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Published in:

Marine Pollution Bulletin

DOI:

[10.1016/j.marpolbul.2020.111433](https://doi.org/10.1016/j.marpolbul.2020.111433)

Publication date:

2020

Link:

[Link to publication in PEARL](#)

Citation for published version (APA):

Rees, A. B., Gallagher, A., Wright, L. A., Wood, J., Cathery, T., Harrison, B., Down, C., & Comber, S. (2020). Leisure craft sacrificial anodes as a source of zinc and cadmium to saline waters. *Marine Pollution Bulletin*, 158(0), 111433-111433. <https://doi.org/10.1016/j.marpolbul.2020.111433>

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1 **This is a preproduction revised copy of the full paper available in**
2 **Marine Pollution Bulletin:** <https://doi.org/10.1016/j.marpolbul.2020.111433>

3 **Leisure craft sacrificial anodes as a source of zinc and cadmium**
4 **to saline waters**

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10

11 **Abstract**

12 Sacrificial anodes are attached to the hulls of boats and marine structures to prevent
13 corrosion. Their use inevitably leads to release of zinc as well as impurities in the zinc alloy
14 such as cadmium to the saline environment. Risk assessments and source apportionment
15 exercises require accurate assessments of the potential loads of chemicals into the
16 environment. This research has surveyed a wide variety of zinc anodes for their composition
17 to compare against a reported industry standard as well as using differing methodologies to
18 determine the dissolution rate of zinc and cadmium from anodes. A zinc dissolution rate of
19 477 g/yr/kg of anode is proposed. Although most anodes tested had concentrations of
20 cadmium within the prescribed limits set by the reported standard, calculated leaching rates
21 from laboratory dissolution experiments suggested as much as 400 g per year of cadmium
22 could leach from zinc anodes used on leisure vessels within UK waters.

23 **Keywords:** Sacrificial anode; zinc; cadmium; dissolution rates; saline water

24 **1. Introduction**

25 Sacrificial anodes attached to the steel on boats (typically on hulls and propeller shafts) and
26 marine structures to prevent corrosion. It is thought they corrode at varying rates due to
27 factors such as salinity variations and stray currents associated with any number of leakages,
28 including for example electrical hook-ups in marinas. This is particularly significant in
29 estuarine environments where salinities can vary from near freshwater to full seawater on
30 each tide (Matthiesen et al., 1999; Deborde et al., 2015). Many fish and shellfish species, as
31 well as other biota, found within such habitats can be sensitive to elevated levels of metals
32 in the water column and therefore in locations where there are high boat densities (e.g. ports,
33 marinas or channel moorings), dissolution characteristics of anodes needs to be assessed

34 (Nam et al., 2005; Denton et al., 2009; Pearson et al., 2018). This in turn would allow for
35 introduction of better management and mitigation measures that would reduce impact on
36 ecosystem health (Rees et al., 2017). Whilst sheltered estuaries such as the Hamble attract
37 1000's of leisure craft to moor throughout its length (Rees et al., 2017), this issue is
38 exacerbated in marinas where lock gates ensure boats are continuously afloat, thereby
39 restricting tidal flushing leading to further elevated zinc concentrations (Bird et al., 1996;
40 Cathery 2014; Harrison 2015; Wood 2014). In addition to zinc, anodes contain a range of
41 impurities which may also present a threat to the aquatic environment. Of particular concern
42 is the highly toxic element cadmium (Cd), a priority hazardous substance under the Water
43 Framework Directive (2000), which regulators are further required to control.

44 Zinc is a specific pollutant under the WFD (2000) and the current Environmental Quality
45 Standard (EQS) in UK estuaries is 7.9 $\mu\text{g/l}$ for dissolved zinc (which includes a background
46 level of 1.1 $\mu\text{g/l}$) (Maycock *et al.*, 2012). This value is significantly lower than the previous
47 value of 40 $\mu\text{g/l}$. Within estuaries and marinas with high boat density, under certain
48 conditions zinc released from anodes has the potential to contribute to concentrations
49 exceeding the EQS (Bird *et al.*, 1996; Boxall *et al.*, 2000). Previous studies have reported
50 concentrations of up to 19.9 $\mu\text{g/l}$ dissolved zinc in Poole Harbour, for example, which was
51 significantly above the control sites of 2 $\mu\text{g/l}$ (Bird et al., 1996). Similarly, elevated
52 concentrations above the revised EQS have been observed on the Hamble and Orwell
53 estuaries, as well as in harbours, bays and estuaries in California (Bird *et al.*, 1996; Boxall
54 *et al.*, 2000; Matthiessen *et al.*, 1999; Singhasemanon *et al.*, 2009). The French port of
55 Camargue in the Mediterranean also had raised zinc levels in sediments likely due to marine
56 paints and zinc anodes. The harbour has around 500 moorings and maintenance yards, with
57 zinc concentrations ranging from 17 and 475 $\mu\text{g/g}$ within the Harbour sediments, an
58 enrichment factor (compared with control areas) of 9 was observed in areas of boat
59 maintenance (Briant *et al.*, 2013). Studies on anode use and dissolution rates were also
60 carried out in the Plymouth area by Wood (2014), Cathery, (2014) and Harrison (2015),
61 which showed marinas to have higher zinc concentrations in water and sediment samples,
62 compared with nearby control sites. The alternative material to zinc anodes in the marine
63 environment is aluminium (Mao *et al.*, 2011), although they seem to be used less frequently
64 than zinc, mainly due to habits of boat owners related to perceived performance and cost.

65 In order to safeguard vulnerable ecosystems it is necessary to manage the sources of
66 contaminants. Therefore, to determine the risk posed by zinc anodes in estuaries, ports and
67 marinas it is necessary to accurately determine their rate of dissolution in order to derive

68 predicted environmental concentrations which can then be compared against environment
69 quality standards to assess risk. However, determining dissolution rates is not necessarily
70 straightforward as environmental factors such as salinity may play a significant role in the
71 dissolution rates. Furthermore, there is also a question as to whether the elemental
72 composition of the anode varies among suppliers and if that could also impact the zinc
73 dissolution rate. Anode impurities may also pose a risk to the aquatic environment,
74 particularly for metals of international concern including cadmium. Concerns regarding the
75 quality and effectiveness of zinc anodes resulted in the current U.S. Military Specification,
76 A-18001K (Boat US, 2016) which was set on the basis of different effectiveness of corrosion
77 control being observed for similar vessels treated with apparently the same zinc anode
78 protection. Some anodes were observed to become passivated when a white crust formed on
79 their surface, identified as iron oxides caused by excessive impurities (mainly iron) in the
80 product. The formation of the crust made the anodes inactive allowing corrosion to take
81 place elsewhere in the vessel. The set specification therefore limited the amount of impurities
82 in the zinc used, resulting in the requirement to use high grade zinc and strict manufacturing
83 practices to guarantee performance.

84 It is imperative that zinc anode composition and its variability across brands is fully
85 understood as well as the dissolution rates, with the objective of deriving a representative
86 dissolution rate for use in environmental risk assessments and source apportionment
87 exercises. A number of methods may be used to estimate metal dissolution rates from anodes
88 of varying complexity, including chemical analysis of anode composition, laboratory based
89 dissolution experiments, field testing, anecdotal boat owner surveys and environmental
90 modelling. The research reported here has determined the composition of a variety of
91 commercially available zinc anodes to compare against the US Military Specification and to
92 determine the levels of impurities present, particularly cadmium owing to its toxicity and
93 regulatory control. Zinc dissolution rates were determined using a variety of survey, *in situ*
94 and modelling methods to propose a definitive dissolution rate.

95

96 **2. Method**

97 A combination of chemical composition analysis combined with survey data and *in situ*
98 monitoring was undertaken to determine zinc anode quality, the presence of impurities which
99 could impact on anode performance (e.g. iron) or negatively impact on the environment (e.g.
100 cadmium) and to determine a definitive dissolution rate with respect to salinity.

101 **2.1 Survey of boat owners**

102 A survey was sent out to boat owners on the Hamble via email covering marinas and mid
103 channel moored boats and to the wider Solent and UK via yachting forums. Furthermore,
104 another paper-based questionnaire was produced for berth holders at Sutton Harbour in
105 Plymouth. Boat owners were also asked what antifouling paint they used to determine if they
106 included zinc based products. The anode survey was piloted by email to four boat owners,
107 with minor adjustments made to question wording before distribution. Boat owners within
108 marinas (with electrical hook-up) and those without electrical supply in mid-channel were
109 approached to determine if they observed different anode corrosion rates. Boat owners
110 supplied information on the length of their boats, how many anodes they used, their
111 approximate weight, how frequently they changed their anodes and the amount of anode
112 remaining when the anode was replaced. In addition to this, the marina manager of Sutton
113 Harbour and a local chandlery (Force 4 Chandlery) were interviewed to provide data
114 regarding the harbour (berth numbers, volume of water, the lock freeflow – period when the
115 gate is open, etc for use when modelling zinc dissolution rates), and the masses of various
116 anodes available on the market.

117 In total 69 responses were obtained from boat owners in the Hamble with boats moored in
118 the channel and 15 responses from boat owners based in marinas. For Plymouth marinas, 42
119 questionnaires were returned for marina based vessels. Other responses included 11 for
120 marina locations in Southampton Water and 13 others from boat owners in marinas around
121 England. Based on initial size, replacement rate and estimated wear, loss rates for zinc per
122 kg of anode could be calculated along with total loads emitted into the receiving water.
123 Additionally, a comparison between the mid channel moorings and marinas could be carried
124 out to see whether possible electrical hooks within marinas could result in increased anode
125 dissolution through stray electrical currents.

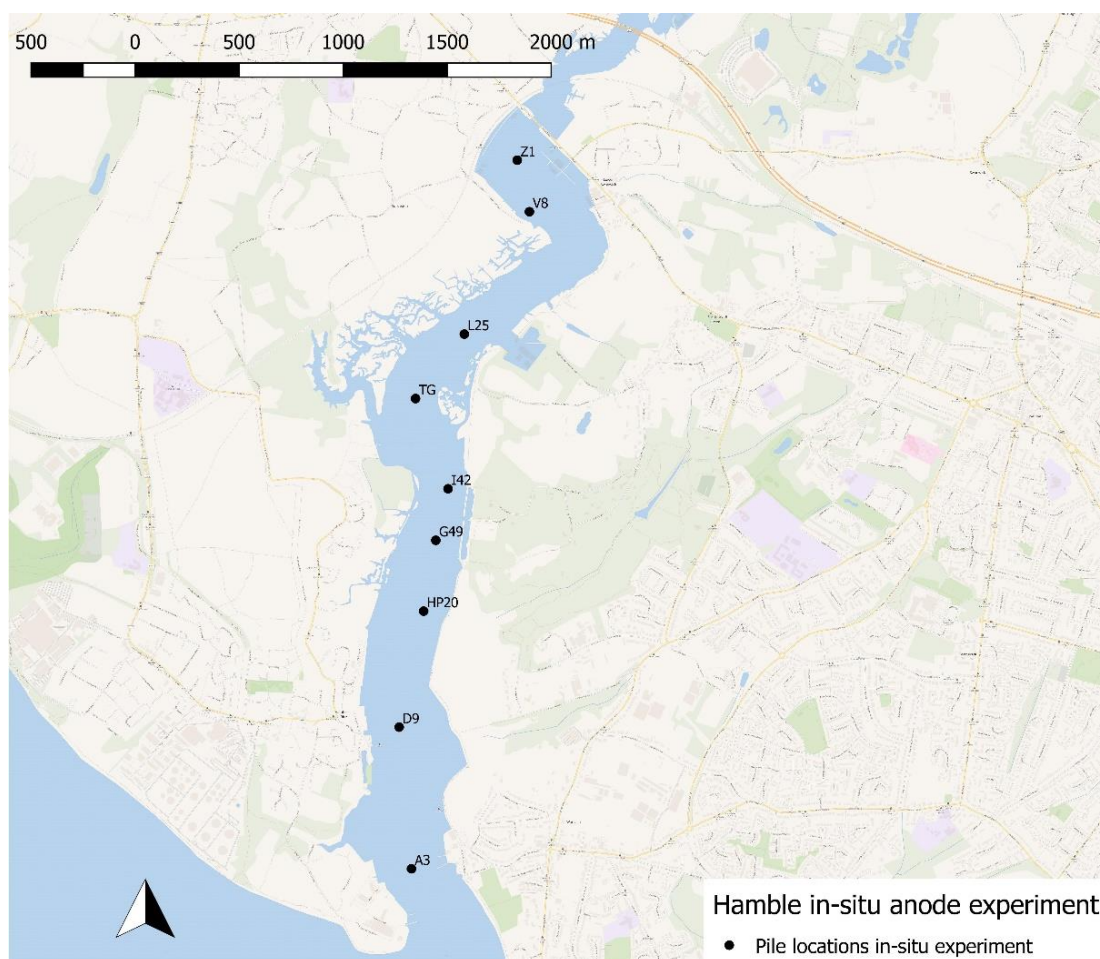
126 Furthermore, detailed data were gathered from one boat owner who had kept extensive
127 records of anode use over a 15 year period, which he weighed to determine their corrosion
128 rates. The corrosion rate for these anodes was estimated using the weight of the new anode
129 installed on the vessel in 2016.

130 **2.2 *In situ* anode dissolution experiment**

131 Hanging anodes were also acquired for an *in situ* anode experiment, these were weighed to
132 two decimal places before the experiment and again after the experiment to determine the

133 dissolution rates at each site in the river. The anodes were analysed using X Ray
134 Fluorescence (XRF) to determine their elemental composition (see section 2.3 for details).
135 Once the anodes were weighed and analysed for initial elemental composition, they were
136 securely attached to steel piles within the estuary from Hamble-Le-Rice up to Bursledon
137 Bridge (Figure 1) at three different depths close to the low water level to maximise the time
138 anodes were in the water during the tidal cycle. The anodes were installed in the estuary for
139 1 year between February 2016 and 2017.

140
141



154 **Figure 1. Location of anode sites for *in-situ* anode experiment (site NGR**
155 **coordinates: A3 = SU487,060; D9 = SU485,069; HP20 = SU487,072; G49 = SU488,075;**
156 **I42 = SU488,079; TG= SU487,083; L25= SU489,087; V8 = SU492,092; Z1=**
157 **SU491,094)**

158

159 Salinity profiling was carried out to determine the salinity variations in the estuary and used
160 along with Environment Agency data to determine salinity regimes. This was carried out at

161 each pile with anodes present at high and low tide on spring and neap tides during 2016 on July
162 4th (spring tide), July 15th (neap tide), October 12th (neap tide) and October 21st (spring tide).
163 The salinity was measured using a YSI 556 MPS probe at 1m intervals from the surface to
164 sediment (between 3 and 8m depending on site and whether neap or spring tides). All data were
165 pooled at each site and the mean used to determine the salinity to which the anodes were
166 exposed. The anodes were gently cleaned during salinity profiling, with a toothbrush to remove
167 algae, mud and any iron and/or zinc oxides/hydroxide that may have built up on the anodes.
168 Care was taken not to abrade the surface of the anodes. This occurred as the anodes were not
169 moving through the water as would be the case on a vessel, although tidal currents either side
170 of slack water would obviously ensure a certain movement of water across the anode surface.
171 Anodes were removed from the estuary in February 2017 after a one year deployment. Once
172 back in the laboratory the three anodes were, cleaned dried at air temperature and then weighed
173 to three decimal places and analysed using XRF. An anode dissolution rate was derived by
174 simply calculating the weight difference of the anodes before and after deployment.

175

176 **2.3 XRF analyses of zinc anodes**

177 A number of new zinc anodes were analysed for their metal content using an XRF (Niton XL
178 3T Gold Plus) instrument. Each anode was analysed 8 times at an exposure time of between 60
179 and 180s, in differing positions to determine the elemental composition at the surface of the
180 electrode (it was assumed that the anodes were of a consistent composition throughout given
181 they are cast. All data are reported as a percentage with a limit of detection of 0.01%. Niton
182 supplied certified reference materials were analysed to provide analytical quality control.
183 Although XRF determination meant only the surface of the material was analysed, it was
184 assumed composition was consistent throughout, and it is noted that any dissolution by saline
185 water is a surface-based process.

186 Zinc anodes of different sizes and weights, from a number of suppliers were tested:

- 187 1) 1 x 2.1kg, pear anode has a code of ZD77 standard size
- 188 2) 1 x Homemade pear electrode (2.1kg), in style of ZD77
- 189 3) 2 x Piranha anodes hull, 4kg each, L310mm x W75mm x H40mm
- 190 4) 1 x MGDuff prop anode 40mm diameter, no weight available online
- 191 5) 1 x Volvo Penta hull anode, Length 267mm, width 85mm, height 30mm.

- 192 6) 3 x Martyr bolt on 50mm diameter disk anode, ca. 65g
- 193 7) 3 x Techno-seal bolt on 50mm diameter disk anode, ca. 80g
- 194 8) 3 x MME (MME 03ZB-UK) bolt on 50mm diameter 35mm deep anode, ca. 250g
- 195 9) 27 x Hanging anodes 2kg each, used for in situ dissolution test
- 196 10) 9 x 700g bar anodes

197 **2.4 Concentrations of zinc in marina water**

198 All samples were collected from subsurface (approximately 0.5m depth), filtered through acid
199 washed (10% HCl) polycarbonate 0.4µm 47mm diameter membranes under vacuum. Analysis
200 was by Inductively Coupled Plasma – Mass Spectrometry – Thermo Scientific X Series 2 (after
201 50% dilution to reduce the salinity). Limits of detection (0.03 µg/l) were based on 3 times the
202 standard deviation of the blank and quality assurance was provided by certified reference
203 waters (SLEW-2, Natural Resources Canada) with recoveries of 99% +/- 5.4% standard
204 deviation.

205 **2.5 Laboratory experiments and water analysis for cadmium dissolution experiment**

206 A laboratory test included nine, 5 litre buckets that were filled with 3 litres of sea water,
207 collected from Queen Anne’s Battery in Plymouth, UK. Three different types of disk anodes
208 were tested in triplicate (Anodes 6, 7 and 8 above). An electrochemical coupling was set up by
209 bolting each anode to a square of sheet steel. One anode was placed in each bucket and the
210 bucket kept covered throughout the duration of the test.

211 Each bucket was sampled 24, 48 and 72 hours after they had been set up. Then weekly for a
212 total of 11 weeks. The study ran for a total of 79 days. Blank control samples were taken to
213 take account of any potential leaching of metal from the plastic buckets. Water samples were
214 taken using a 50ml centrifuge tube and stabilised using 200 µl of 20% nitric acid. Metal
215 concentrations in each sample were determined using a Thermo ICP-MS. Cadmium limit of
216 detection using ICP-MS was 0.016 µg/l based on 3 times the standard deviation of the blank.

217 **2.6 Anode corrosion rate calculation**

218 The corrosion rate was calculated using the weight of each new anode and the percentage of
219 the anode reported to have corroded after one year (the recommended service life for an anode).
220 Where anodes were replaced at longer or shorter time intervals then the weight and percentages
221 were calculated and normalised to a year. To account for the different numbers and sizes of

222 anodes used on different vessels, all calculations were normalised to g of zinc dissolved per
223 year per kg of anode used. Using this basic unit it was then possible to multiply up by the mean
224 or median mass of each anode and mean or median number of anodes per vessel to generate a
225 dissolution rate per vessel.

226 **2.7 Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC)** 227 **modelling**

228
229 To predict the zinc dissolution rate from anodes using a combination of monitoring and
230 modelling data, the MAMPEC model (Deltares, 2019) was utilised as it is simple, requires
231 relatively few inputs, is comprehensive and is open source and hence freely available. The
232 model is designed to predict concentrations of zinc in the surface water based on a number of
233 scenarios including a locked marina. The restricted flow of water into and out of a locked
234 marina, maximises the opportunity for zinc concentrations to build up from leaching from
235 anodes and therefore to register an increase over and above background concentrations.
236 Assuming the model can be parameterised with dimensions and flushing rates to predict
237 dilution, combined with boat numbers and anode dissolution rates, it is possible to predict
238 dissolved concentrations and any partitioning of zinc between the dissolved phase and the
239 sediment. If the sediment and water concentrations and boat numbers are already known, then
240 it is relatively straightforward to adjust the dissolution rate for the anodes attached to boats
241 until the predicted concentration in the marina water is equivalent to that observed; thus
242 arriving at an implied leaching rate for the given scenario.

243
244 Consequently, the model was set up using the tidally locked Sutton Harbour marina in
245 Plymouth as a case study owing to a high boat density and it being well characterised in terms
246 of physical size, tidal range, boat numbers and flushing rate. Furthermore, water quality data
247 was available across a number of years (2013 to 2018) from this and other studies as well as
248 sediment data (2014 and 2015) (Cathery, 2014; Wood, 2014; Harrison, 2015) thereby
249 furnishing a robust set of observed concentrations. Not all zinc in surface waters is derived
250 from anode dissolution, road runoff, minewater drainage, sewage effluent and antifoulant
251 paints would also contribute to the background geological signature. The input for the model
252 background zinc concentration was therefore taken as measured concentrations in Queen
253 Annes Battery directly outside Sutton Marina's lock gates (Table 1). This provided a mean
254 background dissolved zinc concentration of 8.3 µg/L based on 2013 to 2018 data from this
255 study and previous ones (Cathery, 2014; Wood, 2014; Harrison, 2015). The partition

256 coefficient for the distribution of zinc between the sediment and overlying water was calculated
 257 from the measured dissolved and sediment concentrations. With these data input into the
 258 model, it was fully parameterised and the dissolution rate adjusted until the predicted water
 259 zinc concentration matched that of the observed.

260

261 The model is described elsewhere (Deltares, 2019) with the key input parameters provided in
 262 Table 1.

263

264 **Table 1 MAMPEC input values and defaults**

Input parameter	Value assigned
Leaching rate ($\mu\text{g}/\text{cm}^2/\text{day}$)	28
Zn sediment:water partition coefficient (m^3/kg) based on measured dissolved and sediment Zn levels in Sutton Harbour.	20
Background Zn ($\mu\text{g}/\text{l}$) based on concentrations in Queen Anne’s Battery outside of Sutton Marina (includes road runoff, natural and any antifoulant paint addition)	8.3 +/- 1.1 (95% conf, n=57)
Predicted total Zn ($\mu\text{g}/\text{l}$)	21.4
Predicted dissolved Zn ($\mu\text{g}/\text{l}$)	19.4
Observed mean Zn in Sutton Harbour ($\mu\text{g}/\text{l}$) between 2013 and 2018	19.4 +/- 4.8 (95% conf, n=20)
Marina length (m)	280
Marina width (m)	280
Marina depth (m)	5.5
Tidal range (m)	3
Suspended solids concentration (mg/l) measured	5
Background sediment concentration (measured) mg/kg zinc	387
Harbour flushing rate (m^3/s) default	0.1
Ships at berth (<10m) measured (surface area predicted m^2)	462 (20)
Ships at berth (10-50m) measured (surface area predicted m^2)	83 (120)

265

266 **3. Results and Discussion**

267 **3.1 Anode elemental composition and potential to leach impurities**

268 XRF analyses for the surface of new anodes was carried out to determine the metal content and
 269 to see if anodes met the US Military standards for anodes (Wagner et al., 1996; Harris, 2008;
 270 Boat U.S, 2016). Surface samples were used to be representative of the area of the anode

271 directly in contact with the water. Within anode elemental composition was reasonably
272 consistent, but unsurprisingly variation was greater near to the limits of detection, reflecting
273 both the analytical variability near to the detection limits as well as difficulties in
274 manufacturing processes controlling impurities at low levels. Anode-to-anode (or among
275 anode) elemental composition also varied for the same type of product, again relatively low for
276 zinc but much greater for the minor impurities (Table 2) (Wagner *et al.*, 1996; Boat U.S, 2016).
277 Zinc levels ranged from 96.8 to 99.5%, with 8 of the 10 types of anode tested having means
278 less than the US Military specification of 99.3% with 95% confidence (Table 2).

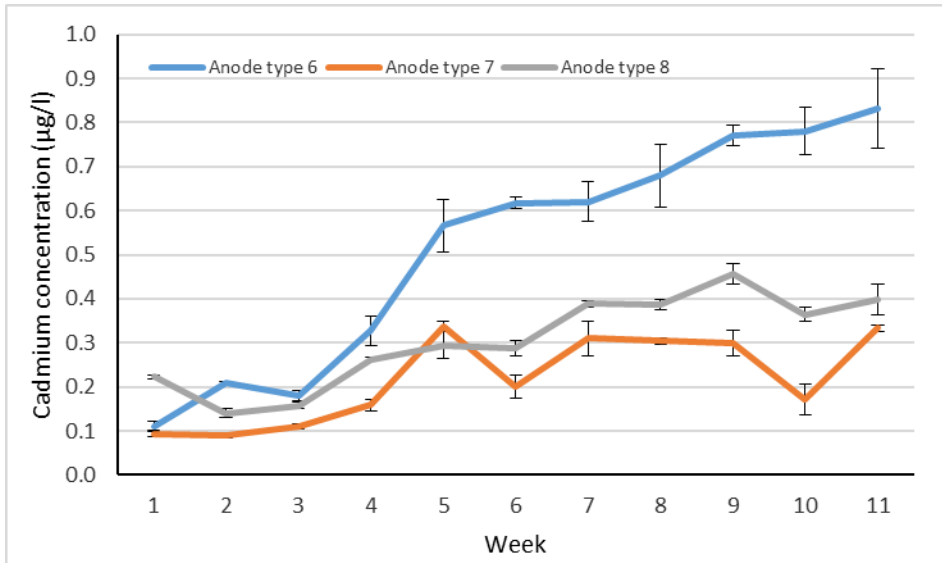
279

280 **Table 3: XRF analyse of new anodes to indicate metal content present (figure in brackets is the 95% confidence interval for 3 replicate**
 281 **determinations per anode tested) green cells show compliance with US military specifications (Boat US, 2016), orange below,**
 282 **red above. n/a means not analysed**
 283

Anode			1	2	3	4	5	6	7	8	9	10
Element %	US Military specification	Description	2.1 kg pear	2.1 kg pear (homemade)	4 kg hull	40mm Prop	5 kg hull	65g disk	80g disk	250g disk	2 kg Hanging anodes	700g Lab anodes
Replicate anodes			1	1	2	1	1	3	3	3	27	9
Zn	99.3	Minimum	96.8 (1.0)	98.0 (0.5)	97.4 (0.4)	96.8 (0.8)	98.7 (0.3)	99.5 (0.11)	99.5 (0.23)	99.1 (0.14)	97.6 (0.18)	98.0 (0.38)
Si	0.1	Maximum	1.2 (0.4)	0.94 (0.2)	0.88 (0.2)	1.4 (0.46)	0.81 (0.1)	n/a	n/a	n/a	0.83 (0.07)	1.47 (0.2)
Al	0.1-0.5	Range	1.4 (0.8)	0.85 (0.09)	2.0 (0.15)	0.15 (0.3)	1.0 (0)	<0.005	<0.005	<0.005	1.2 (0.11)	0.76 (0.2)
Cd	0.025-0.07	Range	0.04 (0.011)	0.03 (0)	0.04 (0)	0.05 (0.01)	n/a	0.057 (0.0001)	0.024 (0.0001)	0.022 (0.0005)	0.034 (0.025)	0.04 (0.007)
Cr	0.1	Maximum	0.11 (0.08)	0.08 (0.045)	0.05 (0.03)	0.1 (0.05)	0.03 (0.01)	0.13 (0.001)	0.29 (0.15)	0.55 (0.12)	0.041 (0.11)	n/a
Cu	0.005	Maximum	n/a	n/a	n/a	0.06 (0)	n/a	<0.005	<0.005	<0.005	n/a	0.02
Fe	0.005	Maximum	0.03	0.03	0.07 (0.02)	0.03 (0.01)	n/a	0.0066 (0.003)	0.005	0.0059 (0.002)	0.032 (0.005)	0.02 (0.004)
Pb	0.006	Maximum	n/a	n/a	n/a	n/a	n/a	<0.005	<0.005	<0.005	0.01	n/a

284

285 Iron impurities are the main concern regarding passivating and poor anode performance and 8
286 out of 10 of the tested anode types exceeded the 0.005% limit set within the US Military
287 specification. The presence of cadmium within anodes is of a concern regarding environmental
288 health. Owing to the environmental toxicity and threat to human health of cadmium, the
289 Environmental Quality Standard Directive (EQSD) (2008/105/EC) requires that all discharges,
290 emissions and losses cease over time with an Environmental Quality Standard of 0.2 µg/L set
291 as an annual average for transitional (estuarine) and coastal waters. Due to the presence of
292 cadmium impurities, anodes 6, 7 and 8 were submerged in seawater for 11 weeks and water
293 samples were collected weekly to establish if any of the cadmium could leach into the water
294 column (Figure 2). Although not necessarily reflective of conditions within an estuary or
295 marina, the fact that there was an increase of cadmium concentration over time in the buckets
296 with the anodes present (compared with the control) may be considered of concern with respect
297 to meeting the requirements of the EU EQSD. Leached concentrations reflected the cadmium
298 content of the anodes with Anode type 6 (0.057%) leaching concentrations up to 0.84 µg/L into
299 the seawater after 11 weeks, compared with only 0.4 µg/L and 0.34 µg/L for Anodes 7 (0.022%)
300 and 8 (0.024%) respectively (Figure 2). A one-way ANOVA applied to the last 3 weeks of data
301 showed a significant difference between the anodes at a 95% confidence level. Concentrations
302 of cadmium in estuaries entering the English Channel range considerably depending on
303 upstream sources (historical mining, smelting, urbanisation, but typically range from a few
304 ng/L to up to 0.2 µg/L (Comber et al., 1995; Mobet 2004) and so observed leaching rates were
305 greater than this level, although environmental concentrations would be subject to a
306 combination of dilution, boat density and anode type. Although the cadmium content of all
307 three anodes was within the range specified by the US Military, from an environmental point
308 of view to meet the WFD objectives of ceasing discharges to the aquatic environment, it would
309 be clearly better to minimise the cadmium content as it would not impact on the passivation or
310 efficacy of the products. Other trace elements were obviously detectable within the anodes (e.g.
311 lead, chromium, copper, aluminium and silicon) but were considered of less concern either
312 because of only because they were present at trace levels or are of lower environmental
313 concern.



314

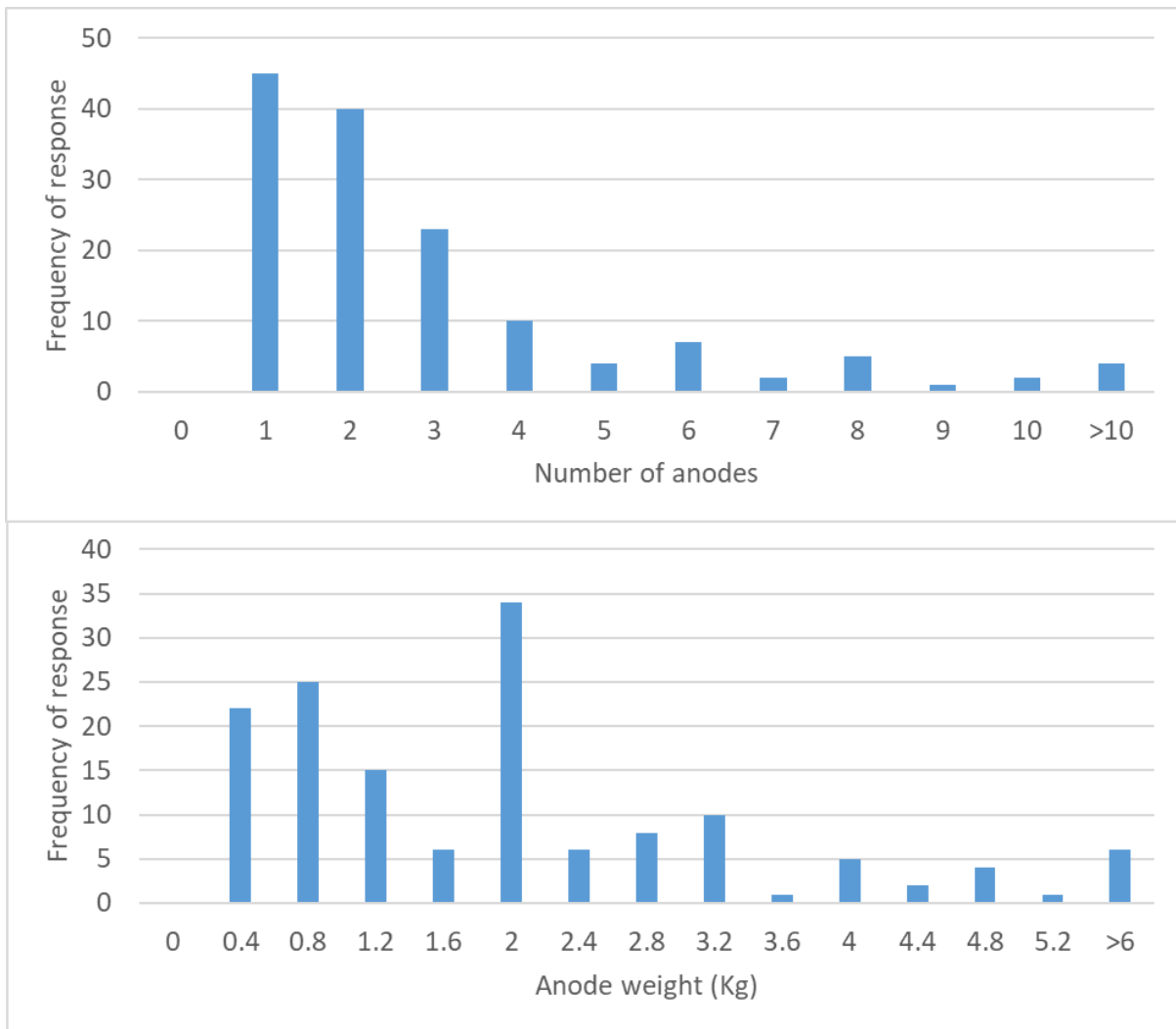
315 **Figure 2. Cadmium concentrations leached into seawater during laboratory testing**
 316 **(error bars are 95% confidence intervals for the ICP analysis)**

317

318 **3.2 Zinc anode corrosion rates calculated using survey data**

319 The survey data provided feedback from 145 boat owners in total. Average replacement rates
 320 were 1.2 years in mid channel moorings in the Hamble Estuary and 1.3 years in marinas within
 321 the estuary, a t-test to compare frequency of anode replacement between mid-channel (M=1.19,
 322 SD=0.47) and marina moorings (M=1.28, SD=0.89) indicated no significant difference in
 323 replacement frequency (t(72)=0.40, P>0.05). A significantly less frequent rate of replacement
 324 of 1.75 (95% CI [2.10, 1.40]) years on average (t(86)=2.27, P<0.01) was reported for Plymouth
 325 in the SW of England than for the Hamble mid-channel replacement rate, although this does
 326 not hold true when compared to Hamble marinas (t(61)=0.24, P>0.05).

327 Using the full dataset, the distribution of number of anodes used (M=3.02, SD=2.70 ;
 328 Mdn=2.00) and their weight (M=2.03kg, SD=2.17 ; Mdn=2.00kg) was highly variable,
 329 reflecting the specific purposes for which they are used. For example propeller shaft anodes
 330 will be smaller in general than hull anodes (Figure 3) consequently there was also an absence
 331 of a relationship between the number of anodes use and the mass of anode. The size of boat,
 332 however, may will have an impact with larger vessels more likely to require more anodes.
 333 Although a Pearson correlation indicated there was no significant correlation between boat
 334 length and number of anodes used (r(77)=0.201, P>0.05) potentially related to the general lack
 335 of understanding of their function or fitment even though advice is available (Harris, 2008;
 336 MGDuff, 2016).



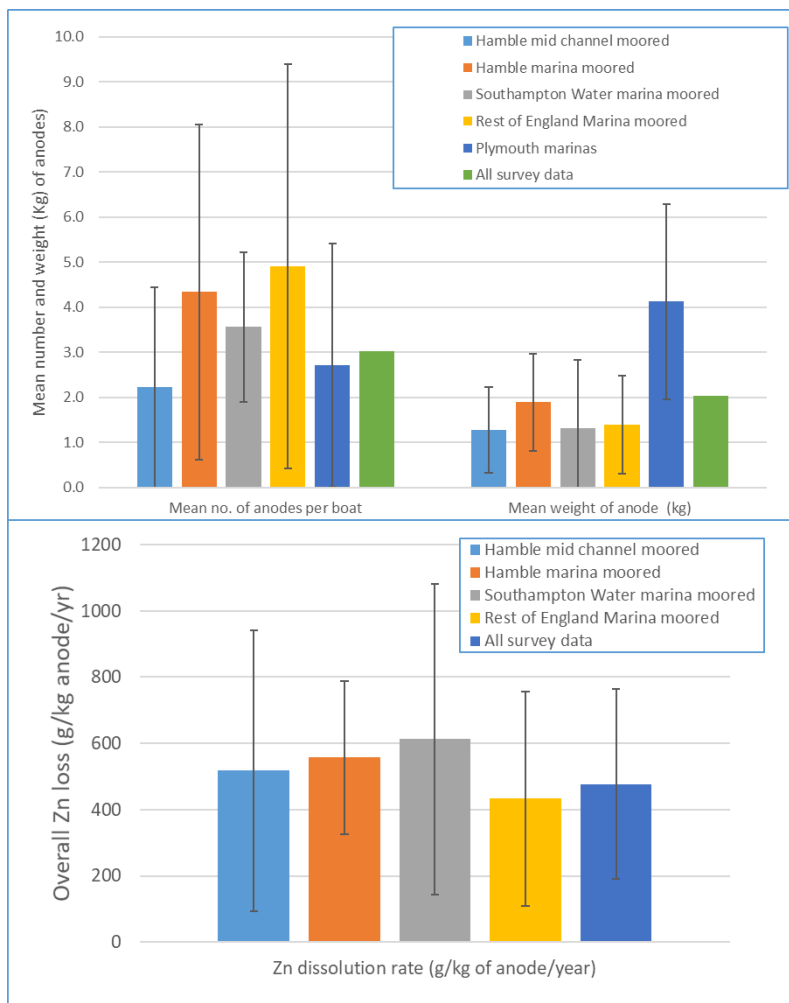
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338 **Figure 3. Histograms for the boat owner survey data from the Hamble estuary, showing**
 339 **number of anodes (top) and weight of anode (bottom) used per vessel**
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341 To account for the variation in anode numbers and weight, zinc dissolution was calculated on
 342 the basis of mass of zinc dissolved per year per kg of anode used. Even taking this into account,
 343 however, there was still significant variability in the dissolution rates for zinc among sites
 344 (Figure 4) which could not be put down to boat size owing to the relatively consistent size
 345 surveyed (M=8.8m, SD=1.8m). A one-way ANOVA indicated no significant differences in the
 346 release rates between locations, either within the Hamble or across the UK ($F(16,72)=0.878$,
 347 $P>0.05$), similarly there was no difference between mid-channel (M=518, SD=0.47 g/yr/kg of
 348 anode) or marina moorings (M=558, SD=0.89 g/yr/kg of anode) ($F(1,97)=0.356$, $P>0.05$).

349 The lack of a significant difference in dissolution rates between the channel moored and marina
 350 moored boats suggests that the potential for stray currents from electrical hook-ups in marinas

351 is unlikely to have a significant impact on zinc anode corrosion rates. Stray currents in the
 352 marine industry are referred to as the portion of current that flows over a path other than the
 353 intended path (ACE Group, 2014). Stray current (DC) corrosion could occur through poor
 354 wiring and earthing within a vessel or possibly a poorly grounded outside power source
 355 (Corrosionpedia, 2015). It is possible to buy galvanic isolators which break the circuit between
 356 vessels, acting as a filter, blocking the flow of low voltage galvanic (DC) currents but at the
 357 same time maintaining the integrity of the earthing circuit (BoatU.S, 2016). Stray current
 358 may therefore be likely to be an issue at an individual boat level, if not significant when
 359 multiplying up to a population level assessment. However, about 50% of respondents had
 360 galvanic isolators fitted on their vessels moored in marinas and mid channel and this may
 361 explain why there was little difference in reported anode corrosion rates between the location
 362 of the boats and why stray currents may not be a significant issue in the observed variable zinc
 363 dissolution rates.



364

365 **Figure 4. Boat owner survey data (131 responses) mean and 95% confidence intervals**
366 **(brackets).**

367 The reasons for such variation are likely due to salinity changes (discussed further below),
368 inaccuracies in estimating the loss of zinc from the anodes at replacement, inaccuracy in the
369 reported replacement frequency, variations in the quality of the anodes impacting their
370 performance as noted above.

371 The boat owners with more anodes on smaller vessels had generally experienced corrosion
372 issues so consequently used more anodes. This once again suggest a lack of knowledge and
373 awareness as more anodes on the same metal item will not protect it better than one, placed
374 correctly. High anode corrosion rates suggest a possible fault with boat wiring or the wrong
375 size anode being used on the vessel (Harris, 2008). A calculation is used by anode
376 manufacturers and retailers to determine the correct anode for a vessel based on size, type of
377 metal components protecting, number of metal items, environment, etc. (Harris, 2008;
378 MGDuff, 2016).

379 Taking all of the survey data together (131 survey results) the loss of zinc to receiving water
380 has a calculated mean of 477 g/yr/kg (SD=287 g/yr/kg) of anode (CI 95% [428 to 526 g/yr/kg]).
381 The median loss rate is 500 g/yr/kg of anode which shows the normalisation of dissolution to
382 mass of anode leads to a more normally distributed dataset. The Plymouth survey (n=25)
383 derived a lower mean rate of 484 g/yr/kg (SD=375 g/yr/kg) (CI 95% [337 to 631 g/yr/kg]) zinc
384 loss of anode, with rates for rest of England (n=13) calculated at the lowest rate of 433 g/yr/kg
385 of anode (SD=324 g/yr/kg) (CI 95% [257 to 609 g/yr/kg]). Suggesting higher corrosion rates,
386 albeit an ANOVA found no significant difference ($F(2,132)=0.499$, $P>0.05$), may be observed
387 in the Hamble and Southampton Water.

388 One owner reported zinc anode usage over the course of 17 years (1999-2016) for a single boat.
389 The boat was moored in a mid-channel mooring around Mercury marina on the Hamble (close
390 to site TG in Figure 1) since December 1998, had kept all the anodes from the vessel since that
391 time. The vessel is in the water for seven months and dry stored ashore for 5 months a year.
392 The anodes used during this period were weighed, along with a new anode which was deployed
393 in 2016, from this corrosion rate predictions were made using the weight of the new anode (the
394 make, and size of anode was consistent) corrected for time in the water. An average rate of 540
395 g/yr/kg of anode (CI 95% [284 g/yr/kg, 796 g/yr/kg]), with a median of 423 g/yr/kg of anode.

396 The mean and median for the dataset were well within the errors reported for the survey data
397 and therefore provided further evidence for the consistency and accuracy of the datasets.

398 Previous estimates for the Hamble have reported 2.4 kg/yr/vessel (based on their own survey
399 data) which equates to 391 and 600 g/yr/kg of anode using mean or median number of anodes
400 per boat and their weight respectively from the survey data (Boxall et al., 2000). This is again
401 within the range reported here.

402 **3.3 In situ zinc anode corrosion rates measured in the Hamble Estuary**

403 Salinity profiles were measured at high and low tide on spring and neap tides in July and
404 October 2016 to determine salinity variations at each site throughout the estuary, which could
405 then be compared with anode corrosion rates (Figure 5). An overall zinc dissolution rate of
406 358 g/yr/kg of anode (CI 95% [272 g/yr/kg, 444 g/yr/kg]) was derived across all sites. This
407 value was lower than the complete set of survey data (M=477 g/yr/kg of anode), although a t-
408 test for differences did not find this to be significant ($t(151)=1.71$, $P>0.05$) (Figure 4). The
409 lower value could reflect the wider range of salinities the in-situ anodes were exposed to,
410 compared with the boat owner survey data owing to the fact that boat density is at its highest
411 further down the estuary where there are more marinas and the estuary is wider.

412 The river water flow into the Hamble estuary is relatively modest compared with the influence
413 of saline intrusions and so salinity variation between high and low water, even during spring
414 tides is relatively low, even for the site furthest up the estuary (site V 8, Figure 1). The data,
415 however, do show an increasing dissolution rate for zinc from the anodes with increasing
416 salinity (Figure 5), with statistically significant differences between salinities below and above
417 30. The dissolution rates at the higher salinities are similar to the calculated values from the
418 boat owner surveys, which would have been biased towards higher salinity data based on boat
419 density increasing down the estuary owing to available space.

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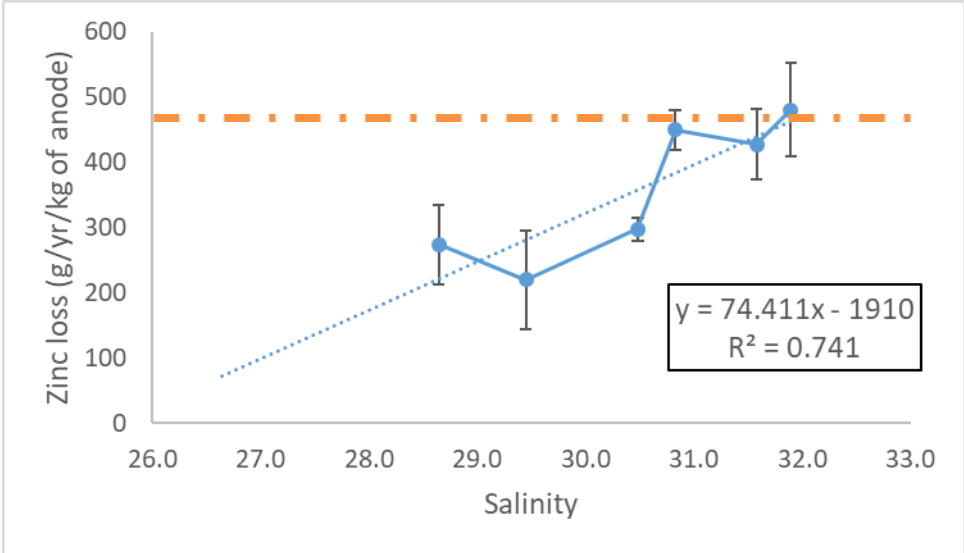


Figure 5. Impact of salinity on zinc loss from anodes versus salinity (95% confidence intervals in brackets). Red dashed line denotes calculated mean zinc loss from anodes from boat owner survey.

Variations in salinity could therefore be a factor in controlling anode corrosion rates. Low salinity waters can cause passivation of the anodes through a build-up of impurities on the anode surface, including hydroxides (often iron-based) and calcareous deposits, which then affects the rate of corrosion (Rousseau *et al.*, 2009; Caplat *et al.*, 2010). The zinc anodes should be made to the US Military specification (Table 1) which are set for seawater conditions. Consequently, they are likely to be less effective in brackish waters and ineffective in freshwater (Wagner *et al.*, 1996; Gavrilu *et al.*, 2000; Jelmert and Van Leeuwen, 2000; Harris, 2008). Freshwater is 10 times less conductive than seawater, zinc (-0.98 to -1.03V) corrodes at a higher voltage than magnesium (-1.60 to -1.63V) so is better suited to seawater (Morgan, 1987). If zinc anodes are removed from water they coat over with a layer of iron and/or zinc hydroxide and calcium which prevents corrosion, this can also occur if boats moorings dry out at low water or if boats are inactive for long periods of time (Gavrilu *et al.*, 2000).

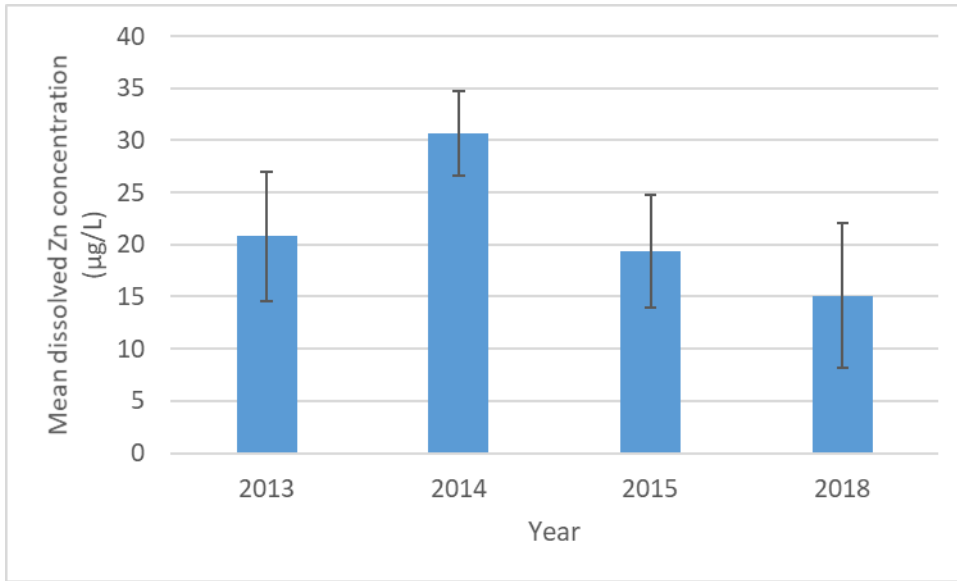
The data in Figure 5 suggests corrosion rates do decrease at lower salinities, but the range is rather narrow. Fitting a trend line to the dataset generates an r^2 of 0.74 and if accepted, then little dissolution of zinc would be expected below a salinity of 26. However, owing to the considerable variability, there is little confidence in this prediction and a further experiment in an estuary with much wider salinity ranges would be required to generate firm conclusions.

Anecdotally from the survey data, most boat owners which have reported a varied and accelerated dissolution rate are moored at Bursledon or upstream of Bursledon on the Hamble

455 estuary (above site V8 in Figure 1). The salinity in this area ranges between 17 Aluminium
456 could be an alternative for some brackish conditions in the upper reaches of the Hamble, as can
457 be used in brackish and seawater (Harris, 2008; MGDuff, 2016). Aluminium is considered less
458 of an environmental concern regarding potential toxicity than zinc in marine waters and
459 currently has no EQS set (Harris, 2008; Mao *et al*, 2011; Gabelle *et al.*, 2012) and so may be
460 more suited. Aluminium anodes are relatively widely used on marine structures such as wind
461 farms and larger vessels, so can become more widely used on pleasure craft (Gabelle *et al.*,
462 2012). The survey and discussions with boats owners indicated that only a very small
463 percentage (4 out of 131 responses) were, however, using aluminium anodes, partly due to zinc
464 being more commonly used in the past and zinc being recommended over aluminium by anode
465 manufacturers and suppliers in high to mid salinity regions. If aluminium anodes became more
466 commonly used this could reduce zinc loads to estuaries (albeit increasing aluminium loads)
467 and boat owners could experience a steadier anode corrosion rate.

468 **3.4 MAMPEC modelled dissolution rates**

469 The use of Sutton Harbour in Plymouth as a study site offered the advantages of water
470 monitoring data available over a number of years (2013 through to 2018) as well as the fact
471 that the marina has lock gates which reduce flushing considerably and therefore makes
472 modelling the dissolution of zinc much easier as the ‘system’ is in steadier state than a fully
473 flushed estuary, for example. The marina has a near full compliment of boats all year round
474 and so year on year number of boats held within the marina is relatively stable. The dissolved
475 zinc concentrations measured in the harbour (20 occasions with at least 3 replicate points within
476 the harbour each time (Figure 6) was statistically analysed to generate means and medians
477 which were input into the MAMPEC model (Deltares, 2019). Combined with measured
478 sediment concentrations (3 sites within the marina on 2 occasions), it was possible to predict
479 concentrations in the water column with relatively few input parameters fed into the model
480 (Table 2). Default values are available where monitoring information is absent. The model had
481 been thoroughly validated and used for the regulation of antifoulant paints. MAMPEC uses a
482 partitioning algorithm along with leaching rates for the anodes (or antifoulant paints) and
483 marina dimensions to apportion any chemical between the dissolved and particulate phases.



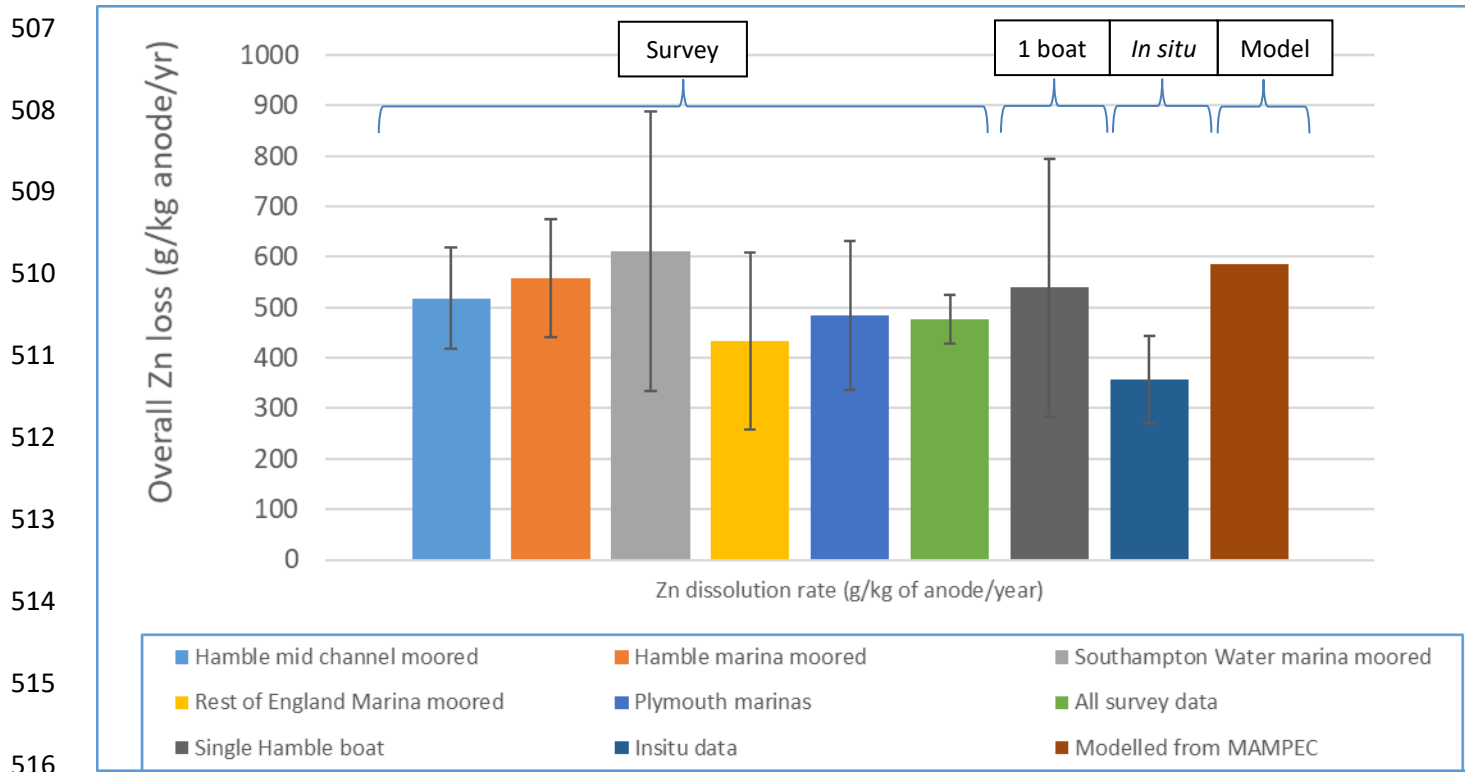
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485 **Figure 6. Measured concentrations of zinc in Sutton Marina Harbour (95% confidence**
 486 **intervals in brackets)**

487

488 The anode leaching rate ($\mu\text{g}/\text{cm}^2/\text{day}$) is derived from an estimate of wetted surface area of a
 489 vessel which is assumed to be painted with antifoulant paint. In the case of zinc dissolution
 490 from anodes, $\text{g}/\text{yr}/\text{kg}$ of anode from the survey data generated in this work can easily be
 491 converted into the appropriate units using a combination of assumed boat lengths in the marina
 492 (mean of 8.8m) from which the wetted surface area is generated from an algorithm within
 493 MAMPEC. The leaching rate was then adjusted until the predicted dissolved concentration of
 494 zinc (taking account of measured sediment and background dissolved zinc concentrations)
 495 matched the observed mean. Using this back calculation a dissolution rate of $28 \mu\text{g}/\text{cm}^2/\text{day}$
 496 required to generate $19.4 \mu\text{g}/\text{l}$ of zinc in the marina produced a zinc dissolution value of 587
 497 $\text{g}/\text{yr}/\text{kg}$ of anode, which was in line with survey estimates taking account of 95% confidence
 498 intervals (Figure 7).

499 It has to be accepted, however, that this is an overestimation as there are a number of other
 500 sources that contribute to Zn loading (e.g. natural background, direct and diffuse sources), also
 501 there are a number of assumptions used to generate this value including flushing rates, the
 502 salinity being stable over time and numbers and weights of anodes, and that variability in these
 503 assumptions or estimates can be considerable. However, the fact that the prediction produces a
 504 dissolution rate similar to the survey data, yet uses a completely different technique to generate
 505 the outcome, provides further confidence that the loss of zinc from anodes of boats is within
 506 this range.



517 **Figure 7. Zinc dissolution rates for all methods tested**

518 **4. Conclusions**

519 Based on the varying methodologies presented here, it is recommended that for future risk
 520 assessments or source apportionment exercises that a value of 477 g/yr/kg of anode be applied.
 521 This is the mean value for all survey data from 131 boat owners across the UK. For a more
 522 conservative value (from the perspective of impacting dissolved zinc concentrations) 526
 523 g/yr/kg of anode which is the mean value for the boat owner survey plus the 95% confidence
 524 interval. Furthermore using a mean weight of 2.0 kg per boat, generates a total loss of zinc per
 525 boat per year of 2.9 and 1.9 kg whether using the mean or median number of anodes per vessel
 526 respectively (using a dissolution rate of 477 g/yr/kg of anode). Scaling up this dissolution rate
 527 for an estimated 382,000 leisure boats in England and Wales (BMF et al, 2013), generates a
 528 total load of zinc from leisure boats of between 740 and 1117 tonnes per year depending on
 529 using the mean or median number of anodes per boat respectively.

530 It may be further concluded that from the laboratory experiments, a cadmium dissolution rate
 531 of between 23 and 173 µg/yr/kg of anode is calculated depending on the anode type, which if
 532 multiplied up by the mass and number of anodes used in England and Wales generates a
 533 cadmium release into estuarine and coastal environments of between 53 and 405kg per year.

534 Accepting that the laboratory tests may not be a true representation of the actual environment
535 this is still a significant discharge for a priority hazardous substance.

536 This data therefore clearly shows that there are significant benefits to limiting the amount of
537 cadmium present in the commercially available anodes, without impacting on their efficiency.
538 It may therefore be recommended that the quality of zinc anodes be more consistent and inline
539 with the specification set out by the US Military, with a review of the cadmium content to set
540 it as low as practicable.

541

542 **Acknowledgments**

543 The authors would like to thank the former Hamble Harbour Masters David Evans and Wendy
544 Stowe for their guidance and help with this survey and everyone else at the Harbour Board who
545 have assisted especially Andy Melhuish and Alison Fowler. Thanks also go to all the boat
546 owners on the Hamble and in Plymouth who took the time to fill out the survey and the marinas
547 and harbour masters who sent out the survey to their berth holders; especially Steve Green who
548 provided his historic anodes. Thanks also goes to the International Zinc Association, Hamble
549 Harbour Board and Solent Protection Society for patially funding the project. Finally we would
550 like to thank Drs Rob Clough and Andy Fisher from the University of Plymouth for their
551 assistance in the sea water analysis.

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