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Metal contamination of intertidal sediment and macroalgae in an area impacted by paint from abandoned boats

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ABSTRACT

Metals commonly employed in boat paint (Ba, Cr, Cu, Pb, Sn and Zn) have been determined in 63- μm -fractionated intertidal sediments and in *Ulva lactuca* and *Fucus vesiculosus* sampled in the vicinity of abandoned vessels. Metal concentrations in sediment were elevated but highly variable, both between sites and amongst replicates from the same site (e.g., mean Cu ~ 100 to 1200 mg kg^{-1} ; mean Pb ~ 130 to 6900 mg kg^{-1}) due to heterogeneous contamination by metal-rich boat paint particles. Concentrations of all metals except Zn were higher in *U. lactuca* than *F. vesiculosus* but in both species metal levels were also elevated and variable. These observations were attributed to contamination by sediment particles and physical and chemical interactions between fine, suspended or deposited paint particles and the algal surface. The latter interactions act as a means by which boat paint metals may enter the foodchain.

1. Introduction

Contamination of the coastal zone by metals has been recognised and studied over many decades. Amongst the most important metal sources in this environment are mining waste, treated and untreated municipal and industrial effluents, urban and agricultural runoff, and discharges from boating and shipping activities (Tanner et al., 2000; Pan and Wang, 2012; Naser, 2013). Regarding the latter, much of the focus has been on metals in antifouling applications, like Cu, Sn and Zn, and their direct release from vessel hulls and other structures into water (Valkirs et al., 2003; Michaud and Pelletier, 2006). However, more recent studies have highlighted that antifouling paint particles derived from unregulated boating and shipping maintenance and repair activities represent a significant, local source of metals (Singh and Turner, 2009; Soroldoni et al., 2018).

In addition to antifouling particles, Rees et al. (2014) identified abandoned boats as an important source of a wider array of paint particles, including old lead-based formulations, derived from multiple parts of the vessel and whose immediate impact is contamination of local coastal sediments. The extent and evolution of boat abandonment along the coast of southern England was recently investigated remotely by Payne and Turner (2022) from Google Earth imagery. Significantly, it was found that the majority of the several hundred boats identified had been abandoned on the mudflats of protected areas, and often in concealed and sheltered locations, and that the scale of the problem had

been steadily increasing over time.

In a field study conducted by Muller-Karanassos et al. (2019) in south west England, it was shown that Cu can accumulate in worms that are exposed to antifouling paint particles in their sandy or silty habitats or through inadvertent ingestion, thereby affording a means by which biocidal metals may enter the foodchain. While most of the study sites identified by these authors were associated with contemporary boating activities, a sheltered embayment (Hooe Lake, Plymouth) was distinctly different in that its shoreline housed several abandoned yachts and trawlers. In the present study, therefore, this site was selected to investigate a broader array of metals associated with paints more generally in both sediments and macroalgae. The latter, primary producers are effective accumulators of metals in coastal waters and serve as useful time-integrated biomonitors of metal bioavailability (Rainbow, 1995).

2. Methods

2.1. Study site

Hooe Lake is a tidal embayment that is connected to the lower Plym Estuary, a small, macrotidal system that is urbanised throughout much of its length (Fig. 1). The lake has an area of 14 ha and is designated as a County Wildlife Site because of the habitats provided by the mudflats. Despite this status, the lake has been a recipient of abandoned boats

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along its southern shoreline that range in length from about 5 to 25 m. The precise study area, noted in Fig. 1c and illustrated in Fig. 2a, contains four timber boats (three trawlers and a yacht) that were abandoned between 1996 and 2007.

2.2. Sampling and sample processing

Sampling took place during the spring of 2016. Samples of paint ($n = 22$) ranging from about 1 to 3 cm in size and <1 mm thick were taken from accessible parts of the four boats where layers were visibly peeling, including the hull, cabin, winch, railings and porthole frames, using a pair of stainless steel tweezers. Samples were transported to the laboratory in individual polyethylene specimen bags and stored in the dark until required for analysis.

Samples of surface (<5 mm) intertidal sediment of about 50 g were taken from fourteen sites within the area shown in Fig. 2a using a plastic shovel and transported in individual polyethylene specimen bags. In the laboratory, large stones and fragments of shell and algae were removed using a pair of polyethylene tweezers before the remaining contents were wet-sieved through a $63 \mu\text{m}$ nylon mesh with the aid of a few mL of Milli-Q water (MQW). The sieved fractions were transferred to a series of polypropylene centrifuge tubes before being centrifuged for 5 min at 3000 rpm using a Centaur 2 centrifuge. Supernatants were discarded and sediments were frozen at -18°C and then freeze-dried in an Edwards Modulyo D freeze-dryer for 48 h. Sediment fractions remaining on the mesh were carefully washed into individual specimen bags with the aid of MQW before being frozen and freeze-dried likewise. All sediment samples were stored under desiccation until required for digestion.

The two most common species of macroalga evident in the study area, the chlorophyte *Ulva lactuca* (sea lettuce) and phaeophyte *Fucus vesiculosus* (bladderwrack), were collected by hand into individual polyethylene specimen bags. In triplicate, growing apical tips of *F. vesiculosus* were sampled at the 14 locations where sediment was taken while triplicate whole individuals of the less abundant *U. lactuca* were sampled from nine of these locations. In the laboratory, algal samples were washed under MQW water to remove epibionts, surficial salts and associated sediments and blotted dry on tissue paper before being frozen, freeze-dried and stored as above.

2.3. Paint particle analysis

Paint particles were analysed for various metals (but with the focus

on metals commonly employed in pigmented or antifouling compounds: Ba, Cr, Cu, Pb, Sn and Zn) by energy dispersive X-ray fluorescence (XRF) spectrometry using a Thermo Scientific Niton hand-held XRF analyser (model XL3t 950 He GOLDD+) housed in a laboratory stand (Turner et al., 2016). Samples were placed centrally over the detector window with the outer surface facedown and were counted for 60 s each in a plastics mode with thickness correction (with the precise thickness having been measured through the central region using digital callipers). Instrument performance was checked by regular analyses of polyethylene reference discs impregnated with Ba, Cr and Pb and detection limits were derived from three counting errors for each sample and element and ranged from about 10 mg kg^{-1} for Pb and Zn to 100 mg kg^{-1} for Ba.

2.4. Sediment and macroalgae digestion and analysis

All glassware used for sample digestions was soaked for >24 h in 10 % HCl and rinsed thoroughly in distilled water before being used. Acids for digestion and standard preparation were purchased from Fisher Scientific and were TraceMetal grade. Sediment and macroalgae digestions were performed in aqua regia (a 3:1 mix of concentrated HCl to concentrated HNO_3) and concentrated nitric acid, respectively (Varma et al., 2011).

In triplicate, 200 mg of both fine ($<63 \mu\text{m}$) and coarse ($>63 \mu\text{m}$) sediment fractions were weighed in to a series of 50 mL Pyrex beakers. Aliquots of 5 mL of aqua regia were added to each beaker and the contents covered by watch glasses. After 15 min of cold digestion, beakers were heated to 90°C on a hot plate for 45 min. Cooled digests and MQW rinsings were vacuum-filtered through Whatman 451 filter papers in a Buchner filtration system before being transferred to 25 mL volumetric flasks and diluted to mark with MQW. For quality assurance purposes, an in-house reference sediment (designed for aqua regia digestion) and controls (in the absence of sediment) were processed likewise in triplicate.

Triplicate digestion of 200 mg portions of macroalgae involved the same protocol but 7 mL of concentrated HNO_3 in place of aqua regia and certified reference sea lettuce (BCR 279) and bladderwrack (ERM CD200) rather than the reference sediment.

Algal digests were analysed for Ba, Cr, Cu, Pb, Sn and Zn by collision cell-inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo X-series II (Thermo Elemental, Winsford UK) with a concentric glass nebuliser and conical spray chamber under operating conditions reported by Rees et al. (2014). The instrument was calibrated externally

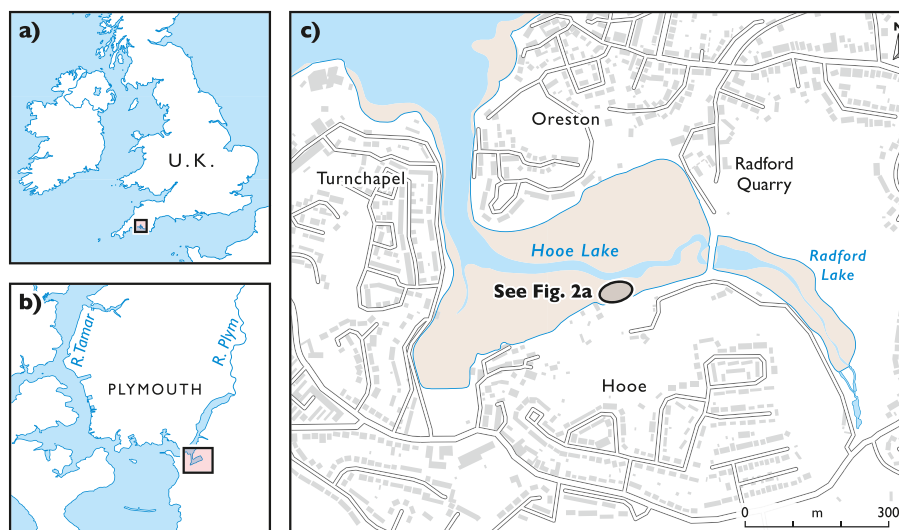


Fig. 1. Location of Hooe Lake in relation to Plymouth and the Plym Estuary, with the precise study area annotated.

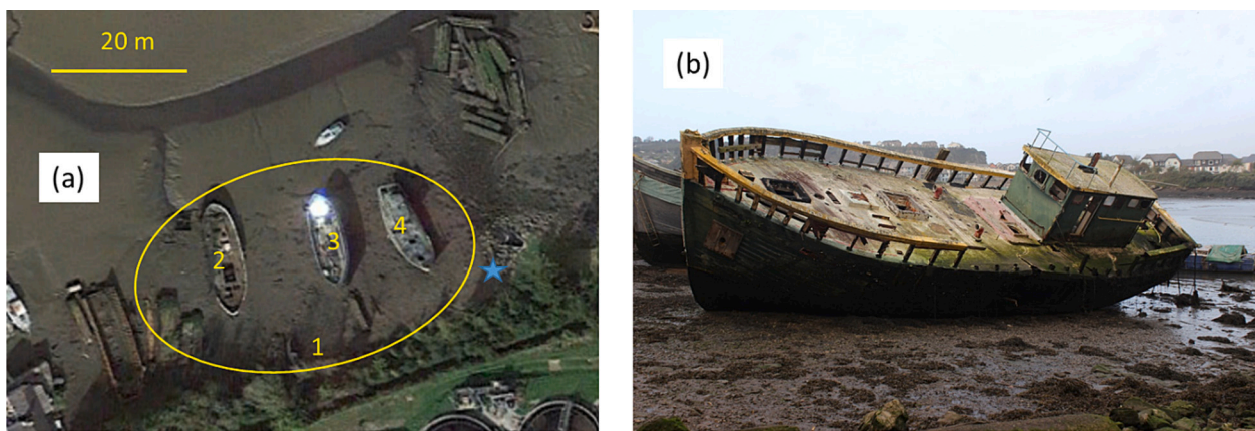


Fig. 2. (a) Google Earth Pro image (dated 2017 and at low tide) of the study area in Hooe Lake (circled in yellow; 50.356, -4.108) and showing the four abandoned boats (numbered), and (b) a photograph of the site taken from the location of the blue star in panel a and illustrating the abundance of *F. vesiculosus* on the mudflats. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Certified or indicative concentrations in the reference materials compared with values determined in the present study. Errors represent 95 % confidence intervals (certified) or one standard deviation (measured).

	BCR 279 (mg kg ⁻¹)		ERM CD200 (mg kg ⁻¹)		In-house sediment (mg kg ⁻¹)	
	Certified	Measured (n = 3)	Certified	Measured (n = 3)	Indicative	Measured (n = 3)
Cu	13.14 ± 0.37	14.68 ± 1.01	1.71 ± 0.18	2.54 ± 0.32	200	200 ± 8.3
Cr	10.7 ^a	5.29 ± 0.42				
Pb	13.48 ± 0.36	13.93 ± 4.39	0.51 ± 0.06	0.85 ± 0.37	117	105 ± 12.3
Zn	51.3 ± 1.2	45.6 ± 4.4	25.3 ± 1.7	21.8 ± 0.9	182	186 ± 8.8

^a Indicative concentration.

using three blanks and five mixed standards in 2 % HNO₃ (within the range 10 to 1000 µg L⁻¹ and depending on the metal) in 2 % HNO₃, and internally by the addition of 50 µg L⁻¹ of ¹¹⁵In and ¹⁹³Ir to all standards, samples and blanks. Sediment digests were analysed for the same metals and both sediment and algal digests were analysed for Al (an indicator of grain size and potential sediment contamination of macroalgae) by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian 725-ES (Mulgrave, Australia) with a Sturman-Masters spray chamber and V-groove nebuliser. The instrument was operated under conditions given in Turner et al. (2016) and was calibrated externally using three blanks and five mixed standards (within the range 1 to 100 mg L⁻¹ and depending on the metal) in 2 % HNO₃.

Measured, dry weight concentrations of Cu, Cr, Pb and Zn in the reference materials are compared with certified or indicative values in Table 1. Agreement between measured and certified values is within 15 % except for Cu and Pb in ERM CD200. Here, low certified concentrations (and considerably lower than corresponding concentrations in the samples) were overestimated and returned with relatively high variation. The Cr concentration measured in BCR 279 is about 50 % lower than its indicative value meaning that some Cr data for macroalgae may be underestimated.

Table 2

Frequency of metal detection and distribution of metal concentrations (in mg kg⁻¹) in paint samples from four abandoned boats in Hooe Lake.

	No. detected	<10 ²	10 ² -10 ³	10 ³ -10 ⁴	10 ⁴ -10 ⁵	>10 ⁵	Min.	Max.	Median
Ba	12		1	5	4	5	2450	389,000	60,500
Cr	6	2	3	1			27.5	2620	544
Cu	18	4	5	4	2	3	1750	184,000	21,600
Pb	14	4	3	5	2		10.7	27,600	997
Sn	6		3	2	1		344	85,700	974
Zn	20	4	7	4	4	1	11.8	276,000	663

3. Results

3.1. Metallic composition of paint samples

Concentrations of the principal metals in the paints sampled from the four abandoned boats are summarised in Table 2. For each metal, concentrations spanned at least two orders of magnitude, with maximum concentrations of Ba, Cu and Zn exceeding 10 % by weight. Amongst the samples, the six different metals were heterogeneously distributed and contributed between <0.1 to about 50 % of the total paint mass. Most samples were layered and this heterogeneity presumably reflected the different histories and functions of these layers, including antifouling coatings and primers of different ages. Significantly, many metal-based compounds in older formulations (e.g. organotin and lead-based pigments) have since been restricted or banned.

3.2. Metal concentrations in sediments

The concentrations of Al in the fractionated Hooe Lake sediments are shown in Table 3. In the fine fraction, concentrations are similar both between sites, and averaging about 13,000 mg kg⁻¹, and within each

Table 3

Mean (\pm one standard deviation; $n = 3$) of Al concentrations (in mg kg^{-1}) in fine ($<63 \mu\text{m}$) and coarse ($>63 \mu\text{m}$) Hooe Lake sediments.

	Al	
	Fine	Coarse
S1	12,820 \pm 181	13,520 \pm 810
S2	12,780 \pm 254	13,880 \pm 99.8
S3	13,240 \pm 994	14,130 \pm 135
S4	12,780 \pm 150	6280 \pm 446
S5	13,350 \pm 797	14,580 \pm 353
S6	13,150 \pm 647	8430 \pm 183
S7	11,010 \pm 3518	14,290 \pm 542
S8	12,810 \pm 349	7720 \pm 105
S9	13,720 \pm 252	13,260 \pm 850
S10	13,170 \pm 35.8	14,390 \pm 98.6
S11	12,980 \pm 245	14,220 \pm 229
S12	13,090 \pm 216	14,080 \pm 281
S13	12,850 \pm 146	7493 \pm 444
S14	12,620 \pm 74.3	5717 \pm 140
Median	12,915	13,700
Mean	12,880	11,570
SD	611	3506

site, with relative standard deviations amongst replicates averaging 4.6 %. In the coarse fraction, concentrations are more variable between sites, ranging from $<6000 \text{ mg kg}^{-1}$ to about $14,500 \text{ mg kg}^{-1}$, but less variable amongst replicates (average relative standard deviation of 3.1 %). These observations suggest that while fine sediments have a consistent granulometry and coarse sediments have a more diverse granulometry, there is relatively little granulometric variation amongst replicated samples.

The concentrations of metals commonly employed in compounds added to paints and identified in Table 2 are shown for Hooe Lake sediments in Table 4. Concentrations of all metals in the fine and coarse fractions are more variable than Al, both between sites and within replicates. For example, average relative standard deviations for fine sediments range from about 13 % for Zn to >30 % for Ba, Cu and Sn, and average deviations for coarse sediments range from about 35 % for Cr and Zn to >60 % for Pb and Sn. Within the coarse fraction of replicate samples, the relative standard deviation sometimes exceeded 100 % for Ba, Cu, Pb and Sn.

According to a series of Wilcoxon sign tests performed in Minitab v19, the only significant differences ($p < 0.05$) in median concentrations between the fine and coarse fractions are for Cr and Pb (and both greater in the coarse fractions). Results of Spearman's rank correlation analysis revealed the strongest associations ($r_s > 0.7$) between Cu in the fine and coarse fractions, Ba—Cr in the fine fraction and Pb—Zn in the coarse

Table 4

Mean (\pm one standard deviation; $n = 3$) of metal concentrations (in mg kg^{-1}) in fine ($<63 \mu\text{m}$) and coarse ($>63 \mu\text{m}$) Hooe Lake sediments.

	Ba		Cr		Cu		Pb		Sn		Zn	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
S1	156 \pm 122	104 \pm 41.6	37.3 \pm 2.5	16.6 \pm 8.9	271 \pm 56.5	168 \pm 46.3	221 \pm 74.2	796 \pm 705	23.2 \pm 0.19	425 \pm 722	294 \pm 45.4	432 \pm 338
S2	81.1 \pm 94.6	81.3 \pm 20.9	25.4 \pm 22.1	28.7 \pm 1.3	268 \pm 164	207 \pm 16.6	147 \pm 156	145 \pm 5.1	17.3 \pm 17.4	15.6 \pm 2.5	329 \pm 3.3	275 \pm 4.7
S3	98.8 \pm 40.7	124 \pm 44.4	28.9 \pm 10.8	38.5 \pm 17.4	254 \pm 101	535 \pm 518	182 \pm 57.0	680 \pm 558	12.1 \pm 5.0	112 \pm 146	264 \pm 35.3	314 \pm 83.9
S4	154 \pm 67.1	143 \pm 24.3	38.8 \pm 0.1	17.6 \pm 7.7	385 \pm 23.6	255 \pm 61.7	490 \pm 15.0	466 \pm 154	12.1 \pm 0.3	6.5 \pm 5.2	395 \pm 5.5	266 \pm 51.1
S5	153 \pm 54.4	122 \pm 81.7	34.5 \pm 2.2	27.9 \pm 9.0	901 \pm 757	1202 \pm 1489	319 \pm 48.8	700 \pm 645	17.5 \pm 3.8	4.8 \pm 1.5	327 \pm 34.2	403 \pm 130
S6	122 \pm 1.8	138 \pm 39.7	35.4 \pm 1.6	17.2 \pm 10.4	500 \pm 15.7	685 \pm 301	424 \pm 4.4	489 \pm 62.2	99.8 \pm 115	32.6 \pm 29.6	329 \pm 12.1	330 \pm 59.8
S7	50.9 \pm 14.5	87.3 \pm 39.1	19.7 \pm 18.2	30.6 \pm 12.0	290 \pm 89.4	655 \pm 496	176 \pm 65.2	672 \pm 769	75.1 \pm 78.9	8.2 \pm 2.7	249 \pm 43.1	354 \pm 153
S8	131 \pm 27.9	71.8 \pm 39.6	27.5 \pm 10.0	16.0 \pm 7.1	163 \pm 55.6	95.5 \pm 16.1	209 \pm 73.9	139 \pm 70.4	12.4 \pm 0.2	10.5 \pm 4.6	223 \pm 77.2	175 \pm 66.8
S9	152 \pm 16.2	90.0 \pm 20.9	33.5 \pm 4.9	40.0 \pm 19.6	255 \pm 33.7	259 \pm 71.0	386 \pm 64.5	6903 \pm 10,528	13.8 \pm 1.2	98.2 \pm 80.8	317 \pm 39.9	428 \pm 123
S10	107 \pm 15.0	112 \pm 65.8	27.8 \pm 2.8	12.7 \pm 4.4	279 \pm 25.5	417 \pm 471	403 \pm 55.1	572 \pm 355	25.7 \pm 24.8	61.8 \pm 43.8	237 \pm 18.7	244 \pm 82.1
S11	73.3 \pm 3.8	53.9 \pm 17.3	27.1 \pm 0.6	24.3 \pm 0.1	696 \pm 589	431 \pm 122	162 \pm 11.3	376 \pm 114	13.3 \pm 1.2	17.3 \pm 11.5	255 \pm 44.0	222 \pm 88.6
S12	77.4 \pm 8.8	45.9 \pm 24.5	28.6 \pm 2.9	14.8 \pm 7.0	773 \pm 700	1233 \pm 442	155 \pm 17.3	133 \pm 46.1	14.3 \pm 0.2	37.5 \pm 30.6	270 \pm 68.9	297 \pm 119
S13	110 \pm 8.0	599 \pm 824	30.6 \pm 2.0	19.1 \pm 3.3	247 \pm 16.0	223 \pm 126	175 \pm 11.5	692 \pm 790	15.8 \pm 0.9	5.8 \pm 1.3	286 \pm 16.2	329 \pm 132
S14	376 \pm 65.8	445 \pm 308	28.7 \pm 4.9	24.2 \pm 2.2	253 \pm 30.9	244 \pm 66.3	298 \pm 39.8	1537 \pm 874	20.7 \pm 0.4	40.8 \pm 25.4	397 \pm 53.2	467 \pm 110
Median	116	108	28.8	21.7	275	338	215	622	16.6	25.0	290	322
Mean	132	158	30.3	23.4	395	472	268	1021	26.7	62.6	298	324
SD	78.1	160	5.1	8.7	231	363	117	1730	26.5	110	54.1	85.8

fraction.

3.3. Metal concentrations in macroalgae

The concentrations of metals, including Al, in *U. lactuca* and *F. vesiculosus* are shown in Tables 5 and 6, respectively. Regarding *U. lactuca*, metal concentrations are variable both between locations and amongst individuals sampled from the same sites, with a range of mean concentrations exceeding an order of magnitude for Ba and Pb. In *F. vesiculosus*, metal concentrations are less variable between sites and amongst apical tips from the same individuals. A series of Mann-Whitney *U* tests performed in Minitab v19 revealed that median concentrations of Cr, Cu, Pb, Sn (and Al) are significantly higher ($p < 0.05$) in *U. lactuca* than *F. vesiculosus* whereas the median concentrations of Zn are significantly greater in the latter.

Spearman's rank correlation analysis revealed a number of significant ($p < 0.05$) relationships between the concentrations of the same metal or different metals in *U. lactuca* or *F. vesiculosus* and in the fine or coarse fraction of sediment, between different metals in either *U. lactuca* or *F. vesiculosus*, and between the same metal or different metals in *U. lactuca* and *F. vesiculosus*. Amongst the strongest positive associations ($r_s > 0.7$) were: Ba—Al, Cu—Cu and Cr—Sn in coarse sediment-*U. lactuca*; Ba—Cu, Ba—Pb, Cr—Cu, Cr—Pb, Cr—Zn, Cu—Pb, Cu—Zn and Pb—Zn in *U. lactuca*; and Pb—Ba, Zn—Pb, Zn—Zn and Zn—Al in *U. lactuca-F. vesiculosus*.

4. Discussion

Metal concentrations in sediments of Hooe Lake in the vicinity of abandoned boats are heterogeneous, in both the fine and coarse fractions, with no relationships evident with granulometry. Such heterogeneity may be attributed to the dispersion of metal-rich boat paint particles of diverse compositions and origins, and as exemplified in Table 1, in the intertidal zone. This effect has been observed in other marine systems impacted by paint from abandoned vessels or boats undergoing maintenance (Singh and Turner, 2009; Takahashi et al., 2012; Rees et al., 2014; Wu et al., 2016; Soroldoni et al., 2018) and was directly visible here from colourful paint fragments retained by the 63 μm mesh after sediment fractionation. Metal concentrations in sediment subject to point source particulate contaminants are also likely to vary temporally. Thus, deposited paint particles are eroded into smaller fragments that become buried or washed away, but are replenished by particles derived from both existing and newly exposed paint layers on boat hulls and other painted surfaces.

Overall, metal concentrations are highly elevated compared with a

Table 5

Mean (\pm one standard deviation; $n = 3$) of metal concentrations (in mg kg^{-1} dry weight) in *U. lactuca* from Hooe Lake.

	Ba	Cr	Cu	Pb	Sn	Zn	Al
S1	5.8 \pm 2.7	3.8 \pm 0.9	73.7 \pm 16.1	43.1 \pm 15.4	7.5 \pm 2.1	46.7 \pm 13.6	1742 \pm 952
S4	11.4 \pm 4.7	7.5 \pm 2.4	142 \pm 15.5	80.0 \pm 24.1	23.3 \pm 5.5	118 \pm 13.0	1407 \pm 824
S5	32.5 \pm 22.1	9.6 \pm 4.5	160 \pm 25.6	115 \pm 54.0	25.7 \pm 26.7	105 \pm 16.1	1173 \pm 275
S8	46.4 \pm 21.7	14.6 \pm 4.9	163 \pm 29.1	231 \pm 158	15.8 \pm 4.7	162 \pm 27.0	2522 \pm 713
S9	31.1 \pm 13.5	10.7 \pm 1.3	225 \pm 75.1	347 \pm 301	20.7 \pm 10.1	215 \pm 137	3154 \pm 186
S10	15.4 \pm 2.2	8.0 \pm 3.9	91.8 \pm 24.3	80.2 \pm 15.5	10.4 \pm 1.9	88.8 \pm 40.9	2304 \pm 791
S11	23.3 \pm 10.7	21.1 \pm 16.6	147 \pm 16.0	632 \pm 455	18.3 \pm 4.9	264 \pm 103	2374 \pm 509
S13	15.5 \pm 5.8	6.7 \pm 1.7	102 \pm 32.0	97.8 \pm 33.2	13.1 \pm 2.8	127 \pm 48.7	1255 \pm 629
S14	82.9 \pm 37.4	9.2 \pm 0.9	166 \pm 82.2	158 \pm 91.8	16.5 \pm 7.0	136 \pm 8.0	1946 \pm 109
Median	23.3	9.2	147	115	16.5	127	1946
Mean	29.4	10.1	141	198	16.8	140	1986
SD	23.6	5.1	46.1	188	5.9	65.9	661

Table 6

Mean (\pm one standard deviation; $n = 3$) of metal concentrations (in mg kg^{-1} dry weight) in *F. vesiculosus* from Hooe Lake.

	Ba	Cr	Cu	Pb	Sn	Zn	Al
S1	11.6 \pm 0.3	3.1 \pm 0.0	47.7 \pm 2.0	20.9 \pm 0.7	16.6 \pm 0.5	122 \pm 4.6	380 \pm 85.5
S2	17.0 \pm 5.7	2.8 \pm 0.4	56.4 \pm 25.3	19.6 \pm 4.5	8.6 \pm 3.2	156 \pm 64.3	353 \pm 72.7
S3	18.2 \pm 1.4	2.7 \pm 0.5	99.4 \pm 13.3	25.1 \pm 4.7	14.0 \pm 9.6	200 \pm 6.1	336 \pm 46.5
S4	13.2 \pm 2.6	2.0 \pm 0.7	54.9 \pm 9.9	17.5 \pm 4.1	8.1 \pm 4.8	196 \pm 59.1	433 \pm 68.1
S5	14.0 \pm 3.6	1.4 \pm 0.7	62.0 \pm 12.5	19.6 \pm 5.8	10.9 \pm 4.0	168 \pm 33.6	419 \pm 46.4
S6	17.4 \pm 2.8	1.6 \pm 0.2	113 \pm 24.2	20.2 \pm 3.5	8.2 \pm 0.1	405 \pm 42.1	415 \pm 105
S7	20.4 \pm 4.8	1.8 \pm 0.5	89.3 \pm 24.4	18.4 \pm 7.7	5.2 \pm 2.3	288 \pm 54.9	377 \pm 68.4
S8	13.3 \pm 5.3	1.1 \pm 0.8	51.0 \pm 22.6	10.1 \pm 6.0	3.7 \pm 3.5	238 \pm 101	415 \pm 66.0
S9	17.6 \pm 1.9	1.9 \pm 0.5	64.8 \pm 9.5	25.8 \pm 5.7	4.8 \pm 1.0	307 \pm 44.3	456 \pm 41.1
S10	13.7 \pm 1.3	1.2 \pm 0.3	57.5 \pm 10.8	14.6 \pm 5.5	7.3 \pm 6.6	260 \pm 24.8	372 \pm 103
S11	22.1 \pm 1.3	3.0 \pm 0.4	91.5 \pm 14.8	23.8 \pm 3.0	7.2 \pm 3.4	387 \pm 79.0	380 \pm 115
S12	17.0 \pm 2.9	2.3 \pm 1.2	88.0 \pm 21.9	25.4 \pm 7.1	4.8 \pm 0.9	259 \pm 34.6	392 \pm 122
S13	18.3 \pm 4.7	1.5 \pm 0.6	45.3 \pm 17.7	13.2 \pm 2.4	3.1 \pm 1.9	232 \pm 94.3	389 \pm 75.6
S14	18.6 \pm 9.4	1.4 \pm 0.8	45.7 \pm 18.5	12.4 \pm 6.1	7.5 \pm 5.4	210 \pm 71.1	366 \pm 104
Median	17.6	1.63	64.8	18.4	5.2	260	389
Mean	16.6	2.0	69.0	19.1	7.9	245	392
SD	3.0	0.7	22.5	5.0	3.8	81.6	32.7

local baseline. Thus, Singh and Turner (2009) report the following mean, aqua regia-available metal concentrations for $<63 \mu\text{m}$ estuarine sediment from the upper Plym where boating activity is impeded by siltation: Cr = 18.0 mg kg^{-1} ; Cu = 98.5 mg kg^{-1} ; Pb = 85.9 mg kg^{-1} ; Sn = 8.2 mg kg^{-1} ; Zn = 129 mg kg^{-1} . Factoring in the granulometry of this baseline (Al = $18,600 \text{ mg g}^{-1}$) yields median enrichment factors (EFs) in Hooe Lake (Al-normalised metal concentrations in fine lake sediment to Al-normalised metal concentrations in upper estuarine sediment) in the order: Cu (EF = 4.0) > Pb (EF = 3.6) > Sn (EF = 2.9) > Zn (EF = 3.3) > Cr (EF = 2.3).

As a measure of the health status of Hooe Lake sediments, mean concentrations of metals in both fine and coarse sediments at each site (Table 4) can also be compared with surficial ($<5 \text{ cm}$) sediment quality guidelines for Cr, Cu, Pb and Zn in marine and estuarine sediment and available to aqua regia as published by the Canadian Council of Ministers of the Environment (1999). Thus, for Cr, interim sediment quality guideline (ISQG) and probable effect level (PEL) concentrations are 52.3 mg kg^{-1} and 160 mg kg^{-1} , respectively, with no exceedances in Hooe Lake sediment. Regarding Zn, the ISQG concentration of 124 mg kg^{-1} is exceeded in all lake sediment samples but the PEL of 271 mg kg^{-1} is only exceeded in six fine and four coarse sediments. For Cu, both ISQG and PEL concentrations of 18.7 mg kg^{-1} and 108 mg kg^{-1} , respectively, are exceeded in the present study for all fine sediments and all but one coarse sediment sample, while for Pb, both ISQG and PEL concentrations of 30.2 mg kg^{-1} and 112 mg kg^{-1} , respectively, are exceeded in all cases.

While these comparisons are useful in providing a general health assessment of Hooe Lake sediment, it should be borne in mind that the forms of Cr, Cu, Pb and Zn upon which quality guidelines are based may be different to those encountered in boat paint particles. For instance, Cr guidelines are centred around toxicological data for the less harmful trivalent form of the metal, whereas many paints contain chromate pigments in which Cr exists in the more toxic, hexavalent oxidation state (La Puma et al., 2001). Aquatic toxicological studies involving Pb and Zn usually refer to the bivalent ions, but in antifouling formulations more hydrophobic organometallic Pb and Zn pyrithione complexes have been employed (Dick and Nowacki, 1970; Turley et al., 2000). With respect to Cu, toxicological data are based on Cu^{2+} but in antifouling paints compounds employ the metal in its lower (I) oxidation state (Blossom et al., 2018) and whose ecotoxicology is unknown. Regarding Sn, Canadian quality guidelines are unavailable for sediment, and although a UK action level of 0.5 mg kg^{-1} for organotins is reported for the management of dredged sediment (Mason et al., 2021), the methods employed in the present study do not discriminate between inorganic and organic forms of the metal.

In most cases, concentrations of metals in *U. lactuca* and *F. vesiculosus* exceed the corresponding ranges of “typical” concentrations in macroalgae for the region, where reported by Rainbow (2020). As bio-monitors, macroalgae are net accumulators of metals over a period of time in which concentrations reflect average bioavailable concentrations (Rainbow, 1995; Villares et al., 2007). In theory, therefore, concentrations are less prone to spatial and temporal variations of metal concentrations than sediments that are directly contaminated by heterogeneous point sources, and correlations between metals in algae and sediments would not necessarily be expected. However, there is still considerable variation in metal concentrations in *U. lactuca* and *F. vesiculosus* sampled a few tens of metres apart in Hooe Lake, and in particular in *U. lactuca* where relative standard deviations ($n = 14$) exceeded 50 % for Ba, Cr and Pb.

Part of this variability could reflect contamination of algae by sediment particles that evade washing under MQW. An estimate of the magnitude of this effect may be gained by assuming that all Al in the macroalgae, $[\text{Al}_{\text{alg}}]$, arises from adherent sediment grains as follows (Luoma et al., 1982):

$$[\text{Me}_{\text{alg}}]^* = [\text{Me}_{\text{alg}}] - ([\text{Al}_{\text{alg}}][\text{Me}_{\text{f}}]/[\text{Al}_{\text{f}}])$$

where $[\text{Me}_{\text{alg}}]$ is the measured metal content of the macroalga, $[\text{Me}_{\text{f}}]$ and $[\text{Al}_{\text{f}}]$ represent, respectively, the metal and Al concentrations of fine sediment sampled at the same site, and $[\text{Me}_{\text{alg}}]^*$ is a “corrected” metal concentration in the macroalga. Results of applying this correction to *U. lactuca* and *F. vesiculosus* are shown in Fig. 3. For the latter, corrected values are not dissimilar to measured concentrations but for the former, correction reduced concentrations considerably in many cases (and for Sn, to $[\text{Me}_{\text{alg}}]^* < 0$). Although it is suspected that the correction applied to *U. lactuca* may have been over-estimated because of the ability of this macroalga to naturally accumulate Al (Olsson et al., 2020), correction

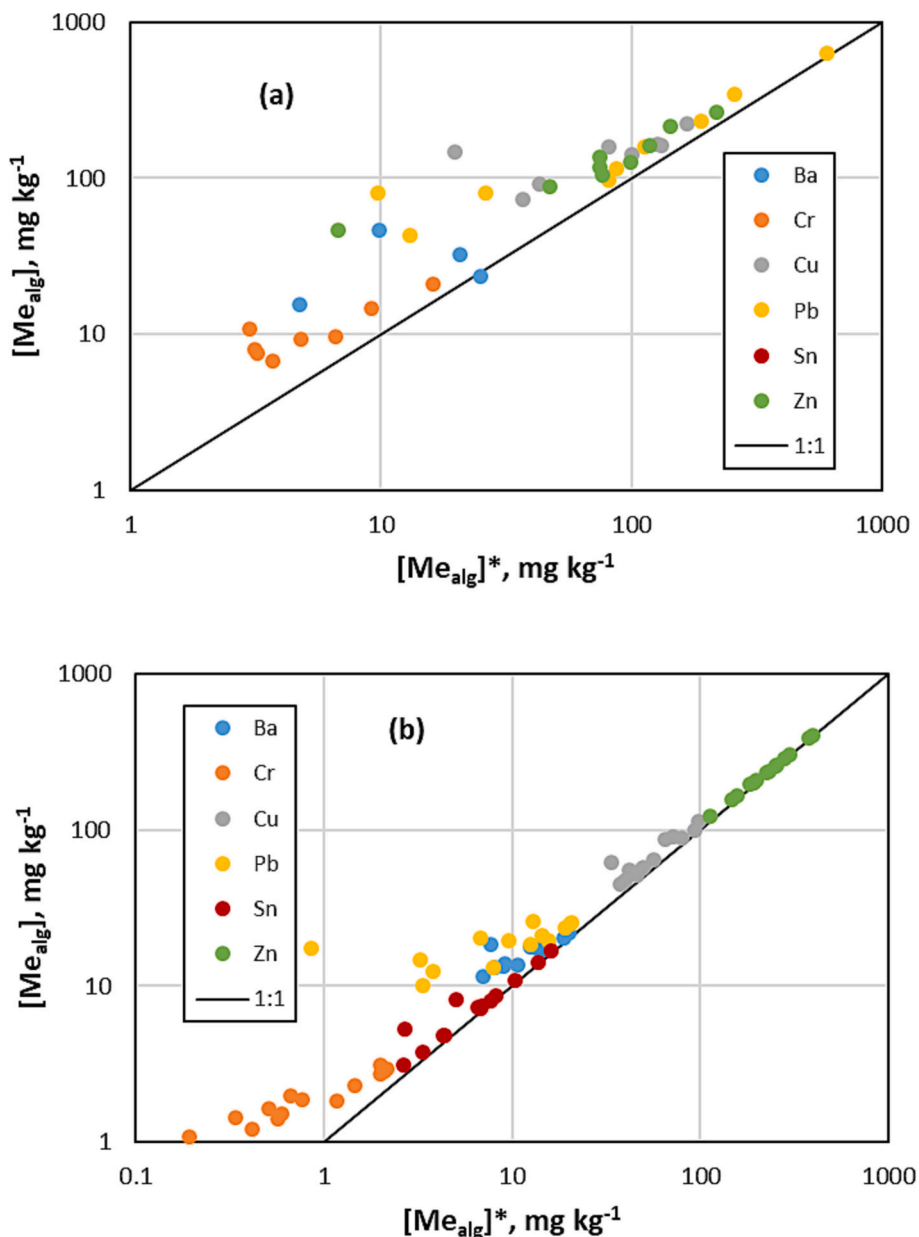


Fig. 3. Measured, dry weight concentrations of metals in (a) *U. lactuca* and (b) *F. vesiculosus* versus the respective dry weight concentrations after correction for potential contamination by adherent sediment grains. Note that for Sn in *U. lactuca*, $[Me_{alg}]^* < 0$.

failed to reduce the variability in metal concentrations observed in either species.

An alternative possibility is that macroalgal surfaces are able to capture and retain microscopic paint particles directly from the water column or from bed sediment at low tide that are not readily removed on cleaning in MQW. Turner et al. (2012) suggested that silver nanoparticles adhered to the polysaccharide-rich mucus layer on the surface of *U. lactuca* could explain the apparent accumulation of Ag by the alga in the absence of any nanoparticle dissolution in controlled laboratory exposures. More recently, Gutow et al. (2016) observed the attachment of microplastic particles to the surface of *F. vesiculosus* in laboratory experiments and suggested that the effect was enabled by both adherence to the mucus layer and electrostatic binding between hydroxyl residues on the surface of polymer surfaces and cellulose. The authors also surmised that such interactions could facilitate the release of additives from the microplastic matrix and their subsequent accumulation by the alga. The stochastic nature of these processes and the greater mobility of metal additives in paint particles than in microplastics or nanoparticles

(Turner, 2022) could account for both the enrichment and variation of metals observed in *U. lactuca* and *F. vesiculosus* in the present study.

These assertions, more generally, imply that macroalgae are not necessarily good indicators of aqueous metal concentrations where heterogeneous, point sources of particulate metals exist. Nevertheless, and regardless of the precise nature of paint-algal interactions, macroalgae may represent an important vector for paint-bound metals to enter the marine food chain.

CRediT authorship contribution statement

Andrew Turner: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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References

- Blossom, N., Szafranski, F., Yacht, A., Lotz, A., 2018. Use of copper-based antifouling paint: a US regulatory update. *Coatings Tech* 15, 63–68.
- Canadian Council of Ministers of the Environment, 1999. Canadian environmental quality guidelines: sediment. <https://ccme.ca/en/resources/sediment> accessed 5/22.
- Dick, R.J., Nowacki, L.J., 1970. Organolead compounds in antifouling paints. *J. Paint Technol.* 42, 535.
- Gutow, L., Eckerlebe, A., Gimenez, L., Saborowski, R., 2016. Experimental evaluation of seaweeds as a vector for microplastics into marine food webs. *Environ. Sci. Technol.* 50, 915–923.
- La Puma, P.T., Fox, J.M., Kimmel, E.C., 2001. Chromate concentration bias in primer paint particles. *Regul. Toxicol. Pharmacol.* 33, 343–349.
- Luoma, S.N., Bryan, G.W., Langston, W.J., 1982. Scavenging of heavy metals from particulates by brown seaweed. *Mar. Pollut. Bull.* 13, 394–396.
- Mason, C., Vivian, C., Griffith, A., Warford, L., Hynes, C., Barber, J., Sheahan, D., Bersuder, P., Bakir, A., Lonsdale, J.A., 2021. Reviewing the UK's action levels for the management of dredged material. *Geosciences* 2022 (12), 3. <https://doi.org/10.3390/geosciences12010003>.
- Michaud, M.H., Pelletier, E., 2006. Sources and fate of butyltins in the St. Lawrence Estuary ecosystem. *Chemosphere* 64, 1074–1082.
- Muller-Karanassos, C., Turner, A., Arundel, W., Vance, T., Lindeque, P.K., Cole, M., 2019. Antifouling paint particles in intertidal estuarine sediments from southwest England and their ingestion by the harbour ragworm, *Hediste diversicolor*. *Environ. Pollut.* 249, 163–170.
- Naser, H.A., 2013. Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: a review. *Mar. Pollut. Bull.* 72, 6–13.
- Olsson, J., Toth, G.B., Albers, E., 2020. Biochemical composition of red, green and brown seaweeds on the Swedish west coast. *J. Appl. Phycol.* 32, 3305–3317.
- Pan, K., Wang, W.X., 2012. Trace metal contamination in estuarine and coastal environments in China. *Sci. Total Environ.* 421, 3–16.
- Payne, M.R., Turner, A., 2022. Remote sensing of boat abandonment using Google Earth™. *Environ. Sci. Pollut. Res.* accepted for publication.
- Rainbow, P.S., 1995. Biomonitoring of heavy metal availability in the marine environment. *Mar. Pollut. Bull.* 31, 183–192.
- Rainbow, P.S., 2020. Mining-contaminated estuaries of Cornwall – field research laboratories for trace metal ecotoxicology. *J. Mar. Biol. Assoc. U. K.* 100, 195–210.
- Rees, A.B., Turner, A., Comber, S., 2014. Metal contamination of sediment by paint peeling from abandoned boats, with particular reference to lead. *Sci. Total Environ.* 494–495, 313–319.
- Singh, N., Turner, A., 2009. Trace metals in antifouling paint particles and their heterogeneous contamination of coastal sediments. *Mar. Pollut. Bull.* 58, 559–564.
- Soroldoni, S., Castro, Í.B., Abreu, F., Duarte, F.A., Choueri, R.B., Möller, O.O., Fillmann, G., Pinho, G.L.L., 2018. Antifouling paint particles: sources, occurrence, composition and dynamics. *Water Res.* 137, 47–56.
- Takahashi, C.K., Turner, A., Millward, G.E., Glegg, G.A., 2012. Persistence and metallic composition of paint particles in sediments from a tidal inlet. *Mar. Pollut. Bull.* 64, 133–137.
- Tanner, P.A., Leong, L.S., Pan, S.M., 2000. Contamination of heavy metals in marine sediment cores from Victoria Harbour, Hong Kong. *Mar. Pollut. Bull.* 40, 769–779.
- Turley, P.A., Fenn, R.J., Ritter, J.C., 2000. Pyrithiones as antifoulants: environmental chemistry and preliminary risk assessment. *J. Bioadhes. Biofilm Res.* 15, 175–182.
- Turner, A., 2022. Paint particles in the marine environment: an overlooked component of microplastics. *Water Res.* X 12, 100110.
- Turner, A., Brice, D., Brown, M.T., 2012. Interactions of silver nanoparticles with the marine macroalga, *Ulva lactuca*. *Ecotoxicology* 21, 148–154.
- Turner, A., Kearn, E., Solman, K.R., 2016. Lead and other toxic metals in playground paints from South West England. *Sci. Total Environ.* 544, 460–466.
- Valkirs, A.O., Seligman, P.F., Haslbeck, E., Caso, J.S., 2003. Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: implications for loading estimation to marine water bodies. *Mar. Pollut. Bull.* 46, 763–779.
- Varma, R., Turner, A., Brown, M.T., 2011. Bioaccumulation of metals by *Fucus ceranoides* in estuaries of south West England. *Mar. Pollut. Bull.* 62, 2557–2562.
- Villares, R., Real, C., Fernández, J.A., Aboal, J., Carballeira, A., 2007. Use of an environmental specimen bank for evaluating the impacts of the Prestige oil spill on the levels of trace elements in two species of *Fucus* on the coast of Galicia (NW Spain). *Sci. Total Environ.* 374, 379–387.
- Wu, C.C., Sao, L.J., Tao, S., Zeng, E.Y., 2016. Significance of antifouling paint flakes to the distribution of dichlorodiphenyltrichloroethanes (DDTs) in estuarine sediment. *Environ. Pollut.* 210, 253–260.