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

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Abstract

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

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

1. Introduction

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

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

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

In order to safeguard vulnerable ecosystems it is necessary to manage the sources of contaminants. Therefore, to determine the risk posed by zinc anodes in estuaries, ports and marinas it is necessary to accurately determine their rate of dissolution in order to derive predicted environmental concentrations which can then be compared against environment quality standards to assess risk. However, determining dissolution rates is not nescessarily straightforward as environmental factors such as salinity may play a significant role in the dissolution rates. Furthermore, there is also a question as to whether the elemental composition of the anode varies among suppliers and if that could also impact the zinc dissolution rate. Anode impurities may also pose a risk to the aquatic environment, particularly for metals of international concern including cadmium. Concerns regarding the quality and effectiveness of zinc anodes resulted in the current U.S. Military Specification, A-18001K (Boat US, 2016) which was set on the basis of different effectiveness of corrosion control being observed for similar vessels treated with apparently the same zinc anode protection. Some anodes were observed to become passivated when a white crust formed on their surface, identified as iron oxides caused by excessive impurities (mainly iron) in the product. The formation of the crust made the anodes inactive allowing corrosion to take place elsewhere in the vessel. The set specification therefore limited the amount of impurities in the zinc used, resulting in the requirement to use high grade zinc and strict manufacturing practices to guarantee performance.

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

2. Method

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

2.1 Survey of boat owners

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

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

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

2.2 *In situ* anode dissolution experiment

Hanging anodes were also acquired for an *in situ* anode experiment, these were weighed to two decimal places before the experiment and again after the experiment to determine the dissolution rates at each site in the river. The anodes were analysed using X Ray Fluorescence (XRF) to determine their elemental composition (see section 2.3 for details).

Once the anodes were weighed and analysed for initial elemental composition, they were securely attached to steel piles within the estuary from Hamble-Le-Rice up to Bursledon Bridge (Figure 1) at three different depths close to the low water level to maximise the time anodes were in the water during the tidal cycle. The anodes were installed in the estuary for 1 year between February 2016 and 2017.

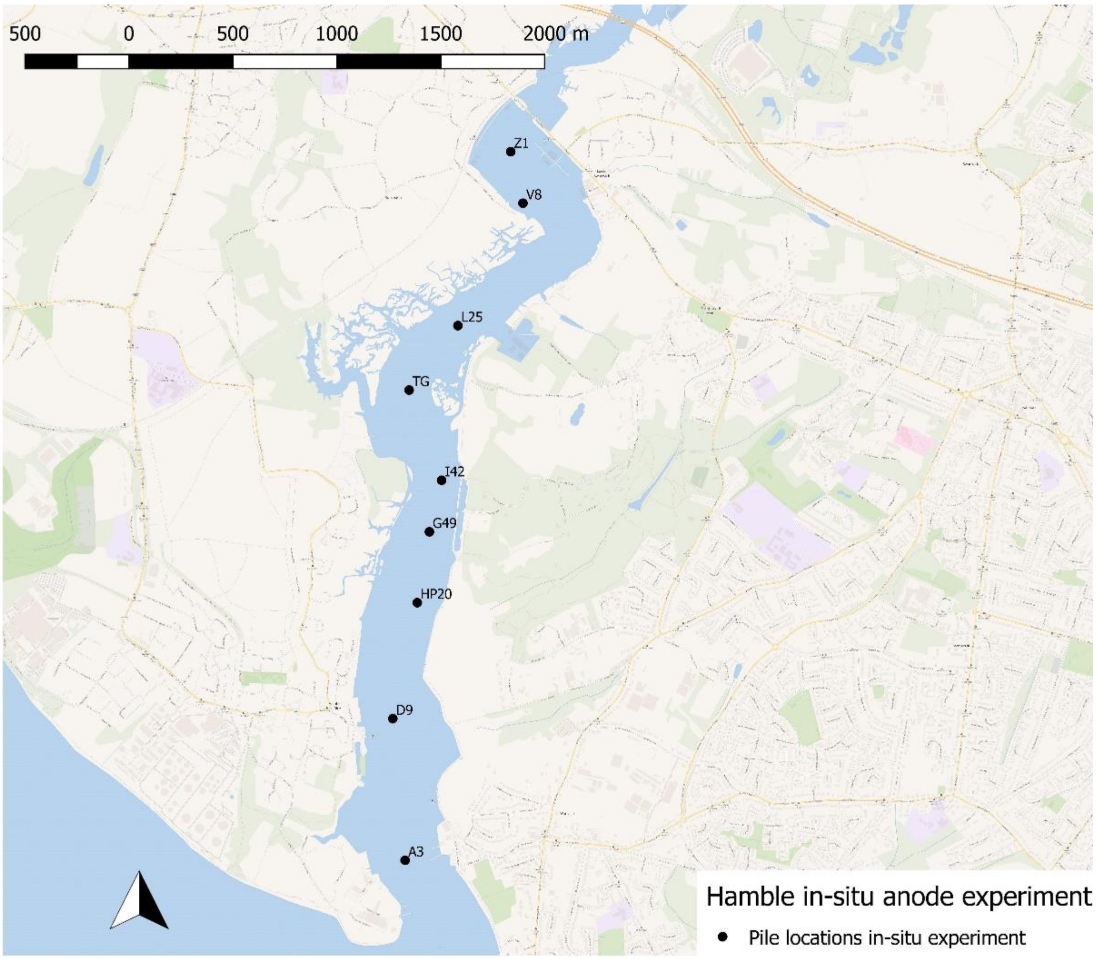

Figure 1. Location of anode sites for *in-situ* anode experiment (site NGR coordinates: A3 = SU487,060; D9 = SU485,069; HP20 = SU487,072; G49 = SU488,075; I42 = SU488,079; TG= SU487,083; L25= SU489,087; V8 = SU492,092; Z1= SU491,094)

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

2.3 XRF analyses of zinc anodes

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

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

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

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

2.4 Concentrations of zinc in marina water

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

2.5 Laboratory experiments and water analysis for cadmium dissolution experiment

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

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

2.6 Anode corrosion rate calculation

The corrosion rate was calculated using the weight of each new anode and the percentage of the anode reported to have corroded after one year (the recommenced service life for an anode). Where anodes were replaced at longer or shorter time intervals then the weight and percentages were calculated and normalised to a year. To account for the different numbers and sizes of anodes used on different vessels, all calculations were normalised to g of zinc dissolved per year per kg of anode used. Using this basic unit it was then possible to multiply up by the mean or median mass of each anode and mean or median number of anodes per vessel to generate a dissolution rate per vessel.

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

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

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

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

Table 1 MAMPEC input values and defaults

Input parameter	**Value assigned**
Leaching rate (µg/cm^2/day)	28
Zn sediment:water partition coefficient (m^3/kg) based on measured dissolved and sediment Zn levels in Sutton Harbour.	20
Background Zn (µg/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 (µg/l)	21.4
Predicted dissolved Zn (µg/l)	19.4
Observed mean Zn in Sutton Harbour (µg/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)

3. Results and Discussion

3.1 Anode elemental composition and potential to leach impurities

XRF analyses for the surface of new anodes was carried out to determine the metal content and to see if anodes met the US Military standards for anodes (Wagner et al., 1996; Harris, 2008; Boat U.S, 2016). Surface samples were used to be representative of the area of the anode directly in contact with the water. Within anode elemental composition was reasonably consistent, but unsurprisingly variation was greater near to the limits of detection, reflecting both the analytical variability near to the detection limits as well as difficulties in manufacturing processes controlling impurities at low levels. Anode-to-anode (or among anode) elemental composition also varied for the same type of product, again relatively low for zinc but much greater for the minor impurities (Table 2) (Wagner *et al.*, 1996; Boat U.S, 2016). Zinc levels ranged from 96.8 to 99.5%, with 8 of the 10 types of anode tested having means less than the US Military specification of 99.3% with 95% confidence (Table 2).

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

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

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

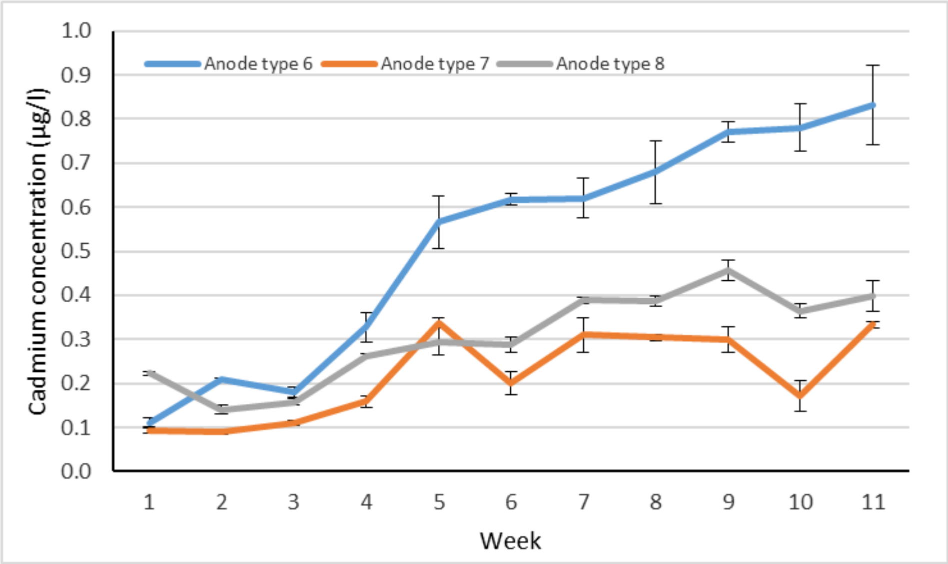

Figure 2. **Cadmium concentrations leached into seawater during laboratory testing (error bars are 95% confidence intervals for the ICP analysis)**

3.2 Zinc anode corrosion rates calculated using survey data

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

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

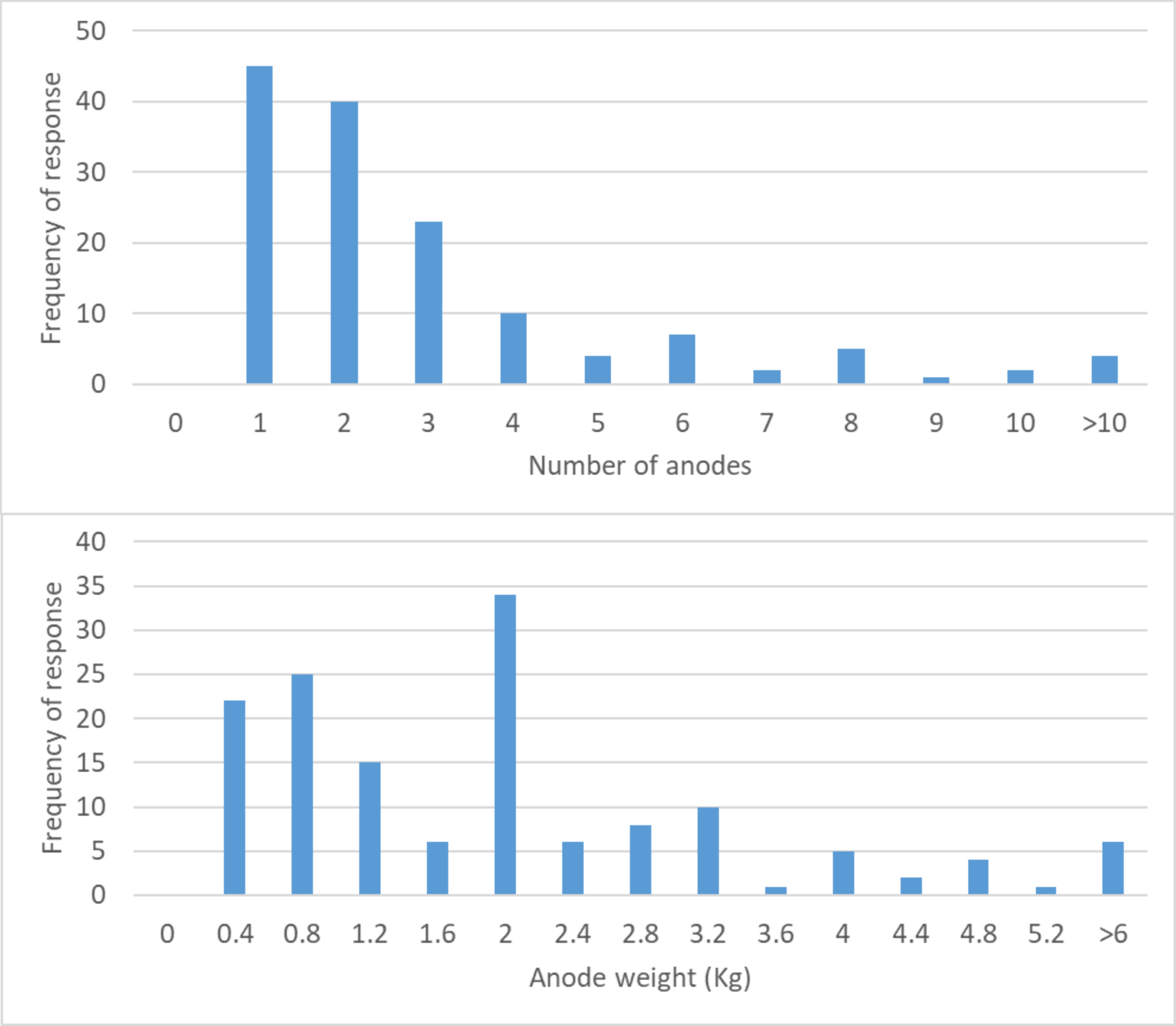

Figure 3. Histograms for the boat owner survey data from the Hamble estuary, showing number of anodes (top) and weight of anode (bottom) used per vessel

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

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

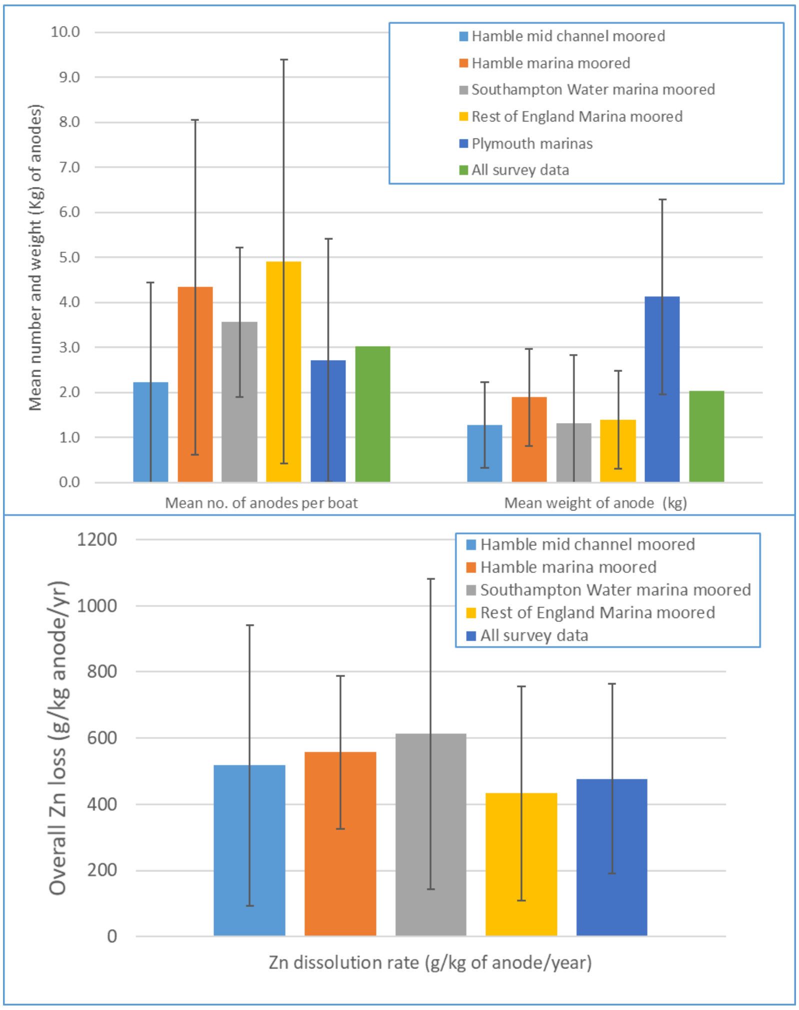

Figure 4. Boat owner survey data (131 responses) mean and 95% confidence intervals (brackets).

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

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

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

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

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

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

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

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

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

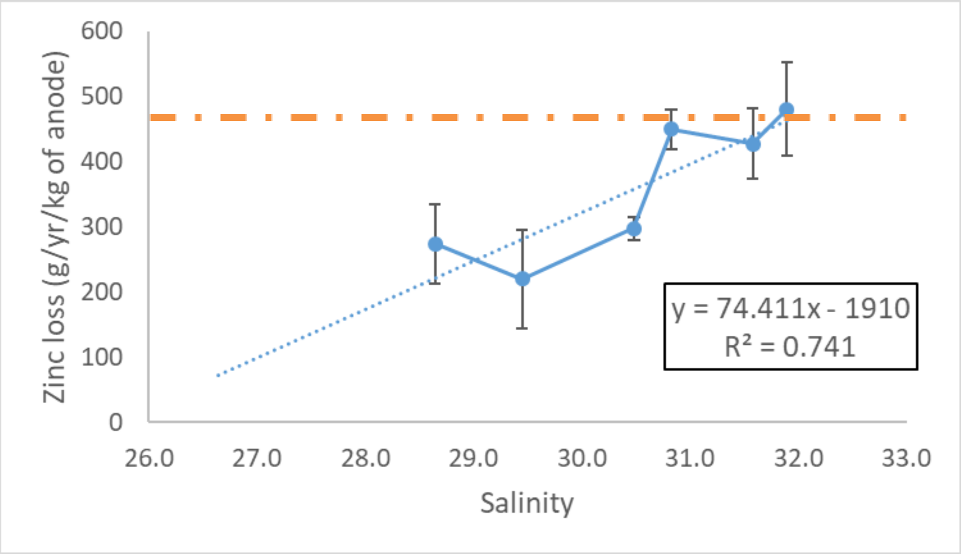

Figure 5. Impact of salinity on zinc loss from anodes versus salinity (95% confidence intervals in brackets). Red dashed line denotes calculated mean zinc loss from anodes from boat owner survey.

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

3.4 MAMPEC modelled dissolution rates

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

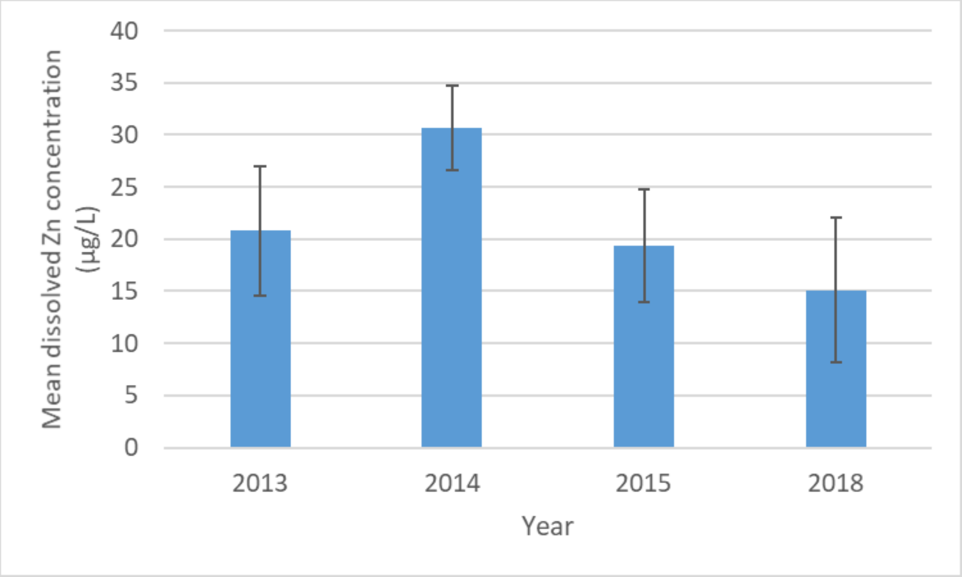

Figure 6. **Measured concentrations of zinc in Sutton Marina Harbour (95% confidence intervals in brackets)**

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

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

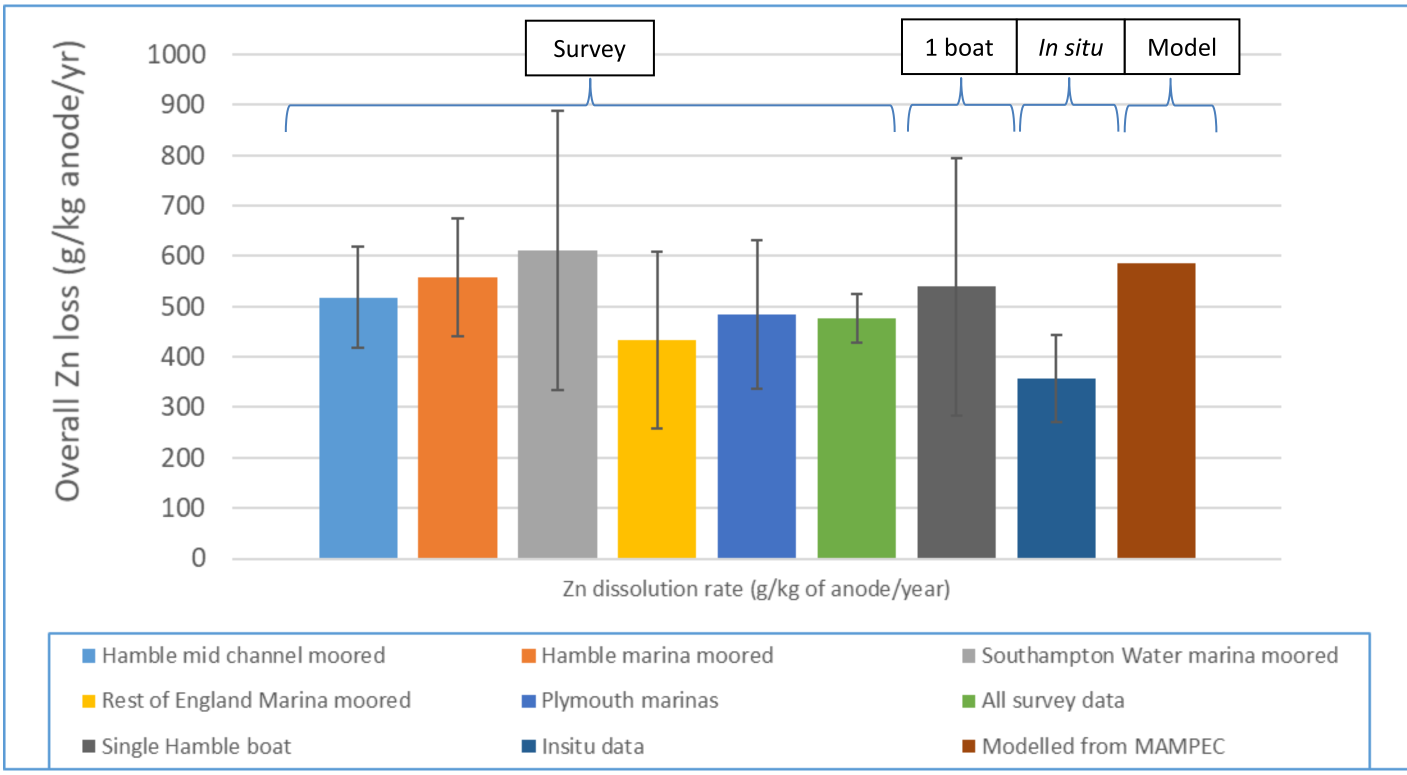

Figure 7. Zinc dissolution rates for all methods tested

4. Conclusions

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

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

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

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

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References

ACE Group, (2014), Stray electric current safety checklist for marinas and yacht clubs, available online: http://www.acegroup.com/us-en/assets/marine-facilities-insurance-stray-electric-current-tip-sheet.pdf last accessed 17/10/2016.

Bird P., Comber S.D.W., Gardner M.J. & Ravenscroft J. (1996) Zinc inputs to coastal waters from sacrificial anodes. The Science of the Total Environment, 181: 257-264.

Briant N., Bancon-Montigny C., Elbaz-Poulichet F., Freydier R., Delpoux S and Cossa D., (2013) Trace elements in the sediments of a large Mediterranean marine (Port Camargue, France): Levels and contamination history, *Marine Pollution Bulletin,* 73: 78 – 85

British Marine Federation, (2014) Watersports Participation Survey, available online: http://www.rya.org.uk/SiteCollectionDocuments/sportsdevelopment/Watersports_survey_Market_Review_2013_Executive_Summary_.pdf last accessed 16/02/ 2016..

BoatU.S, (2016), Types of Marine Corrosion, available online: http://www.boatus.com/boattech/articles/marine-corrosion.asp last accessed 08/04/2016

Boxall A.B.A., Comber S.D, Conrad A.U., Howcroft J. and Zaman N., (2000) Inputs, monitoring, and fate modelling of Antifouling Biocides in UK estuaries, Marine Pollution Bulletin, 4: 898-905.

Caplat, C., Oral, R., Mahaut, M.L., Mao, A., Barillier, D., Guida, M., Della Rocca, C., and Pagano, G., (2010) Comparative toxicities of aluminum and zinc from sacrificial anodes or from sulfate salt in sea urchin embryos and sperm. Ecotoxicology and Environmental Safety 73: 1138–1143.

Cathery, T.M., (2014). An evaluation into the impacts of marinas as a source of zinc concentrations to the Tamar Estuary and Plymouth Sound. Plymouth University Bsc Thesis.

Comber S D W, Gunn A M and Whalley C (1995) Comparison of the partitioning of trace metals in the Humber and Mersey estuaries. Marine Pollution Bulletin, 30, 12, 851-860.

Corrosionpedia, (2015), Stray Current Corrosion, available online: https://www.corrosionpedia.com/definition/1033/stray-current-corrosion last accessed 08/04/2016.

Deborde J., Refait P., Bustamante P., Caplat C., Basuyaux, O. (2015) Impact of Galvanic Anode Dissolution on Metal Trace Element Concentrations in Marine Waters. Water, Air, and Soil Pollution, Springer Verlag, 226 (423), 1-14.

Deltares (2019) MAMPEC Marine antifoulant model. Accessible at: https://www.deltares.nl/en/software/mampec/.

Denton G. R. W., Morrison R. J., Bearden B. G., Houk P., Starmer J. A., and Wood H. R., (2009) Impact of a coastal dump in a tropical lagoon on trace metal concentrations in surrounding marine biota: A case study from Saipan, Commonwealth of the Northern Mariana Islands (CNMI), *Marine Pollution Bulletin,* 58: 424 – 455.

Environment Agency, (2016), Water quality data archive, available online: http://environment.data.gov.uk/water-quality/view/landing last accessed 13/10/2016.

Gabelle C., Baraud F., Biree L., Gouali S., Hamdoun H., Rousseau C., van Veen E., Leleyter L., (2012), The impact of aluminium sacrificial anodes on the marine environment: A case study, Applied Geochemistry, 27; 2088-2095.

Gavrila M., Millet J. P., Mazille H., Marchandise D and Cuntz J. M., (2000), Corrosion behaviour of zinc–nickel coatings, electrodeposited on steel, Surface and Coatings Technology, 123: 164–172.

Harris C., (2008, March) How to conquer corrosion, Sailing Today, P102 – 107.

Harrison B., (2015) The extent to which sacrificial anodes act as a zinc source within marinas in Plymouth Sound, BSc Dissertation, University of Plymouth.

Jelmert A., and J. H., Van Leeuwen., (2000), Harming local species or preventing the transfer of exotics? Possible negative and positive effects of using zinc anodes for corrosion protection or ballast water tanks, Water Research, 34: 1937-1940.

Mao A., Mahaut M. L., Pineau S., Barillier D. and Caplat C., (2011) Assessment of sacrificial anode impact by aluminium accumulation in mussel Mytilus edulis: A large scale laboratory test, Marine Pollution Bulletin, 62: 2707 – 2713.

Matthiessen P., Reed J., Johnson M. (1999) Sources and potential effects of copper and zinc concentrations in the estuarine waters of Essex and Suffolk, United Kingdom. Marine Pollution Bulletin, 38: 908-920.

Maycock, D., Peters, A., Merrington, G., and Crane, M. (2012) Proposed EQS for Water Framework Directive Annex VIII substances: zinc (For consultation). Water Framework Directive - United Kingdom Technical Advisory Group (WFD-UKTAG). SNIFFER / Environment Agency.

MGDuff, (2016) Cathodic Protection, available online: http://mgduff.co.uk/ last accessed 08/04/2016.

Monbet, P. (2004) Seasonal cycle and mass balance of cadmium in an estuary with an agricultural catchment: The Morlaix River estuary (Brittany, France). Estuaries 27, 448–459.

Morgan J. H., (1987) Cathodic Protection, 2nd edition, National Association of Corrosion Engineers, Houston, Texas.

Nam D. H., Anan Y., Ikemoto T., Kim E. Y., and Tanabe S., (2005), Distribution of trace elements in subcellular fractions of three aquatic birds, Marine Pollution Bulletin, 51: 750 – 756.

Pearson H., Comber S., Braungardt C., Worsfold P, Stockdale A. and Lofts S. (2018) Determination and prediction of zinc speciation in estuaries. Environmental Science and Technology. 52(24), 14245-14255.

Rees A. B., Gallagher A., Comber S., and Wright L. A., (2017), An analysis of variable dissolution rates of sacrificial zinc anodes: A case study of the Hamble estuary, UK, *Environmental Science and Pollution Research,* 24: 21422 – 21433.

Rousseau C., Baraud F., Leleyter L and Gil O. (2009) Cathodic protection by zinc sacrificial anodes: Impact on marine sediment metallic contamination. *Journal of Hazardous Materials*, 167: 953-958.

Singhasemanon N., Pyatt E. and Bacey J, (2009), Monitoring for indicators of antifouling paint pollution in California Marinas, California Environmental Protection Agency, EH08-05, available online: https://pdfs.semanticscholar.org/1201/041ca105f38e28b40ad3a3b380de6e5107b1.pdf

Wagner P., Little B., Hart K., Ray R., Thomas D., Trzakoma-Paulette P and Lucas K., (1996) Environmental fate of sacrificial zinc anodes and influence of a biofilm, International biodeterioration and biodegradation, 151-157.

Wood J (2014) The importance of zinc sacrificial anodes within two Plymouth Marinas, MSc Thesis, Plymouth University.