nebuliser coupled with a conical spray chamber and with acquisition parameters and gas flow rates described elsewhere (Turner et al., 2010). External calibration was achieved using 5 matrix-matched, multi-element standards and three blanks, and 50 μg L^{-1} of both ^{115}In and ^{193}Ir were added to all standards, blanks and samples to compensate for instrumental drift and variations in plasma conditions. Metal concentrations in the digests were corrected for any contamination encountered in the controls and then converted to a dry wt/wt basis. Measured concentrations of Cu, Pb and Zn in the reference sediment were 2655 ± 9.8, 1574 ± 80 and 3934 ± 230 μg g^{-1}, respectively, compared with certified concentrations of 2400 ± 1.2, 1685 ± 1.0 and 3530 ± 1.2 μg g^{-1}, respectively. Aluminium, as a proxy for sediment grain size, was analysed by ICP-optical emission spectrometry inductively using a Varian 725-ES operated under conditions outlined in Jessop and Turner (2011).

3. Results

3.1. Metals in paint fragments

Results of the XRF analyses of paint fragments (*n* = 155) from the 18 abandoned boats are summarised in Table 2. Here, the median, minimum and maximum concentrations of surficial Cu, Pb and Zn are reported for the pooled results arising from single and multiple analyses of all fragments from each boat. Lead was detected in all XRF analyses performed (*n* = 430), while Zn was undetected in four cases and Cu was undetected in 153 cases. Among the metals, and based on median concentrations, Pb was highest in 15 boats and Zn in 3 boats. For a given boat, concentrations of Cu and, in general, Zn were greatest in hull paints, while the highest concentrations of Pb were measured in samples from a variety of regions, including the hull, nameboard, transom and cabin.

Other metals detected in fewer cases by XRF included Cr (*n* = 100), Ni (*n* = 107) and Sn (*n* = 34) and at concentrations up to 13,400, 860 and 2620 μg g^{-1}, respectively. The highest concentrations of Ni and Sn were always encountered on lower hull paints, while the highest Cr concentrations were found on paints from various interior or exterior components.

In Figure 3, surficial concentrations of Cu, Pb and Zn determined by multiple XRF analyses of each paint fragment are compared with total metal concentrations in each fragment as ascertained by ICP-MS analysis following acid digestion (or the method employed to determine metals in sediment). In each case, a significant correlation was observed and data were dispersed roughly equally either side of unit slope. This suggests that both analytical techniques deliver a similar response to Cu, Pb and Zn in the paint matrix, or, strictly, that the total metal concentration for a fragment is comparable with an average concentration derived from multiple analyses of the paint surface. Clearly, and at least with respect to paint fragments, XRF has the advantage in being able to map the spatial distribution of metals at the sample surface.

3.2. Metals in sediment

The concentrations of Cu, Pb and Zn in the sediment samples are summarised in Table 3. Here, the mean (and standard deviation) of concentrations determined in three samples collected in the vicinity of each boat (or pair of boats) are shown. Also given, in italics and coded 0, are mean concentrations of metals at the control sites for each environment under study. With the exception of Cu and Zn in two cases each, mean concentrations in the sediment samples in the vicinity of the abandoned boats exceeded mean concentrations of the corresponding controls. In most cases, the variability in metal concentrations was also greater in the vicinity of boats than in the controls. For example, the relative standard deviation in the controls was always less than 20% for Cu and Pb and less than 10% for Zn compared with respective relative standard deviations of up to 70%, 140% and 80% around the abandoned vessels.

According a series of two-sample *t*-tests, mean concentrations of Pb were always significantly greater ($p < 0.05$) in the vicinity of boats than the corresponding control concentrations. For Cu, significant enrichment relative to the controls occurred in the samples from Pin Mill and Heybridge Basin and in three samples from Tollesbury Fleet; no significant enrichment was observed at Heybridge Creek, however. For Zn, significant enrichment occurred at Heybridge Basin and Tollesbury Fleet and in two and three samples from Pin Mill and Heybridge Creek, respectively.

In order to account for possible effects arising from grain size variations among the sediment samples, enrichment of each metal, Me, was also determined following normalisation to Al as follows:

$$EF = \frac{[Me]_s/[Al]_s}{[Me]_c/[Al]_c}$$

where EF is a dimensionless enrichment factor and subscripts s and c denote the sample and control, respectively. The distribution of EF among the sediment samples, shown in Figure 4, was largely consistent with the distribution of absolute concentrations since the Al content of the samples from the vicinity of the boats was similar to the Al content of the corresponding controls. For Cu, the maximum EF was about 110 in a sample from Tollesbury Fleet (TL3), and the overall median value was about 1.3. For Pb and Zn, respective values for maximum EF and median were about 440 and 1.9 and 20 and 1.3 respectively, with the greatest enrichment observed at the same Tollesbury site.

4. Discussion

The present study has revealed an abundance of peeling paint on a variety of abandoned boats, and in various stages of dereliction, along the foreshores of two estuaries of eastern England. While the service histories and ownership of many of the boats can be ascertained from the relevant literature, the nature, origin and age of the paints employed are unknown. For example, in some cases remnants of original formulations may remain on exterior or internal surfaces, while in other cases, and in particular where boats have changed ownership and/or function, more recent paints are likely to be prevalent. Regardless of the precise history of paint application, many fragments analysed by XRF contain concentrations of metals that are sufficiently high to be of concern in respect of both contamination of the local aquatic environment and risk to human health.

The occurrence of Cu was largely in fragments collected from the lower hulls of decaying vessels. Clearly, this reflects the use of the metal (e.g. as Cu_2O or CuCNS) in antifouling formulations, with or without other organic or organometallic biocides. Concentrations of Cu in the present study are, however, considerably lower than those reported for antifouling paints themselves or for paint particles derived from recently renovated vessels. For example, Paradas and Filho (2007) report a Cu concentration of about 32% for a contemporary antifouling formulation while Bellinger and Benham (1978) report concentrations of Cu up to about 68% for various antifouling paints available in the 1970s. Adopting a more indirect approach, Singh and Turner (2009) analysed a composite of paint fragments collected from a small boatyard in south west England and found a mean Cu concentration of over 30%. Presumably, lower concentrations observed in paint fragments from abandoned boats reflect the continued, slow release of cuprous ions from the paint matrix during the boats operational life and post abandonment from periods of tidal inundation or precipitation (Jessop and Turner, 2011). On this basis, therefore, it would be reasonable to expect an inverse relationship between the concentration of Cu and the age of paint and its degree of exposure to sea water and rainfall.

The more widespread occurrence of Zn among our paint fragment samples reflects both the use of the metal in antifouling formulations, as a component of certain co-biocides, acrylic polymers or soluble pigments (Yebra et al., 2006), and its application in paints more generally (Abel, 2000). Unlike the case for Cu, the highest concentrations of Zn measured, and mainly on the hulls of abandoned boats, are consistent with concentrations in contemporary and historical antifouling formulations (around 15-20%; Bellinger and Benham (1978); Paradas and Filho (2007)), suggesting that Zn-based compounds are more persistent than those involving Cu(I).

Despite health concerns about its use in paint, Pb was encountered in all paint fragments sampled and at variable concentrations. This observation reflects the variety of uses of the metal in historical paints, including those used on boats. For example, Pb was used as a drying agent, as a pigment for colour or to enhance opacity and as an anticorrosion agent (Booher, 1988). Lead was also used in organometallic form in antifouling paints before the 1970s and was found to be particularly effective in combatting tubeworm fouling (Dick and Nowacki, 1970). Unlike Cu, compounds of Pb used in paints (other than those employed as biocides), including lead chromate and lead carbonate, are rather insoluble. Thus, greater concentrations of Pb than Cu (and, to a certain extent, Zn) in paint fragments from abandoned boats can be attributed to both the historical, general use of Pb and its greater overall persistence. A consequence of the latter is that, in contrast to Cu, the wt/wt concentration of Pb in fragments from old boats may exceed concentrations in the original formulations through the gradual dissolution of more soluble components from the paint matrix.

Given its abundance, persistence and toxicity, Pb is the metal of most concern among those considered in the present study in respect of both risks to human health and aquatic wildlife. In 13 out of 18 of the boats sampled, median concentrations of Pb in paint fragments determined in the current study exceed a human health related 5000 $\mu g\ g^{-1}$ ‘safety level’ (based on a 1977 EC Directive and a 1990 US Department of Housing and Urban Development abatement action; Horner, 1994). Deteriorating paint itself therefore presents a health hazard if disturbed during the salvage, renovation or disposal of abandoned boats. Strictly, material for disposal should be regarded as hazardous waste, and the use of boat components for firewood or the burning of abandoned boats in situ, practices which we have been made aware of by members of the public, are clearly unsafe and irresponsible.

We have also observed swans pecking at loose paint on poorly maintained leisure craft and note that the incidental ingestion of antifouling paint particles is believed to be responsible for cases of Cu toxicosis and critically high hepatic Cu concentrations (Molnar, 1983; Degernes, 2008). High concentrations of Pb in peeling paint therefore present a potential means by which waterfowl may be poisoned, a condition that has been directly observed in sea birds having ingested leaded paint from a decommissioned military base (Finkelstein et al., 2003).

Clearly, both elevated and more variable metal concentrations in sediment in the vicinity of abandoned boats compared with control sites reflect contamination arising from paint fragments of various sizes. Contamination may be direct, in that discrete paint fragments are heterogeneously dispersed among sediment grains, or indirect, whereby metals ions dissolved from the paint matrix adsorb to neighbouring sediment particles. That contamination is greatest for Pb reflects its abundance and persistence in boat paints coupled with a high affinity of aqueous Pb^{2+} for the surface of geosolids (O'Reilly and Hochella, 2003; Hua et al., 2012). Presumably, therefore, variations in the precise degree of sediment contamination result from differences in (i) the concentrations and labilities of metals in paints from the various boats, (ii) the rates of input of paint fragments through weathering, and (iii) local hydrodynamics and sedimentation rates.

Regarding marine sediment and according to the CCME (Canadian Council of Ministers of the Environment, 2012), quality guidelines for the protection of aquatic life (as predicted effect concentrations; PELs) for Cu, Pb and Zn are 108, 112 and 271 μg g^{-1}, respectively. Thus, out of the 16 sites in which sediment was sampled near to abandoned boats, mean concentrations of Cu and Zn exceed the respective quality guidelines in one case each, while the mean concentration of Pb exceeds the corresponding guideline in five cases (Table 3); based on individual sediment samples, the number of exceedances for Cu, Pb and Zn are four, thirteen and six, respectively. Although in most cases metal concentrations do not exceed quality guidelines, it is important to appreciate that the forms and species of metals in boat paints (e.g. organolead compounds, Cu(I) and Zn pyrithione) are likely to be more hazardous than those bound to sediment and which form the basis of predicted effects.

5. Conclusions

This study has revealed high concentrations of Cu, Pb and Zn in peeling paint sampled from boats abandoned on the mudflats of two estuaries in eastern England. Among the metals considered, Pb is of greatest concern due to its abundance in a wide variety of paints coupled with a relatively high environmental persistence and high toxicity to aquatic life, waterfowl and humans. The abundance and persistence of Pb results in significant contamination of local sediment, with Al-normalised enrichment factors > 10 in many cases and concentrations exceeding available quality guidelines in several instances.

To our knowledge, this is the first study to quantify contamination of the coastal environment from flaking paint on abandoned boats and the first to highlight the hazards associated with old leaded paints on these vessels. Clearly, contamination from peeling paint is likely to be a general problem where boat abandonment occurs, although the precise metals that pose the greatest threat may vary depending on the age and nature of the boats. For example, it is anticipated that old antifouling paints containing biocidal (and organo-) forms of As, Hg and Sn may well present an environmental hazard on boats that have been abandoned for several decades. Although more work into the scale and nature of the problem is called for, including an assessment of the bioavailabilities and toxicities of paint components to a variety of organisms, immediate recommendations are clear legislation for the prevention of boat abandonment and facilities specifically designed for the safe disposal of end-of-life vessels.

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Figure 1: Map under construction.

Figure 2: Photographs of a selection of abandoned boats sampled in the present study: (a) PM3; (b) PM5; (c) HC1; (d) HC2; (e) TL2; (f) TL3.

Figure 3: A comparison of metal concentrations in paint fragments from the abandoned boats (Pin Mill, ■; Heybridge Basin, ○; Heybridge Creek, ●; Tollesbury Fleet, Δ) ascertained by multiple, surficial XRF analyses and by whole fragment digestion-ICP analysis.

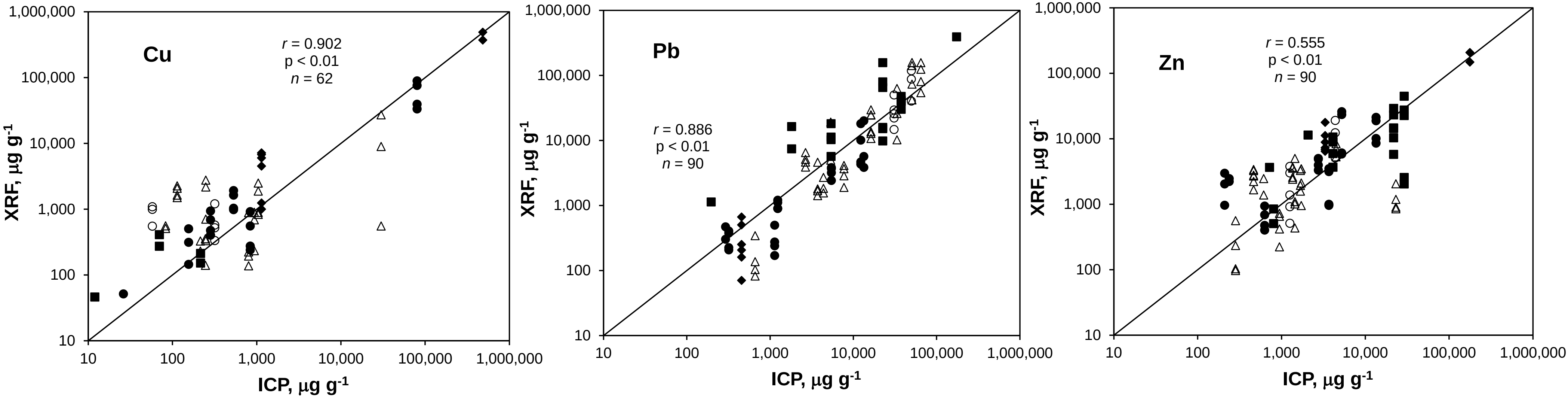

Figure 4: Aluminium-normalised factors defining the enrichment of metals in sediments in the vicinity of the abandoned boats relative to control sediments.

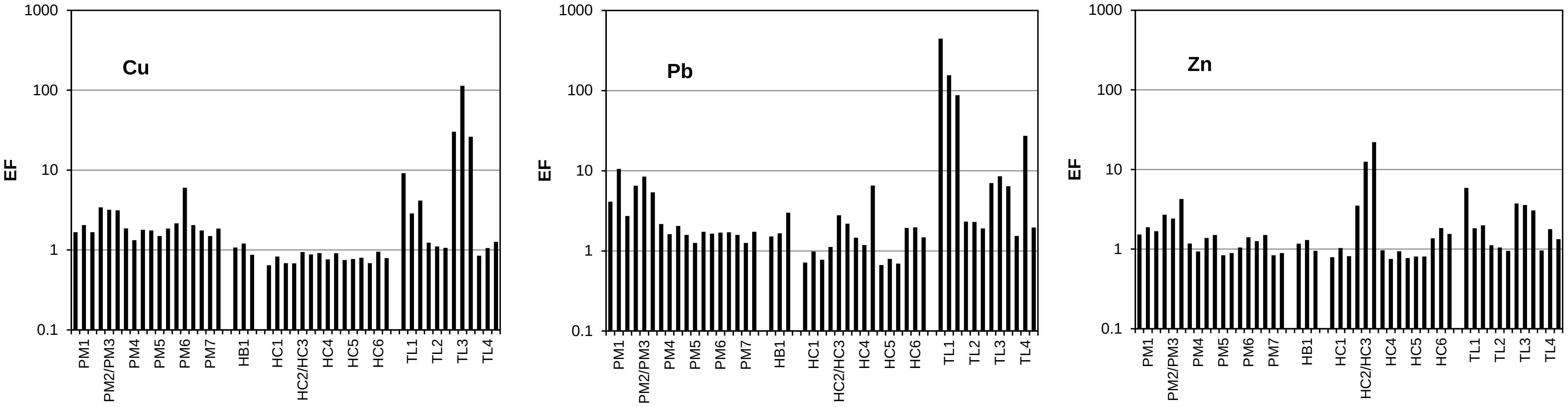

Table 1: Location, characteristics and coding of the abandoned boats, and the regions of each boat sampled for paint fragment analysis. Note that all boats were of wooden construction except where otherwise mentioned.

location	boat number	boat name	boat type	year commissioned	year abandoned	sampling areas	no. samples	no. XRF analyses
Pin Mill	PM1	Mousme	Thames barge	1924	2006	outer hull, transom, nameboard, railing	11	16
	PM2	Venture	Thames barge	1900	1993	outer hull, nameboard	8	15
	PM3	Waterlily	Thames barge	1902	1986	outer hull, nameboard, bow post	5	16
	PM4	Rainbow	trawler		late 1990s	outer hull, railing	5	19
	PM5		pleasure boat		2006-2007	outer cabin, outer hull, inner hull	6	30
	PM6		lightship tender, fishing boat		2010-2011	outer hull, inner hull, transom	6	17
	PM7	MV Hainault	ferry	1914	1999	deck, outer cabin, inner cabin, outer hull, inner hull	12	34
Heybridge Basin	HB1	Charles Burley	Thames barge	1902	1980s	deck, outer hull	15	35
Heybridge Creek	HC1		houseboat		2000-2005	deck, outer cabin, inner hull, outer hull, bow post	17	54
	HC2		pleasure boat		2000-2005	deck, outer cabin, outer hull	3	12
	HC3		fibreglass pleasure boat		2000-2005	outer hull	2	4
	HC4		pram dinghy		2009	outer hull, topside	4	7
	HC5		plyboard motorboat		2000-2005	deck, outer hull, inner hull	7	17
	HC6	Beaumont Belle	Thames barge	1894	1960s	outer hull, bow post	4	6
Tollesbury	TL1		houseboat		before 2000	deck, outer hull, transom	15	47
	TL2		river cruiser		unknown	outer cabin, inner cabin, outer hull, inner hull	14	47
	TL3		yule		2000-2005	deck, outer hull	9	22
	TL4	Memory	Thames barge	1904	1995	outer hull, transom, winch, nameboard	12	32

Table 2: Summary of metal concentrations in the paint fragments sampled from the abandoned boats as ascertained by XRF analysis and in μg g^{-1}. Note that *n* refers to the number of analyses in which each metal was detected.

	Cu				Pb				Zn			
boat	*n*	median	min	max	*n*	median	min	max	*n*	median	min	max
PM1	5	332	46.1	665	16	34,900	1030	736,000	16	3100	656	44,600
PM2	11	374	94.0	1630	15	7420	167	157,000	15	866	88.0	33,200
PM3	10	283	151	3020	16	9490	151	55,871	16	5810	1030	46,300
PM4	6	249	165	513	19	15,800	5040	483,000	19	10,300	4190	117,000
PM5	17	314	166	1410	30	9060	659	30,500	29	3100	208	21,600
PM6	12	533	199	18,800	17	2860	372	9570	17	5220	562	19,400
PM7	26	1100	77.5	9130	34	6080	153	282,000	32	2010	167	23,300
HB1	16	535	63.6	1210	36	16,200	195	139,000	35	4130	67.3	44,900
HC1	40	608	145	4690	54	4760	55.6	144,000	54	1980	310	20,400
HC2	12	414	147	1910	12	1,930	170	3830	12	4650	960	25,900
HC3	nd				4	9930	1270	16,300	4	46.1	29.5	93.0
HC4	1	965			7	16,300	1650	44,400	7	628	442	3690
HC5	12	698	172	89,000	17	405	194	43,800	17	2650	902	239,000
HC6	1	51.5			6	339	244	15,300	6	1550	344	9480
TL1	40	877	124	150,000	46	14,200	2280	313,000	46	907	166	29,500
TL2	32	418	107	2420	47	2860	82.2	62,500	47	2800	97.1	16,500
TL3	22	1860	104	172,400	22	5040	1200	72,700	22	3610	579	8400
TL4	14	793	64.4	2264	32	10,800	87.6	157,000	32	1240	111	4485

Table 3: Mean (± one standard deviation) of metal concentrations in sediments (µg g^{-1}) sampled from the vicinity of abandoned boats (or boat pairs) and in the control sites (in italics and coded ‘0’). Concentrations in bold are significantly greater than concentrations in the corresponding controls.

boat	Cu	Pb	Zn
PM0	*8.9 ± 0.4*	*9.7 ± 1.0*	*26.7 ± 0.7*
PM1	**17.8 ± 2.4**	**63.6 ± 46.7**	**50.6 ± 6.2**
PM2/PM3	**36.4 ± 0.8**	**83.5 ± 18.1**	**107 ± 39.6**
PM4	**14.1 ± 4.4**	**18.2 ± 5.5**	29.4 ± 7.1
PM5	**13.1 ± 1.5**	**12.8 ± 0.7**	25.0 ± 7.4
PM6	**26.7 ± 20.0**	**13.9 ± 1.3**	28.3 ± 6.0
PM7	**13.1 ± 1.5**	**12.8 ± 0.7**	25.0 ± 8.0
HB0	*20.1 ± 3.0*	*24.3 ± 0.5*	*64.2 ± 4.0*
HB1	**27.6 ± 2.7**	**72.4 ± 47.7**	**96.8 ± 9.7**
HC0	*40.1 ± 5.3*	***58.5 ± 10.6***	*113 ± 8.4*
HC1	41.7 ± 5.4	**68.6 ± 6.6**	**145 ± 17.8**
HC2/HC3	25.8 ± 3.5	**87.5 ± 25.0**	**1120 ± 906**
HC4	45.6 ± 6.6	**228 ± 217.0**	133 ± 14.5
HC5	40.9 ± 2.1	**54.8 ± 2.5**	120 ± 4.3
HC6	40.1 ± 2.5	**129 ± 20.9**	**224 ± 10.4**
TL0	*17.8 ± 3.3*	*34.4 ± 3.9*	*59.3 ± 5.9*
TL1	**90.3 ± 37.3**	**7377 ± 4719**	**180 ± 90.4**
TL2	**29.3 ± 4.7**	**109 ± 9.7**	**89.8 ± 11.9**
TL3	**1154 ± 791**	**317 ± 17.5**	**261 ± 45.5**
TL4	23.6 ± 2.7	**431 ± 612**	**101 ± 24.0**