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

Comber, SDW

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| 7 | Aldous B. Rees, Andrew Turner [*] , Sean Comber |
| 8 9 | School of Geography, Earth and Environmental Sciences |
| 10 | Plymouth University |
| 11 | Drake Circus |
| 12 | Plymouth PL4 8AA |
| 13 | UK |
| 14 | |
| 15 | |
| 16 | |
| 17 | *Corresponding author. Tel: +44 1752 584570; Fax: +44 1752 584710; e-mail: |
| 18 | aturner@plymouth.ac.uk |
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22 Abstract

23 Fragments of boat paint have been sampled from eighteen boats (including sailing 24 barges, houseboats, a trawler and a ferry) abandoned on the intertidal mudflats of two 25 estuaries in eastern England. The surfaces of each sample were analysed for Cu, Pb 26 and Zn by field portable X-ray fluorescence (XRF) spectroscopy while total metals 27 were determined in fragments by inductively coupled plasma-mass spectrometry 28 (ICP-MS) following acid digestion. Lead was detected by XRF in all cases (430 29 analyses of 155 fragments) and median concentrations on each boat ranged from about 350 to 35,000 μ g g⁻¹, with individual concentrations exceeding 20% in several 30 31 cases. Zinc was detected in most samples with median concentrations ranging from 32 about 50 to 10,000 μ g g⁻¹ and a maximum individual concentration of 24%. Copper 33 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 μ g g⁻¹ and an 34 35 individual maximum concentration of 17%. For all metals, multiple, surficial XRF 36 analyses of each fragment were correlated significantly with single, total analyses 37 conducted by ICP.

38

39 The relatively high abundance and persistence of Pb in the paints resulted in greatest 40 contamination of local sediment by this metal, with concentrations exceeding quality guidelines (of 112 μ g g⁻¹) in several instances. Among the metals considered, 41 42 therefore, Pb is of greatest concern from both environmental and human health 43 perspectives. Contamination arising from peeling paint on abandoned craft is likely to 44 be a general, albeit localised problem, whose significance depends on the size, age, 45 condition and nature of the boat. Although further research into the problem is 46 required, including an assessment of the aquatic toxicities of metals in old paints,

| 47 | immediate recommendations are clear legislation preventing the abandonment of |
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| 48 | boats and the creation of facilities designed to assist boat owners with the disposal of |
| 49 | end-of-life vessels. |
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51

- 52 **Keywords:** *abandoned boats; paint; antifouling; hull; metals; contamination;* 53 sediment
- 54

55 **1. Introduction**

56 The abandonment of boats appears to be either a practice that is exempt from any 57 clear or direct legislation or an illegal activity that is essentially unenforceable (Lord-58 Boring et al., 2004; Lord-Boring and Zelo, 2006; National Association of State 59 Boating Law Administrators, 2009; Washington State Department of Natural 60 Resources, 2013; Stevenson, undated). Consequently, abandoned boats in various 61 states of disrepair are commonly observed on the foreshores, intertidal flats, reefs and 62 mangroves of the coastal zone. As well as an eye sore, and depending on their size, 63 location and state of dereliction, abandoned boats can present both a physical and 64 navigational hazard. From an environmental perspective, they are also responsible for 65 a loss of habitat, pose an entrapment risk to wildlife and can act as a local source of 66 contamination. With respect to the latter, leaking oil presents an immediate, albeit 67 significant threat (Lord-Boring and Zelo, 2006), while deteriorating and flaking paint 68 potentially represents a longer-term environmental problem (Turner, 2010). 69

70 Studies conducted in the vicinity of shipyards and boatyards have revealed that local

71 sediment is often considerably contaminated by antifouling paint waste containing

72 biocidal components, including Cu(I) and various organic compounds, that are toxic 73 to marine life (Takahashi et al., 2012; Turner, 2013). Regarding abandoned boats, an 74 additional concern is that old, peeling paint from the hulls and other structural 75 components may contain substances that are currently restricted in use or that have 76 been banned since their original application. In a recent study, for instance, high 77 concentrations of Sn, presumably as organotin (e.g. tributyltin), and Pb (as various 78 inorganic pigments and, possibly, organolead biocides) were measured in various 79 paint fragments sampled from boats abandoned on sediment flats of UK estuaries 80 (Turner et al., 2014).

81

82 In the present study, we measure metals in paint fragments sampled directly from 83 boats abandoned on the intertidal mudflats of two estuaries in eastern England. 84 Specifically, we have targeted locations where there are clusters of a variety of 85 decaying wooden vessels, many of which are more than a hundred years old, and use 86 both non-destructive surface mapping and total analysis following acid digestion to 87 determine the distributions and concentrations of metals in paint fragments collected 88 from various regions of each boat. We also measure metals in surficial sediment 89 samples surrounding each boat or cluster of boats and compare concentrations with 90 those in local control sites in order to ascertain the degree and significance of 91 contamination arising from peeling paint on abandoned vessels. 92

93

- 94 **2. Materials and methods**
- 95 2.1. Sampling and sample locations

96 Sampling was conducted during December 2012 on the intertidal mudflats of two 97 estuaries in eastern England (Orwell and Blackwater; Figure 1a) at locations where a 98 variety of abandoned boats were known to be present (and have been for many years) 99 and where there were no obvious confounding sources of contamination (for example, 100 from slipways or boatyards). The Orwell is a mesotidal, coastal plain estuary of 20 km 101 in length and with a shoreline of about 50 km. Here, sampling was undertaken near 102 the community of Pin Mill (PM), located about half way along the southern shores of 103 the estuary (Figure 1b). The Blackwater is a macrotidal, coastal plain estuary of 21.3 104 km in length and with a shoreline length of about 110 km. Here, sampling was 105 undertaken in Heybridge Creek (HC) and Heybridge basin (HB), towards the head of 106 the estuary (Figure 1c), and in Tollesbury Fleet (TF), a managed realignment area on 107 the north bank towards the mouth of the estuary (Figure 1d). 108

109 At each location, paint was sampled from different regions of accessible boats, as 110 defined and coded in Table 1 and exemplified photographically in Figure 2, using a 111 pair of plastic tweezers. Samples were carefully cleared of any visible extraneous 112 material (algae, shell debris, grit) before being stored in individual zip-lock bags and 113 in the dark until required for analysis. The name and type of boat, year of 114 commissioning and port of registration were ascertained by visual inspection and/or 115 consultation with the appropriate literature (e.g. The Society for Sailing Barge Research, 2012). The approximate year of boat abandonment was established from the 116 117 literature or by using the time slider facility in Google Earth. 118

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.

126

127 2.2. XRF analysis

128 The surfaces of the paint fragments were analysed for a variety of metals, of which 129 Cu, Pb and Zn are the focus of the present study, by energy dispersive X-ray 130 fluorescence (XRF) spectrometry using a Thermo Scientific Niton hand-held XRF 131 analyser (model XL3t 950 He GOLDD+). The instrument is fitted with an X-ray tube 132 with Ag anode target excitation source and a geometrically optimised large area drift 133 detector, and data are transferred using Thermo Scientific Niton data transfer (NDT) 134 PC software. In the present study, the instrument was operated in the laboratory in an 135 accessory stand. Each paint fragment was carefully placed in the centre of a 6 µm 136 polypropylene slide, outer face downwards, and the slide was then placed over a 3 137 mm small-spot collimator above the detector. Overall measurement time was between 138 120 and 150 seconds and spectra up to 30 keV were quantified by standardless 139 analysis in 'plastics' mode. Where possible, measurements were repeated after 140 repositioning the fragment with respect to the collimator and after the inversion of the 141 fragment to expose the inner face to the detector (the total number of analyses 142 undertaken depended on the size and apparent heterogeneity of the sample). 143

144 Metal concentrations were reported in parts per million ($\mu g g^{-1}$) with an error of 2σ 145 (95% confidence). Instrumental detection limits, supplied by the manufacturer and for

- 146 a SiO₂ matrix analysed using the optimum ('mining') mode and for a period of 60
- seconds, were 12, 4 and 6 μ g g⁻¹ for Cu, Pb and Zn, respectively. Triplicate

148 measurements of a polyethylene reference material (Niton PN 180-554) containing

- 149 1002 μ g g⁻¹ of Pb returned a mean (± one sd) concentration of 922 (± 3) μ g g⁻¹ (Note
- 150 that the reference plastic had not been amended with Cu and Zn.)
- 151
- 152 2.3. Paint fragment and sediment digestion

153 For comparative purposes, the total concentrations of metals in selected paint

154 fragments (n = 27) were also measured by inductively coupled plasma-mass

155 spectrometry (ICP-MS) after acid digestion. Thus, whole fragments or pieces thereof

156 weighing up to 0.1 g were accurately weighed into individual 25 ml Pyrex beakers to

- 157 which 5 ml of aqua regia (3:1 HCl:HNO₃; both Fisher Scientific TraceMetal grade)
- 158 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
- 160 individual 100 ml Pyrex volumetric flasks and diluted to mark with Millipore Milli-Q

161 water (> 18 M Ω cm).

162

163 One g aliquots of freeze-dried sediment samples and triplicate 1 g aliquots of a

164 reference material certified for metal concentrations available to aqua regia (Harbour

165 Sediment, LGC6156) were accurately weighed into Pyrex beakers to which 8 ml of

- 166 aqua regia were added. The contents were digested as above before being transferred
- 167 to individual 50 ml volumetric flasks and diluted with Milli-Q water. Procedural
- 168 controls were performed in triplicate likewise but in the absence of paint fragments or

169 sediment.

171 *2.4. ICP analysis*

Digests and, as necessary, dilutions thereof, were analysed for ⁶⁵Cu, ²⁰⁸Pb and ⁶⁶Zn by 172 inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-Series 173 174 ICP mass spectrometer with collision cell (ThermoElemental, Winsford, UK). 175 Samples were introduced via a concentric glass nebuliser coupled with a conical spray 176 chamber and with acquisition parameters and gas flow rates described elsewhere 177 (Turner et al., 2010). External calibration was achieved using 5 matrix-matched, multi-element standards and three blanks, and 50 μ g L⁻¹ of both ¹¹⁵In and ¹⁹³Ir were 178 179 added to all standards, blanks and samples to compensate for instrumental drift and 180 variations in plasma conditions. Metal concentrations in the digests were corrected for 181 any contamination encountered in the controls and then converted to a dry wt/wt 182 basis. Measured concentrations of Cu, Pb and Zn in the reference sediment were 2655 \pm 9.8, 1574 \pm 80 and 3934 \pm 230 µg g⁻¹, respectively, compared with certified 183 concentrations of 2400 ± 1.2 , 1685 ± 1.0 and $3530 \pm 1.2 \ \mu g \ g^{-1}$, respectively. 184 Aluminium, as a proxy for sediment grain size, was analysed by ICP-optical emission 185 spectrometry inductively using a Varian 725-ES operated under conditions outlined in 186 187 Jessop and Turner (2011).

188

189

190 **3. Results**

- 191 *3.1. Metals in paint fragments*
- 192 Results of the XRF analyses of paint fragments (n = 155) from the 18 abandoned
- 193 boats are summarised in Table 2. Here, the median, minimum and maximum
- 194 concentrations of surficial Cu, Pb and Zn are reported for the pooled results arising
- 195 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.

202

203 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

205 highest concentrations of Ni and Sn were always encountered on lower hull paints,

206 while the highest Cr concentrations were found on paints from various interior or

207 exterior components.

208

209 In Figure 3, surficial concentrations of Cu, Pb and Zn determined by multiple XRF 210 analyses of each paint fragment are compared with total metal concentrations in each 211 fragment as ascertained by ICP-MS analysis following acid digestion (or the method 212 employed to determine metals in sediment). In each case, a significant correlation was 213 observed and data were dispersed roughly equally either side of unit slope. This 214 suggests that both analytical techniques deliver a similar response to Cu, Pb and Zn in 215 the paint matrix, or, strictly, that the total metal concentration for a fragment is 216 comparable with an average concentration derived from multiple analyses of the paint 217 surface. Clearly, and at least with respect to paint fragments, XRF has the advantage 218 in being able to map the spatial distribution of metals at the sample surface. 219

220 3.2. Metals in sediment

221 The concentrations of Cu, Pb and Zn in the sediment samples are summarised in 222 Table 3. Here, the mean (and standard deviation) of concentrations determined in 223 three samples collected in the vicinity of each boat (or pair of boats) are shown. Also 224 given, in italics and coded 0, are mean concentrations of metals at the control sites for 225 each environment under study. With the exception of Cu and Zn in two cases each, 226 mean concentrations in the sediment samples in the vicinity of the abandoned boats 227 exceeded mean concentrations of the corresponding controls. In most cases, the 228 variability in metal concentrations was also greater in the vicinity of boats than in the 229 controls. For example, the relative standard deviation in the controls was always less 230 than 20% for Cu and Pb and less than 10% for Zn compared with respective relative 231 standard deviations of up to 70%, 140% and 80% around the abandoned vessels. 232 233 According a series of two-sample *t*-tests, mean concentrations of Pb were always 234 significantly greater (p < 0.05) in the vicinity of boats than the corresponding control 235 concentrations. For Cu, significant enrichment relative to the controls occurred in the 236 samples from Pin Mill and Heybridge Basin and in three samples from Tollesbury 237 Fleet; no significant enrichment was observed at Heybridge Creek, however. For Zn, significant enrichment occurred at Heybridge Basin and Tollesbury Fleet and in two 238 239 and three samples from Pin Mill and Heybridge Creek, respectively. 240

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:

244

$$245 \qquad \text{EF} = \frac{[\text{Me}]_{s}/[\text{Al}]_{s}}{[\text{Me}]_{c}/[\text{Al}]_{c}}$$

| 247 | where EF is a dimensionless enrichment factor and subscripts s and c denote the |
|-----|--|
| 248 | sample and control, respectively. The distribution of EF among the sediment samples, |
| 249 | shown in Figure 4, was largely consistent with the distribution of absolute |
| 250 | concentrations since the Al content of the samples from the vicinity of the boats was |
| 251 | similar to the Al content of the corresponding controls. For Cu, the maximum EF was |
| 252 | about 110 in a sample from Tollesbury Fleet (TL3), and the overall median value was |
| 253 | about 1.3. For Pb and Zn, respective values for maximum EF and median were about |
| 254 | 440 and 1.9 and 20 and 1.3 respectively, with the greatest enrichment observed at the |
| 255 | same Tollesbury site. |
| 256 | |
| 257 | |
| 258 | 4. Discussion |
| 259 | The present study has revealed an abundance of peeling paint on a variety of |
| 260 | abandoned boats, and in various stages of dereliction, along the foreshores of two |
| 261 | estuaries of eastern England. While the service histories and ownership of many of the |
| 262 | boats can be ascertained from the relevant literature, the nature, origin and age of the |
| 263 | paints employed are unknown. For example, in some cases remnants of original |
| 264 | formulations may remain on exterior or internal surfaces, while in other cases, and in |
| 265 | particular where boats have changed ownership and/or function, more recent paints |
| 266 | are likely to be prevalent. Regardless of the precise history of paint application, many |
| 267 | fragments analysed by XRF contain concentrations of metals that are sufficiently high |
| 268 | to be of concern in respect of both contamination of the local aquatic environment and |
| 269 | risk to human health. |
| 270 | |

271 The occurrence of Cu was largely in fragments collected from the lower hulls of 272 decaying vessels. Clearly, this reflects the use of the metal (e.g. as Cu₂O or CuCNS) 273 in antifouling formulations, with or without other organic or organometallic biocides. 274 Concentrations of Cu in the present study are, however, considerably lower than those 275 reported for antifouling paints themselves or for paint particles derived from recently 276 renovated vessels. For example, Paradas and Filho (2007) report a Cu concentration 277 of about 32% for a contemporary antifouling formulation while Bellinger and Benham 278 (1978) report concentrations of Cu up to about 68% for various antifouling paints 279 available in the 1970s. Adopting a more indirect approach, Singh and Turner (2009) 280 analysed a composite of paint fragments collected from a small boatyard in south west 281 England and found a mean Cu concentration of over 30%. Presumably, lower 282 concentrations observed in paint fragments from abandoned boats reflect the 283 continued, slow release of cuprous ions from the paint matrix during the boats 284 operational life and post abandonment from periods of tidal inundation or 285 precipitation (Jessop and Turner, 2011). On this basis, therefore, it would be 286 reasonable to expect an inverse relationship between the concentration of Cu and the 287 age of paint and its degree of exposure to sea water and rainfall. 288 289 The more widespread occurrence of Zn among our paint fragment samples reflects 290 both the use of the metal in antifouling formulations, as a component of certain co-

291 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

293 concentrations of Zn measured, and mainly on the hulls of abandoned boats, are

294 consistent with concentrations in contemporary and historical antifouling formulations

295 (around 15-20%; Bellinger and Benham (1978); Paradas and Filho (2007)),

suggesting that Zn-based compounds are more persistent than those involving Cu(I).

298 Despite health concerns about its use in paint, Pb was encountered in all paint 299 fragments sampled and at variable concentrations. This observation reflects the 300 variety of uses of the metal in historical paints, including those used on boats. For 301 example, Pb was used as a drying agent, as a pigment for colour or to enhance opacity 302 and as an anticorrosion agent (Booher, 1988). Lead was also used in organometallic 303 form in antifouling paints before the 1970s and was found to be particularly effective 304 in combatting tubeworm fouling (Dick and Nowacki, 1970). Unlike Cu, compounds 305 of Pb used in paints (other than those employed as biocides), including lead chromate 306 and lead carbonate, are rather insoluble. Thus, greater concentrations of Pb than Cu 307 (and, to a certain extent, Zn) in paint fragments from abandoned boats can be 308 attributed to both the historical, general use of Pb and its greater overall persistence. A 309 consequence of the latter is that, in contrast to Cu, the wt/wt concentration of Pb in 310 fragments from old boats may exceed concentrations in the original formulations 311 through the gradual dissolution of more soluble components from the paint matrix. 312

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,

320 renovation or disposal of abandoned boats. Strictly, material for disposal should be 321 regarded as hazardous waste, and the use of boat components for firewood or the 322 burning of abandoned boats in situ, practices which we have been made aware of by 323 members of the public, are clearly unsafe and irresponsible.

324

325 We have also observed swans pecking at loose paint on poorly maintained leisure

326 craft and note that the incidental ingestion of antifouling paint particles is believed to

327 be responsible for cases of Cu toxicosis and critically high hepatic Cu concentrations

328 (Molnar, 1983; Degernes, 2008). High concentrations of Pb in peeling paint therefore

329 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).

332

333 Clearly, both elevated and more variable metal concentrations in sediment in the 334 vicinity of abandoned boats compared with control sites reflect contamination arising 335 from paint fragments of various sizes. Contamination may be direct, in that discrete 336 paint fragments are heterogeneously dispersed among sediment grains, or indirect, 337 whereby metals ions dissolved from the paint matrix adsorb to neighbouring sediment 338 particles. That contamination is greatest for Pb reflects its abundance and persistence in boat paints coupled with a high affinity of aqueous Pb²⁺ for the surface of geosolids 339 340 (O'Reilly and Hochella, 2003; Hua et al., 2012). Presumably, therefore, variations in 341 the precise degree of sediment contamination result from differences in (i) the 342 concentrations and labilities of metals in paints from the various boats, (ii) the rates of 343 input of paint fragments through weathering, and (iii) local hydrodynamics and 344 sedimentation rates.

| 346 | Regarding marine sediment and according to the CCME (Canadian Council of |
|-----|---|
| 347 | Ministers of the Environment, 2012), quality guidelines for the protection of aquatic |
| 348 | life (as predicted effect concentrations; PELs) for Cu, Pb and Zn are 108, 112 and 271 |
| 349 | μ g g ⁻¹ , respectively. Thus, out of the 16 sites in which sediment was sampled near to |
| 350 | abandoned boats, mean concentrations of Cu and Zn exceed the respective quality |
| 351 | guidelines in one case each, while the mean concentration of Pb exceeds the |
| 352 | corresponding guideline in five cases (Table 3); based on individual sediment |
| 353 | samples, the number of exceedances for Cu, Pb and Zn are four, thirteen and six, |
| 354 | respectively. Although in most cases metal concentrations do not exceed quality |
| 355 | guidelines, it is important to appreciate that the forms and species of metals in boat |
| 356 | paints (e.g. organolead compounds, Cu(I) and Zn pyrithione) are likely to be more |
| 357 | 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.

369 To our knowledge, this is the first study to quantify contamination of the coastal 370 environment from flaking paint on abandoned boats and the first to highlight the 371 hazards associated with old leaded paints on these vessels. Clearly, contamination 372 from peeling paint is likely to be a general problem where boat abandonment occurs, 373 although the precise metals that pose the greatest threat may vary depending on the 374 age and nature of the boats. For example, it is anticipated that old antifouling paints 375 containing biocidal (and organo-) forms of As, Hg and Sn may well present an 376 environmental hazard on boats that have been abandoned for several decades. 377 Although more work into the scale and nature of the problem is called for, including 378 an assessment of the bioavailabilities and toxicities of paint components to a variety 379 of organisms, immediate recommendations are clear legislation for the prevention of 380 boat abandonment and facilities specifically designed for the safe disposal of end-of-381 life vessels.

382

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489 Figure 1: Map under construction.

491 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.





497 Tollesbury Fleet, Δ) ascertained by multiple, surficial XRF analyses and by whole fragment digestion-ICP analysis.





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

512 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

| 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 |

513 were of wooden construction except where otherwise mentioned.

515 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

516 to the number of analyses in which each metal was detected.

517

| | 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 |

| 533 | boat | Cu | | Pb | | Zn | | |
|-----|---------|---------------|------|--------|-------------|--------------|------|--|
| 534 | PM0 | 8.9 ± | 0.4 | 9.7 ± | 1.0 | 26.7 ± | 0.7 | |
| 535 | PM1 | 17.8 ± | 2.4 | 63.6 ± | 46.7 | 50.6 ± | 6.2 | |
| 536 | PM2/PM3 | 36.4 ± | 0.8 | 83.5 ± | 18.1 5 5 | 107 ± | 39.6 | |
| 000 | PIM4 | 14.1 ± | 4.4 | 18.2 ± | 5.5 | 29.4 ± | 7.1 | |
| | PIM5 | $13.1 \pm$ | 1.5 | 12.8 ± | 0.7 | 25.0 ± | 7.4 | |
| | PIM6 | 26.7 ± | 20.0 | 13.9 ± | 1.3 | 28.3 ± | 6.0 | |
| | PM7 | 13.1 ± | 1.5 | 12.8 ± | 0.7 | $25.0 \pm$ | 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 <i>±</i> | 2.1 | 54.8 ± | 2.5 | 120 <i>±</i> | 4.3 | |
| | HC6 | 40.1 ± | 2.5 | 129 ± | 20.9 | 224 ± | 10.4 | |
| | TLO | 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 | |
| | | | | | | | | |

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.