



XRF measurements of tin, copper and zinc in antifouling paints coated on leisure boats[☆]



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ABSTRACT

Tributyltin (TBT) and other organotin compounds have been restricted for use on leisure boats since 1989 in the EU. Nonetheless, release of TBT is observed from leisure boats during hull maintenance work, such as pressure hosing. In this work, we used a handheld X-ray Fluorescence analyser (XRF) calibrated for antifouling paint matrixes to measure tin, copper and zinc in antifouling paints coated on leisure boats in Sweden. Our results show that over 10% of the leisure boats ($n = 686$) contain $>400 \mu\text{g}/\text{cm}^2$ of tin in their antifouling coatings. For comparison, one layer (40 μm dry film) of a TBT-paint equals $\approx 800 \mu\text{g Sn}/\text{cm}^2$. To our knowledge, tin has never been used in other forms than organotin (OT) in antifouling paints. Thus, even though the XRF analysis does not provide any information on the speciation of tin, the high concentrations indicate that these leisure boats still have OT coatings present on their hull. On several leisure boats we performed additional XRF measurements by progressively scraping off the top coatings and analysing each underlying layer. The XRF data show that when tin is detected, it is most likely present in coatings close to the hull with several layers of other coatings on top. Thus, leaching of OT compounds from the hull into the water is presumed to be negligible. The risk for environmental impacts arises during maintenance work such as scraping, blasting and high pressure hosing activities. The data also show that many boat owners apply excessive paint layers when following paint manufacturers recommendations. Moreover, high loads of copper were detected even on boats sailing in freshwater, despite the more than 20 year old ban, which poses an environmental risk that has not been addressed until now.

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1. Introduction

Marine biofouling, i.e. the attachment and colonization of microorganisms, plants and animals on submerged structures is a severe problem for both leisure crafts and the shipping industry (Yebra et al., 2004). The adverse effects include higher friction between the hull surface and water which will lead to increased fuel consumption and higher costs for hull maintenance. For example, the effect of not having a sufficient antifouling protection have been estimated to result in up to 40% increase in fuel consumption (Champ, 2000). The principal strategy to prevent fouling is to coat the hull with antifouling paints that are designed to leach biocides

from the coating's surface. In the early 1960s organotin compounds (OTs) were introduced as biocides to the paint formulations, most commonly in the form of tributyltin (TBT) and triphenyltin (TPHT) (Dafforn et al., 2011). TBT containing antifouling paints became extremely popular due to their efficiency in controlling biofouling and at low concentrations and, as a consequence, dominated the market during the 1970 and 1980s. However, due to adverse environmental effects, organotin compounds were restricted for use in antifouling paints on leisure boats (<25 m in length) in several countries in the late 1980s (Directive 89/677/EEC). The most sensitive organisms for OTs are gastropods and bivalves and the effects include endocrine disruption, impaired larval recruitment and shell malformations (Bryan et al., 1986; Alzieu et al., 1986; Alzieu, 1991). For example, it has been shown that 1–2 ng TBT/L can cause the development of male sexual characteristics in female genitalia in gastropods (termed imposex) (Bryan et al., 1986; Garaventa et al., 2006; Antizar-Ladislao, 2008). Today, TBT and TPHT are considered to be among the most hazardous compounds

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that have ever deliberately been released to the marine environment. Due to adverse effects on the marine environment, the coatings were prohibited in 1989 in the European Union for use on leisure boats (<25 m in length), and since 2008 there is a global ban on TBT for all ships through the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS-convention) adopted by the International Maritime Organization (IMO). Since the degradation of TBT in sediments has shown to be slow, with reported half-lives ranging from years to decades (Cornelissen et al., 2008; Viglino et al., 2004), harbours and marinas worldwide still hold sediment concentrations exceeding environmental quality standards (EQS). For example, the status classification of TBT in the Baltic Sea shows 65% of the sites to be classified as either “bad” or “poor” (HELCOM, 2010a). The highest concentrations are reported from harbours, but also sediments in the deep central parts of the Baltic Proper contained TBT at levels above the threshold value for “bad status” (>50 µg/kg ww) (HELCOM, 2010b).

Today, the antifouling paint market is dominated by copper- and zinc-based paints. Unlike most marine areas within the EU, the Baltic Sea faces special conditions in terms of salinity and tides, as well as the high number of vessels. Therefore, the Swedish Chemicals Agency (KEMI) has developed a different model for assessing the environmental risk of antifouling paints, applying more protective PNECs (Predicted No Effect Concentrations) for brackish water than for marine water. This allows the use of paints containing maximum 8.5% Cu₂O in the Baltic Sea and up to 35% Cu₂O on the Swedish West coast (i.e. the North Sea). In freshwater, all biocide-containing paints have been prohibited since 1993 (Debourg et al., 1993).

In 2012, the Swedish Agency for Marine and Water Management (SWAM) initiated a study to assess if maintenance work, i.e. pressure hosing of leisure boats contributes to the spread of contaminants to the marine environment. The results from the study showed that the wastewater produced from pressure hosing contained TBT concentrations as high as 14,000 ng/L (median value 1600 ng/L n = 15) (Ytreberg, 2012). That can be related to the annual environmental quality standard (EQS) value of TBT according to the Marine Strategy Framework Directive (MSFD) which is set at 0.2 ng/L.

Standardized protocols exist for chemical analysis of organotin compounds in several matrices including soil, sediment and water. However, the analytical method is time consuming, costly and involves several critical derivatization steps. Therefore, it is not an ideal method for screening purposes of large numbers of boats and ships. In a recent publication (Ytreberg et al., 2015), we describe a new cost-efficient method to screen for tin, copper and zinc in antifouling paints coated on boat hulls. The method is based on X-ray fluorescence spectroscopy (XRF) and utilizes a handheld XRF instrument which has been calibrated to analyse tin, copper and zinc concentrations in antifouling paints. The analysis is fast (30s), non-destructive and the metal concentration is expressed as µg/cm². As compared to the unit mg/kg, the advantage with expressing the concentrations in µg/cm² is that the data can be used to determine the total load of hazardous metallic compounds in antifouling paints applied on boats. No information is however given on the speciation of elements, i.e. if tin is in the form of inorganic or organic species. However, since tin is not used in paint formulations nowadays and has not, to our knowledge, been added to paint formulations in other forms than organotin it was hypothesized that if tin is present in the paint, the main fraction is in organotin forms. This was also verified by analysing five different antifouling paints for tin using the XRF method described in Ytreberg (Ytreberg et al., 2015). All paints showed tin concentrations below the instruments LOQ (own unpublished data). The aim of the current study was to determine how widespread the use of tin is on

leisure boat hulls coated with antifouling paints in Sweden. An additional aim was to determine the loads of copper and zinc in coatings on boats that are used in marine, brackish and inland waters.

2. Material and methods

2.1. XRF field measurements

A handheld XRF-analyser was used to screen and quantify the concentrations of tin, copper and zinc in antifouling paints applied on leisure boat hulls. The XRF analyser (Delta-50, Innov-X, Olympus) is powered with a 4 W, 50 kV X-ray tube. The empirical module described in Ytreberg, Lundgren, Bighiu and Eklund (Ytreberg et al., 2015) was used for the measurements. The method has a Limit of Quantification (LOQ) of 9.4 µg/cm², 35.9 µg/cm² and 73 µg/cm² (Champ, 2000), for Sn, Cu and Zn, respectively, and a 90% prediction interval (PI) of 0.78–1.28 (Sn), 0.5–2.02 (Cu) and 0.64–1.58 (Zn), respectively. The analytical time was set to 30s per measurement and the Compton normalized adjusted intensities of the K_α signals were used to derive Sn, Cu and Zn concentrations.

Leisure boats from nine different boat yards were analysed. Three of the boat yards are located in the Stockholm area (Baltic Sea), four boatyards are located in the Gothenburg area (Kattegat) and two are located in Lake Mälaren. In total 686 leisure boats were analysed and distributed as follows: 256 in the Stockholm area (i.e. brackish water), 202 in the Gothenburg area (i.e. saltwater), and 228 in Lake Mälaren (i.e. freshwater) (Fig. 1). The measurements were carried out in 2012 (N = 125), 2013 (N = 365) and 2014 (N = 196).

2.2. Calculation of metal concentrations in commercial antifouling paints

For comparison to the XRF-analysed concentrations, two different commercial copper-based antifouling paints, Mille Extra (Hempel) which is approved for the Swedish West coast and Cruiser One (International) which is approved for the Baltic Sea, were used to calculate area concentrations. In addition, tin concentrations in a TBT paint were also determined. The area concentrations were calculated using the CEPE mass-balance calculation method (Finnie, 2006), a method which is also accepted in the EU for estimating the release rate of biocides (report-workshop-report, 2006). The method calculates the total area concentration of biocides in the dry antifouling paint and estimates the sum of a 14-d cumulative initial release and a steady-state release (µg/cm²/d) for the remainder of the specified lifetime by the use of Equations (1) and (2).

$$X + \left(Y \times \left(\frac{365 \times t}{12} - 14 \right) \right) = La \times a \times Wa \times \frac{100}{vs} \rho \times DFT \quad (1)$$

$$\frac{X}{Y} = 30 \quad (2)$$

Where X is the cumulative release (µg/cm²) during the initial 14 days, Y is the steady-state release rate during the remainder of the specified lifetime of the paint (µg/cm (Champ, 2000)/d), t is the specified lifetime (months) of the paint, La is the proportion of the active ingredient in the dry film released during the life time t, a is the weight fraction (%) of active ingredient in the biocide, Wa is the percentage (w/w) of biocide in the paint formulation, vs is the volume solid content in %, ρ is the density (kg/L) of the wet paint, and DFT is the dry film thickness (µm) specified for the lifetime t.

With the exception of La and a, all the above listed parameters

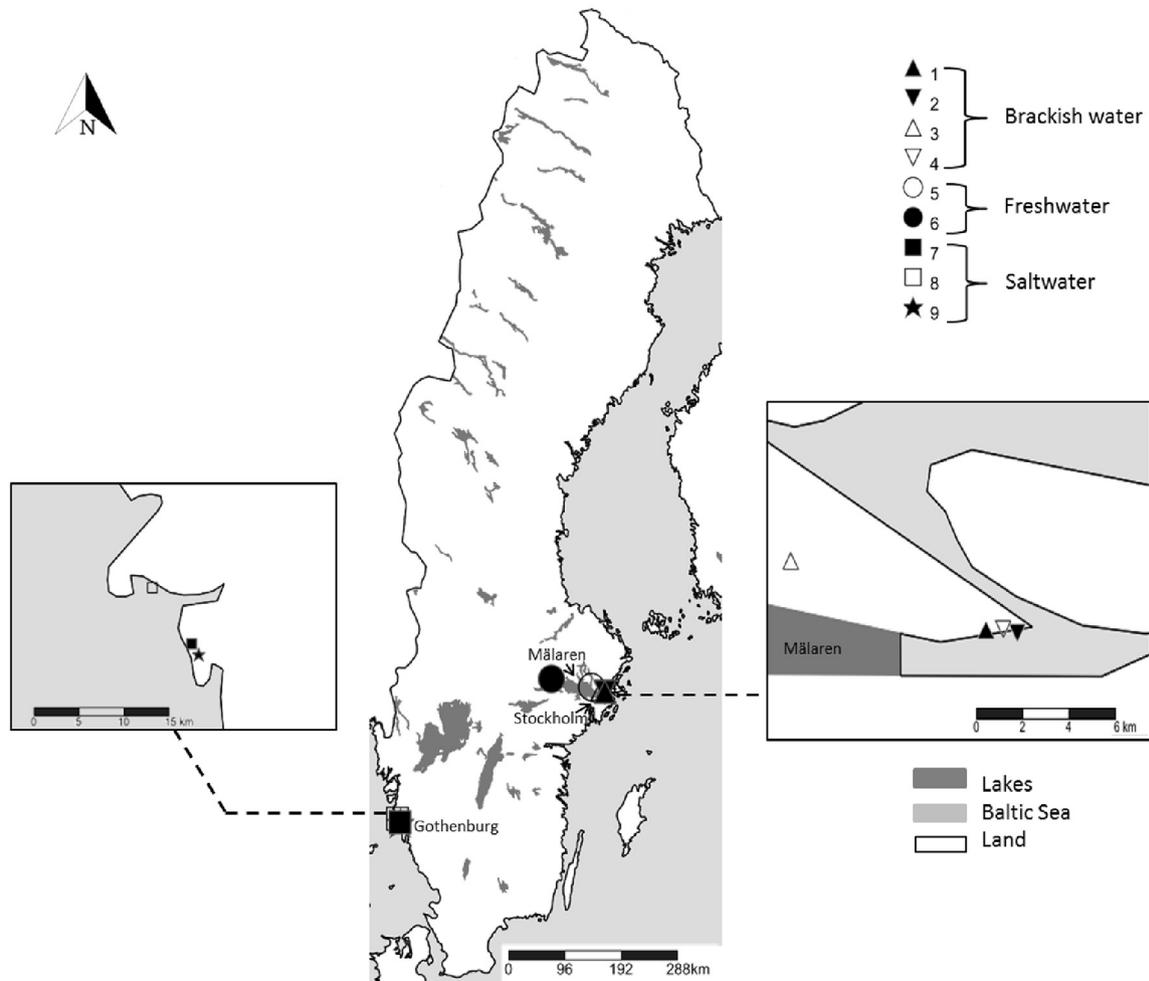


Fig. 1. Locations of the boat yards where the XRF-measurements were performed.

were taken from the safety and product data sheets of two different commercial copper-based antifouling paints (see SI table 2). The paints hold a Cu_2O concentration of 34.6% (Mille Xtra) and 8.54% (Cruiser One), i.e. W_a . The ZnO concentration is only given in an interval in the safety data sheet and thus the average value was used, i.e. 13.75% (Mille Xtra) and 17.5% (Cruiser One). The right side of Equation (3) equals the total area concentration of the specific biocide when L_a is set to 1. The weight fraction, a , in Equation (3) is for Cu 0.89 (based on Cu_2O) and for Zn 0.80 (based on ZnO). The DFT corresponding to one layer of paint was used, i.e. 40 μm (Mille Xtra) and 46 μm (Cruiser One).

The area concentration of tin in two theoretical TBT paints was determined using the same parameters as for Mille Xtra and Cruiser One, with the exception that TBT was included instead of copper and zinc. First, the average percentage (w/w) of TBT was calculated based on 14 different previously registered and by KEMI approved TBT-based antifouling paints (SI table 1). The paints contained both bis(TBTO) and Tributyltin methacrylate. Secondly, the average percentage (w/w) of Sn was calculated (corresponds to the product of a^*W_a) and used to determine the area concentration of tin in the two TBT paints.

2.3. Statistical analysis

The data was analysed using JMP software v. 12 (SAS, USA). Due to the strong skewness of the distributions, nonparametric tests

were applied, namely Kruskal-Wallis followed by Steel-Dwass multiple comparisons to check for 1) differences between boat clubs from the same region and 2) differences between regions. The level of significance was set at 0.05.

3. Results

3.1. XRF field measurements

For the saltwater region, no significant difference in metal concentrations on the boats from the three different boat clubs was observed ($p > 0.05$) (Tables 2 and 3). Similar behaviour was observed for the freshwater localities, except for copper where boat club 1 had significantly higher copper concentrations than boat club 2 ($p = 0.0003$). For the brackish water region significant differences were observed for all metals (Tables 2 and 3). However, to check for significant differences between the salinity regions, the data from all the boat clubs within each region were pooled.

3.1.1. Tin

Of all leisure boats, 67.2% showed tin concentrations $>9.4 \mu\text{g}/\text{cm}^2$, i.e. concentrations exceeding the XRF instruments' LOQ. The proportion of boats containing tin was higher in saltwater (85.6%) compared to brackish water (55.9%) and fresh water (63.6%) (Table 1a,b,c). The area concentration of tin was also significantly higher on boats from saltwater locations (median 53 $\mu\text{g}/\text{cm}^2$)

Table 1a

Distribution of tin on leisure boats from areas with different salinities; the values represent percentage of boats.

Region	$\mu\text{g}/\text{cm}^2$ Sn						
	n.d.	9.4–99	100–199	200–399	400–799	800–1599	>1600
freshwater (n = 228)	36.4	37.3	9.6	6.6	6.6	3.1	0.4
brackish water (n = 256)	44.1	39.1	5.9	4.7	3.1	2.7	0.4
saltwater (n = 202)	14.4	56.9	6.9	5.9	8.4	5.9	1.5
All boats (n = 686)	32.8	43.7	7.4	5.7	5.8	3.8	0.7

n.d. = not detected.

Table 1b

Distribution of copper on leisure boats from areas with different salinities; the values represent percentage of boats.

Region	$\mu\text{g}/\text{cm}^2$ Cu						
	<35.9	35.9–999	1000–1999	2000–3999	4000–7999	8000–15,999	>16,000
freshwater (n = 228)	20.6	31.6	10.5	19.7	11.8	3.9	1.8
brackish water (n = 256)	7.8	22.7	17.2	14.1	19.1	14.1	5.1
saltwater (n = 202)	0.0	7.9	8.9	10.9	16.3	25.2	30.7
All boats (n = 686)	9.8	21.3	12.5	15.0	15.9	14.0	11.5

Table 1c

Distribution of zinc on leisure boats from areas with different salinities; the values represent percentage of boats.

Region	$\mu\text{g}/\text{cm}^2$ Zn						
	<73	73–999	1000–1999	2000–3999	4000–7999	8000–15,999	>16,000
freshwater (n = 228)	20.2	35.1	14.5	9.2	14.0	6.1	0.9
brackish water (n = 256)	11.7	28.1	12.1	11.7	16.4	16.8	3.1
saltwater (n = 202)	1.5	7.9	8.4	19.3	31.7	26.7	4.5
All boats (n = 686)	11.5	24.5	11.8	13.1	20.1	16.2	2.8

Table 2Significant differences ($p < 0.05$) in metal concentrations between boat clubs (1–9) from the same region. Statistical differences were based on Steel-Dwass comparisons for all pairs and Wilcoxon (for freshwater, i.e. 2 groups only).

Metal	Freshwater	P value	Brackish water	P value	Saltwater	P value
Sn	N/A	N/A	6 ≠ 3	0.0142	N/A	N/A
Cu	1 ≠ 2	0.0003	5 ≠ 3; 5 ≠ 4	0.0176; 0.0195	N/A	N/A
Zn	N/A	N/A	6 ≠ 4	0.0271	N/A	N/A

Table 3

Mean and median concentrations of tin (Sn), copper (Cu) and zinc (Zn) on leisure boats from boat clubs located in freshwater, brackish water and saltwater regions.

Region	Boat club	Boats (n)	Mean ($\mu\text{g}/\text{cm}^2$)			Median ($\mu\text{g}/\text{cm}^2$)		
			Sn	Cu	Zn	Sn	Cu	Zn
Freshwater	1	32	105	5008	2050	17.0	3647	972
	2	196	130	1764	2219	17.0	702	684
Brackish water	3	138	79	4851	3440	10.7	2940	1253
	4	34	91	6612	2990	15.5	3447	1715
	5	72	84	3750	4976	11.0	1333	2927
	6	12	189	4737	5889	50.2	2083	5344
Saltwater	7	65	191	10,480	5535	28.0	7034	4439
	8	32	160	13,820	7655	38.8	10,687	6109
	9	105	192	13,681	6733	62.0	12,274	5815

(Champ, 2000)) compared to brackish (median 13 $\mu\text{g}/\text{cm}$ (Champ, 2000)) or freshwater (median 17 $\mu\text{g}/\text{cm}$ (Champ, 2000)) ($p < 0.0001$). The distribution of tin was skewed with a domination of low (9.5–100 $\mu\text{g}/\text{cm}^2$) tin concentrations (Table 1a,b,c, Fig. 2a). Nonetheless, high (>400 $\mu\text{g}/\text{cm}^2$) tin concentrations were observed on 15.8, 6.3 and 10.1% of the boats moored in saltwater, brackish and freshwater, respectively.

3.1.2. Copper

The concentrations of copper were significantly higher on leisure boats in saltwater (median 9536 $\mu\text{g}/\text{cm}$ (Champ, 2000)) in comparison to boats from brackish water (2400 $\mu\text{g}/\text{cm}^2$) and freshwater (900 $\mu\text{g}/\text{cm}^2$) ($p < 0.0001$). In saltwater, all boats (n = 202) contained copper above the XRF instrument's LOQ of 35.9 $\mu\text{g}/\text{cm}^2$. About 8% of the boats from the brackish water region showed no copper (concentrations <35.9 $\mu\text{g}/\text{cm}^2$) in their coatings.

For the freshwater region, the corresponding proportion was higher: 20.6% of the leisure boats displayed copper concentrations lower than 35.9 $\mu\text{g}/\text{cm}^2$. The proportion of boats containing copper concentrations >16,000 $\mu\text{g}/\text{cm}^2$ was considerable higher in saltwater (30.7%) compared to brackish water (5.1%) and freshwater (1.8%) (Table 1a,b,c, Fig. 2b).

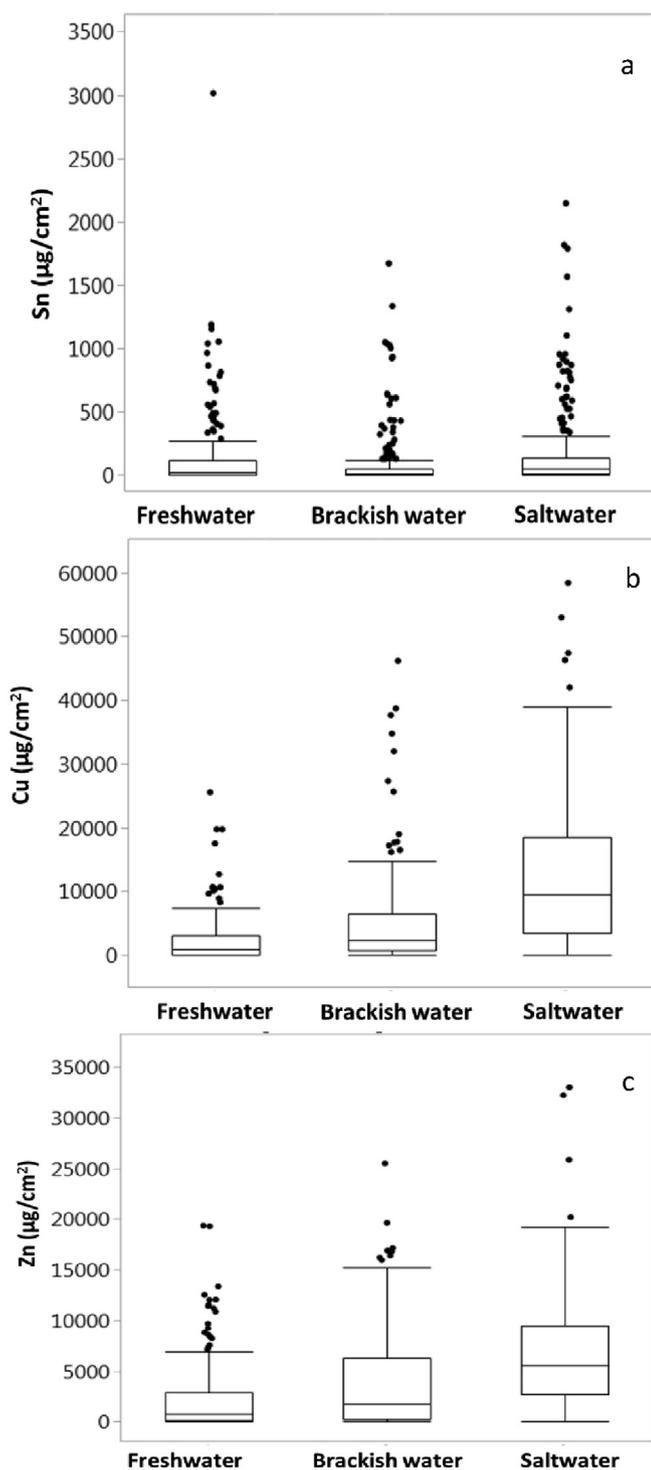


Fig. 2. a,b,c Area concentrations of tin (Sn), copper (Cu) and zinc (Zn) on boats from regions with different water salinities; the horizontal line within the boxes is the median and the lower and upper limits of the box represent the 25th and 75th quantiles, respectively.

3.1.3. Zinc

As for copper, the concentration of zinc was highest on leisure boats in saltwater (median 5571 $\mu\text{g}/\text{cm}^2$ (Champ, 2000)) followed by brackish water (median 1808 $\mu\text{g}/\text{cm}^2$ (Champ, 2000)) and freshwater (median 791 $\mu\text{g}/\text{cm}^2$ (Champ, 2000)) ($p < 0.0001$) (Table 1a,b,c, Fig. 2c). Only 1.5% of the boats from the “saltwater”

category had no zinc ($<73 \mu\text{g}/\text{cm}^2$) in their coatings. About 9% of the boats from brackish water showed no zinc in their coatings. The corresponding proportion was 26.8% for the freshwater boats.

3.2. Metal concentrations in commercial antifouling paints

The calculated copper and zinc concentration in one layer (40 μm) of Mille Xtra was 4019 $\mu\text{g}/\text{cm}^2$ (Champ, 2000) and 1625 $\mu\text{g}/\text{cm}^2$ (Champ, 2000), respectively. For Cruiser One, the corresponding copper concentration in one layer (46 μm) was lower, 1107 $\mu\text{g}/\text{cm}^2$, while the zinc concentration was higher, 2009 $\mu\text{g}/\text{cm}^2$. The calculated tin concentration in one layer of the TBT paint was 772 $\mu\text{g}/\text{cm}^2$ (Champ, 2000) (based on the properties of Mille Xtra) and 861 $\mu\text{g}/\text{cm}^2$ (Champ, 2000) (based on the properties of Cruiser One).

4. Discussion

4.1. Tin

OT coatings, primarily based on TBT and TPhT compounds, were used extensively in the 1970 and 1980s. To our knowledge, tin has never been added into paint formulations in other non-toxic forms such as inorganic species. The XRF analysis of three different primers and seven different commercial antifouling paints did not show the presence of tin in any of the coatings (data not shown here).

The XRF-results presented here show that the majority of the boats had tin present on their hulls mostly in concentrations $<100 \mu\text{g}/\text{cm}^2$. A lower proportion, 4.5% of all boats, contained tin concentrations $>800 \mu\text{g}/\text{cm}^2$. For comparison, one layer of coating of the theoretical TBT-paints equals $\approx 800 \mu\text{g Sn}/\text{cm}^2$. On 10 boat hulls where tin was detected, we performed additional XRF measurements by progressively scraping off the top coatings and analysing each underlying layer. When tin was detected, it originated in the paint layer closest to the hull and was covered with several layers of other coatings. Thus, leaching of OT compounds from the hull to the water is presumed to be negligible. The risk for environmental impacts arises during maintenance work such as scraping, blasting and high pressure hosing activities (Eklund et al., 2014; Turner et al., 2015; Turner, 2010; Eklund and Eklund, 2014).

Since the XRF analysis does not provide any information on tin speciation, the results presented here cannot be seen as a quantitative measurement of organotin compounds. The successive degradation of TBT to the less toxic compounds dibutyltin (DBT) and monobutyltin (MBT) and ultimately inorganic tin has shown to be governed primarily by microbial activity (Barug, 1981). Also UV radiation and increasing temperature have been shown to accelerate the degradation (Antizar-Ladislao, 2008; Navio et al., 1993). The half-life of TBT in sediments has been reported to be in the range of years to decades (Cornelissen et al., 2008; de Mora et al., 1995). To our knowledge, no data is available on the degradation of OT compounds in antifouling paints, but since the microbial mediated degradation is assumed to be negligible in paint formulations, the XRF measured tin concentration on the boat hulls can be assumed to hold a high proportion of OT compounds.

4.2. Copper and zinc

The median area concentrations of copper and zinc followed the expected trend with highest concentrations on boats originating from saltwater areas followed by brackish water and freshwater areas. In freshwater, approximately 20% of the boats showed no copper or zinc in their coatings. In addition, one third of the boats had low ($<1000 \mu\text{g}/\text{cm}^2$) concentrations of copper and zinc. As shown previously, the CEPE-calculated area concentrations of

copper and zinc in one layer of the Baltic Sea paint Cruiser One is 1107 and 2009 $\mu\text{g}/\text{cm}^2$ (Champ, 2000), respectively. The corresponding area concentration of copper and zinc in the West coast paint Mille Xtra was 4019 $\mu\text{g}/\text{cm}^2$ (Champ, 2000) and 1625 $\mu\text{g}/\text{cm}^2$ (Champ, 2000), respectively. Approximately 17.5% of the freshwater boats had copper concentrations $>4000 \mu\text{g}/\text{cm}^2$, which corresponds to four layers of Cruiser One or one layer of Mille Xtra. Because the use of biocides is restricted in antifouling paints applied on boats moored in freshwater, copper and zinc may instead leach both into the water and on land during maintenance work (Eklund et al., 2014; Turner et al., 2015).

The data suggest that there is an overuse of paints, particularly on the boats originating from saltwater locations: almost one third of the boats had copper concentrations $>16,000 \mu\text{g}/\text{cm}^2$, i.e. more copper than four layers of Mille Xtra. Thus, a leisure boat with an average copper concentration of $16,000 \mu\text{g}/\text{cm}^2$ and a painted surface area of 20 m^2 would hold a total copper load of 3.2 kg. According to the CEPE-mass balance module, the leached copper load during the first 14d from Mille Xtra is $550 \mu\text{g}/\text{cm}^2$ and the steady state release rate during the rest of the paints' lifetime is $6.3 \mu\text{g}/\text{cm}^2/\text{d}$. Thus, the total copper load leached from a 20 m^2 leisure boat during a Scandinavian boating season (5 months) is 0.28 kg. Nonetheless, the paint manufacturer recommends that two layers of Mille Xtra should be applied for Scandinavian waters per season, which equals 1.6 kg Cu, assuming the same hull area of 20 m^2 . This is an overuse of paints and by following these recommendations, boat owners will only build up unnecessary layers of coatings on their hulls every year.

5. Conclusions

This is, to our knowledge, the first study that has used handheld XRF to measure metals in antifouling coatings applied on leisure boats. Since the analysis is fast (30s), a rapid overview of the use of antifouling paints in different boating areas can be achieved. The current study showed the majority of the boats from freshwater environments to hold copper in their coatings despite a more than 20 year old ban. The data also showed tin to be present in high concentrations in antifouling paints on leisure boats. Of all leisure boats analysed ($n = 686$), 10.3% contained tin concentrations $> 400 \mu\text{g}/\text{cm}^2$. This work can have important implications for regulatory authorities in their ongoing efforts to apply necessary measures to cease out, in particular, emissions of TBT to the marine environment. This is particularly important since wastewater produced during hull cleaning has been shown to contain TBT concentrations that exceed the EQS-value by a factor of 10,000. Hence, by using this XRF application leisure boats with high area concentration of Sn (indicative that the paint consists of TBT) can be identified and appropriate measures can be adopted, e.g. removal of paint.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.03.029>.

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