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Antifouling paints leach copper in excess – study of metal release rates and efficacy along a salinity gradient

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ABSTRACT

Antifouling paints are biocidal products applied to ship and boat hulls in order to prevent the growth and settlement of marine organisms, i.e. fouling. The release of biocides from the surface of the paint film act to repel or poison potential settling organisms. Currently, the most commonly used biocide in antifouling paints is cuprous oxide. In the EU, antifouling products are regulated under the Biocidal Products Regulation (BPR), which states that the recommended dose should be the minimum necessary to achieve the desired effect. For antifouling products, the dose is measured as the release rate of biocide(s) from coating. In this study, the release rates of copper and zinc from eight different coatings for leisure boats were determined through static exposure of coated panels in four different harbors located in Swedish waters along a salinity gradient ranging from 0 to 27 PSU. The results showed the release rate of copper to increase with increasing salinity. Paints with a higher content of cuprous oxide were also found to release larger amounts of copper. The coatings' ability to prevent biofouling was also evaluated and no significant difference in efficacy between the eight tested products was observed at the brackish and marine sites. Hence, the products with high release rates of copper were equally efficient as those with 4 – 6 times lower releases. These findings suggest that current antifouling paints on the market are leaching copper in excess of the effective dose in brackish and marine waters. Additionally, the results from the freshwater site showed no benefit in applying a copper-containing paint for the purpose of fouling prevention. This indicates that the use of biocidal paints in freshwater bodies potentially results in an unnecessary release of copper. By reducing the release rates of copper from antifouling paints in marine waters and restricting the use of biocidal paints in freshwater, the load of copper to the environment could be substantially reduced.

1. Introduction

Antifouling paints are biocidal products applied to boat and ship hulls in order to avoid the colonization of the hull surface by fouling organisms (Almeida et al., 2007). In the EU, these products are regulated under the Biocidal Products Regulation (BPR) (European Parliament and Council, 2012). The BPR (Annex VI Art. 77) states that the recommended dose of a biocidal product should be the minimum necessary to achieve the desired effect. For antifouling products, the dose represents the speed at which active substances are delivered from the surface of the coating to the surrounding water, i.e. its biocidal release rate which is measured in µg/cm^2/day. Art. 19 (1) of the BPR further states that authorization of a biocidal product will only be granted according if that product is shown to be sufficiently effective.

The efficacy of an antifouling paint is typically evaluated through simulated field tests whereby treated panels are exposed in seawater under static and/or dynamic conditions (Kojima et al., 2016). Static raft tests are generally considered to represent worst case scenarios as static hydrodynamic conditions are generally more favorable for the settlement of fouling organisms (Cassé and Swain, 2006). Patch tests can also be performed which involve painting patches or strips with the coating on vessel hulls (European Chemical Agency, 2018). Whereas static tests may indeed be considered a worst case scenario for ship paints, the conditions of such tests are not far removed from those of recreational vessels which tend to be idle for large periods of time. In Sweden, leisure boats are for example only actively used during 10%

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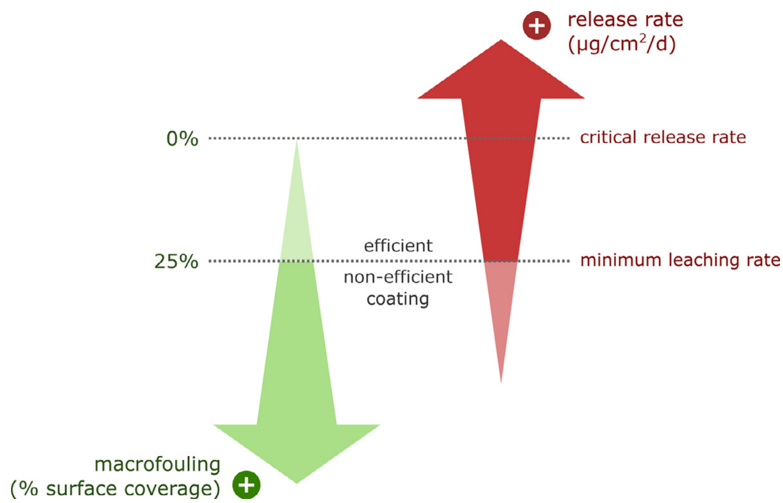

Fig. 1. Schematic overview of the relationship between macrofouling coverage and biocidal release rate for antifouling paints. The efficacy threshold of 25% surface coverage of macrofouling is that of the EU efficacy guidelines for biocidal products (European Chemical Agency, 2018). The minimum leaching rate is the lowest necessary release rate to achieve the desired effect, in accordance with the BPR (European Parliament and Council, 2012). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Critical release rates of Cu for some marine organisms determined for Atlantic waters (* Scotland, UK or **Netherlands).

Organism	Critical Cu release rate (µg/cm2/d)	Reference
Algae		
"Brown Mats" (algal growth)	20*	Barnes, 1948
Unspecified	22**	de la Court, 1988
Ectocarpus, filamentous brown algae	10*	Barnes, 1948
Tube worms (*Tubularia*)	10*	Barnes, 1948
Barnacles	9*	Barnes, 1948
(*Balanus*)	16**	de la Court, 1988
Hydrozoans (*Obelia*)	4*	Barnes, 1948
Calcareous worms (*Pomotoceros*)	3*	Barnes, 1948

of the boating season according to a national survey (The Swedish Transport Agency, 2015). After exposure, the type and degree of fouling organisms present on the panel are used to assess the paint's performance. Biofouling can generally be categorized as either microfouling (bacterial and diatomic biofilms) or macrofouling (e.g., macroalgae, barnacles, mussels, oysters, tubeworms, bryozoans) (Little and Depalma, 2013). Typically, the efficacy will be determined based on the amount of macrofouling present, as this fouling type will have the largest effect on a vessel's fuel consumption as a result of the increase in drag (Holm et al., 2004). According to recent EU efficacy guidelines for biocidal products, antifouling paints in marine waters may be considered effective if static tests show a surface coverage of macrofouling $< 25\%$ (European Chemical Agency, 2018).

The critical release rate describes the leaching rate of an active substance needed to prevent the attachment of a given fouling organism (WHOI, 1952). If macrofouling is considered as a whole, the critical leaching rate (0% surface coverage of macrofouling) is thus distinct from, and should not be confused with, the minimum dose i.e. the minimum leaching rate ($< 25\%$ macrofouling). A paint with a leaching rate below the critical release rate can thus still be deemed efficient according to the EU efficacy guidelines (Fig. 1). Knowledge of the critical release rate can nonetheless give an indication of the required minimum leaching rate. There are currently ten approved active substances under the BPR (European Chemical Agency, 2020), amongst which Cu_2O (cuprous oxide) is the most commonly used (Amara et al., 2018). However, studies of the critical release rates of copper for various marine organisms are few, dated and limited to Atlantic waters (Table 1). A critical release rate of 10 µg Cu/cm^2/day has generally been assumed to be sufficient to prevent the attachment of most animal forms, although some algae may still attach at even higher leaching rates (Barnes, 1948; WHOI, 1952). This leaching rate should however only be considered as indicative, as it was determined under laboratory conditions and subsequent studies have shown that even lower leaching rates may be efficient against the settlement of e.g. barnacles (de Wolf and van Londen, 1966). Additionally, differences in fouling pressure, i.e. quantity and type of fouling organisms present, may result in differences in the critical release rate between geographic areas. Species living in the brackish water Baltic Sea are subject to constant osmotic stress, making them more sensitive to hazardous compounds (Magnusson and Norén, 2012). The critical release rates of biocides may therefore be lower in this particular sea area, as compared to marine waters.

Here, eight antifouling paints for recreational vessels containing copper and zinc were immersed along a salinity gradient (0 – 27 PSU) at four different locations along the Swedish coast during one yachting season (5 months). ZnO is typically added to most antifouling paints and serves, according to the European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE), to control the polishing rate of the paint (CEPE, 2011). The type and amount of fouling present at the end of the season was assessed, as well as the effects of salinity and metal content on the Cu and Zn release rates. With these results, the performance of the antifouling paints was assessed in relation to their Cu release rates to determine whether the products were following the guidelines of the BPR with respect to minimum leaching rate. Ultimately, the results from this and previous studies were used to estimate and

Table 2
Overview of the investigated paints. Information about the content of active substance was collected from the Swedish Chemicals Agency public pesticide register and used to derive the Cu content. The ZnO content range, as specified in the products' safety data sheets is also shown. The Zn content (± 1 standard deviation) was estimated from the reported Cu content and the average Cu:Zn ratio determined through X-Ray Fluorescence measurements ($n = 96$) on the panels prior to immersion.

Paint	Product name	Manufacturer	Color	Active substance	Cu (wt%, ww)	ZnO (wt%, ww)	Zn (wt%, ww)
H1	Lefant Nautica Copper	Lefant	Red	Cu_2O (7.0 wt%)	6.2	20 – 100	16.8 ± 0.6
H2	VC17m	International	Graphite	Cu powder (17.96 wt%)	18.0	–	–
H3	Racing VK	Jotun	Red	Cu_2O (22.02 wt%)	19.6	10 – 25	19.7 ± 0.2
H4	Hard Racing Xtra	Hempel	Red	Cu_2O (33.1 wt%)	29.4	10 – 25	13.3 ± 0.2
P1	Mille Light Copper	Hempel	Red	Cu_2O (6.1 wt%)	5.4	10 – 25	7.4 ± 0.4
P2	Cruiser One	International	Red	Cu_2O (8.5 wt%)	7.5	2.5 – 25	22.8 ± 0.4
P3	Biltema Antifouling	Biltema	Red	Cu_2O (13 wt%)	11.5	20 – 25	19.9 ± 1.1
P4	Micron Superior	International	Red	Cu_2O (31.93 wt%)	28.4	2.5 – 25	8.0 ± 0.1
Control	Underwater Primer	hempel	gray	–	–	–	–

Table 3
Information about the study sites. The temperature shown here is the average temperature ± 1 standard deviation at 1 m depth during the release rate determination.

Site	Location	Latitude	Longitude	Salinity (PSU)	Temperature (°C)
1	Lake Mälaren (Strängnäs Marina)	59.379274°	17.027013°	0	23 ± 2
2	Swedish East Coast, Baltic Sea (Nynäshamn Marina)	58.899576°	17.951985°	6.4	20 ± 3
3	Swedish West Coast, Baltic Sea (Limhamn Marina)	55.584070°	12.916962°	7.5	21 ± 3
4	Swedish West Coast, Kattegat (Kristineberg Marine Research Center)	58.250031°	11.446905°	27	21 ± 1

map the critical release rates of Cu for the Baltic Sea and Kattegat area.

2. Materials & methods

2.1. Paints and study sites

Eight antifouling paints available on the Swedish market for amateur use with copper contents ranging from ~ 6 to 30 wt% (ww) were evaluated in this study (Table 2). No booster biocides were present in any of the coatings. Four of the paints are classified as hard coatings (H1 – H4) while the other four are polishing coatings (P1 – P4) according to the paints' product data sheets. The paints were applied to 10 × 10 cm PVC (Poly Vinyl Chloride) panels. Two sets of panels were prepared: one set for efficacy (fouling) evaluation and one set for release rate determination of copper and zinc. Prior to any paint application, the panels were lightly rugged with sandpaper and a layer of primer coating (Hempel Underwater Primer) was applied. This specific primer paint was selected as it was found to contain no measurable concentrations of Cu or Zn by X-Ray Fluorescence and would thus not interfere with the release rate determination. Once coated with antifouling paint, the panels were attached to grids and immersed statically at ~1 m depth during the summer season of 2018 at four locations along the Swedish coast (Table 3). Temperature loggers (HOBO Pendant® Temperature Logger, UA-002–08) were immersed at all study sites to monitor the water temperature at 1 m depth.

2.2. Efficacy evaluation

For the panels intended for fouling rate evaluation, two coats of paint (primer and antifouling paint) were applied using 10 cm wide paint rollers. Four replicate panels were prepared for each paint and site, as well as control panels coated only with primer. The control panels were coated in order not to underestimate the fouling pressure as a previous study showed that panels painted with a biocide-free coating were significantly more fouled than unpainted panels (Wrange et al., 2020a). The panels were mounted in random order on grids and exposed for 5 months (June – October 2018) at the four study sites. Upon retrieval, the fouling on the panels was characterized and classified according to the fouling rate (FR) scale from the Naval Ships' Technical Manual (NSTM) of the US Navy (US Navy, 2006). The scale consists of 10-point increments between 0 and 100, where FR0 represents a clean hull and increasing numbers (FR10 – FR100) reflect increasing severity of fouling (Table 4). FR10 – FR30 are classifications of various types of soft fouling (from micro- to macroalgae growth), whereas FR40 – FR100 represent variations in hard fouling (calcareous fouling in the form of tubeworms and/or barnacles, oysters, mussels). The surface coverage of each identified FR class was also estimated according to ASTM D 6990, 2005. To assess the overall efficacy of the coatings, a single weighted fouling rate, FR_w, was also determined for each panel whereby the values of the FR categories (0 – 100) were multiplied with their corresponding observed surface coverage (in%) and summed according to the following equation (where $n = 100$):

$$FR_w = \sum_{i=0}^{n} \frac{FR_i \times Surface\ coverage_i}{100} \quad (1)$$

2.3. Release rate determination

The release rates of Cu and Zn were estimated through X-Ray Fluorescence (XRF) measurements using an Innov-X Delta-50 XRF instrument. The method, whose principle has been described in previous publications (Ytreberg et al., 2017; Lagerström et al., 2018), utilizes a specific calibration for the measurement of Cu and Zn in µg/cm^2 in antifouling paints. Full details of the calibration used for the measurements in this study are found in Lagerström and Ytreberg, 2020. In brief, paint standards with chemically determined concentrations of Cu and Zn were prepared and analyzed by XRF using a 20 s measurement time. The same type of panel coated with primer as used for the panels in the field test were used as background during the measurements. Standards of ten different antifouling coatings were prepared and analyzed to establish a calibration curve between the area concentration in

Table 4
Naval Ships' Technical Manual fouling rate scale (US Navy, 2006).

Fouling Rate	Fouling Type	Description
0	–	Clean, foul-free surface
10	Soft	Incipient slime, painted surfaces visible beneath the fouling
20	Soft	Advanced slime, painted surfaces obscured by the fouling
30	Soft	Soft fouling up to 76 mm in length and up to 6.4 mm in height (e.g. filaments, sea cucumbers)
40	Hard	Tubeworms less than 6.4 mm in height or diameter
50	Hard	Barnacles less than 6.4 mm in height or diameter
60	Hard	Combination of tubeworms and barnacles less than 6.4 mm in height or diameter
70	Hard	Combination of tubeworms and barnacles greater than 6.4 mm in height or diameter
80	Hard	Closely packed tubeworms or barnacles (less than 6.4 mm in height) growing on top of each other
90	Hard	Dense growth of tubeworms with barnacles, 6.4 mm or greater in height
100	Composite	Soft and hard fouling present, with soft fouling growing over various forms of hard growth.

µg/cm^2 and the measured XRF signal intensities of Cu and Zn. Linear calibration curves with $r^2 \geq 0.99$ were established for both elements and the measurement of validation samples confirmed the accuracy of the measurements. For the panels prepared for release rate determination, single coats of the paints (primer and antifouling paint) were applied at a wet film thickness of 100 µm using an automatic, motorized film applicator (TQC AB3120) to ensure thin layers and a smooth finish. Paint rollers were used to apply two of the paints (H1 and H2) as these were not viscous enough to be applied with the motorized applicator. The XRF method typically requires a dry film thickness (DFT) $<$ 40 µm for most antifouling paints in order to be within the linear range of the XRF and avoid absorption effects of the X-Ray signal (Ytreberg et al., 2017). The two paints were therefore also rolled onto 80 µm Mylar® films to enable the determination of their DFT. A DFT $<$ 40 µm was consequently confirmed through measurements with a film thickness gage (Defelsko Positector 6000).

The XRF method was used to determine the average release rates between days 14 and 56. In a previous study, the release rates from five antifouling paints were measured by XRF for two different salinities, 5 and 14 PSU (Lagerström et al., 2018). The release rates were determined after various immersion times (7, 14, 28, 56 and 84 days) and the study found the release rates to be typically highest between days 14 and 56 compared to days 0 – 14 (5 PSU) and days 56 – 84 (14 PSU). At the lower salinity, the release rate of copper generally increased and stabilized after 14 days. At the higher salinity, the release rate instead decreased after 56 days. Ideally, the changes in release rate over the whole boating season (150 days) would be studied but is technically difficult given the restriction on paint thickness imposed by the XRF method. Such an investigation may be possible at lower salinities given the lower depletion rate of copper from the paint films at such conditions. However, for the purpose of comparison, the same exposure time was used regardless of site in this study. The chosen time period (days 14 – 56) represents nonetheless roughly a third of a full boating season. Additionally, determining release rates during a time interval when they are likely the highest is the most relevant from an environmental point of view (precautionary principle) and reduces the risk of underestimating the critical release rate needed to deter macrofouling.

Duplicate sets of panels to be collected after 14 and 56 days respectively were therefore prepared, mounted randomly on grids and immersed at each study site. For each set, triplicate panels were prepared for all antifouling paints. The concentrations of Cu and Zn were measured by XRF in 4 designated points on each panel before and after immersion. A beam energy of 40 kV (Ø 10 mm beam size) and a measurement time of 20 s was used. The raw spectra from the XRF analyses were exported from the instrument and processed using a script in Matlab (see Lagerström and Ytreberg, 2020 for full method description). Triplicate measurements were performed on each designated measurement point and their concentrations averaged prior to any further calculation. In order to evaluate the precision of the instrument, three standards holding low (~200 µg/cm^2), medium (~800 µg/cm^2) and high (~2000 µg/cm^2) concentrations of Cu and Zn were measured between every three panels. With a relative standard deviation (RSD) $\leq$ 0.8%, the variation within one measurement session, i.e. one day, was found to be very low and on par with the day-to-day variation (RSD $\leq$ 0.5%).

2.4. Data processing and statistical analyses

To calculate the average release rate between day 14 and day 56, the difference in concentration (i.e. loss of metals in µg/cm^2) between days 0 – 14 and days 0 – 56 were firstly determined as the average difference in concentration before and after exposure (for either 14 or 56 days) for the triplicate panels of each paint at each site. Measurement points with $>$ 80% depletion of either Cu or Zn after exposure were excluded from the data set. This was only the case for a few points (12 out of 768 measurement points). The average loss between day 0 – 14 was then subtracted from that between day 0 – 56 to. The standard deviation σ of this resulting calculated release between days 14 and 56 was propagated from the individual standard deviations of the two measurement sets using the following formula:

$$\sigma_{release} = \sqrt{(\sigma_{d0-14})^2 + \ (\sigma_{d0-56})^2} \quad (2)$$

The average release, as well as the propagated standard deviation were then divided by the difference in exposure time (56 – 14 = 42 days) to obtain an estimate of the release rate between days 14 and 56.

All statistical tests were performed in JMP® Pro 15 with a significance level of 5% (α=0.05). To assess for statistical differences in antifouling performance between treatments (antifouling paints and control) at each of the four study sites, one-way ANOVAs with post hoc testing (Tukey HSD) were performed on the weighted fouling rates, FR_W. Single and multiple linear regression analyses were employed to assess the effect of various parameters on the release rates of Cu and Zn. For the multiple linear regression models, five parameters were considered (salinity, Cu content, Zn content, temperature and paint type) and stepwise backward selection (criterion of $p = 0.05$) employed to only retain significant parameters in the final model. For the paints for which a significant regression between release rate and salinity could be established, the regression slope estimates were grouped based on paint type and compared using a *t*-test in order to assess any difference based on paint type (hard vs polishing). Linear regression analyses between release rates (Cu or Zn) and the weighted fouling rates, FR_W, were also performed.

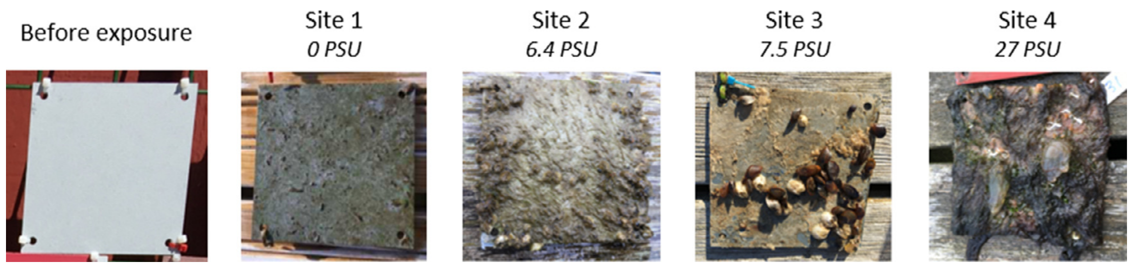

Fig. 2. Local fouling pressure, as captured by the control panels, at the four sites (see Table 3) after 5 months exposure. Site 1: thin algal cover and clay-tubes formed by (terrestrial) Chironomidae larvae, Site 2: filamentous algae and barnacles, Site 3: bryozoans, mussels and barnacles, Site 4: long filamentous algae, tunicates, tubeworms and barnacles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

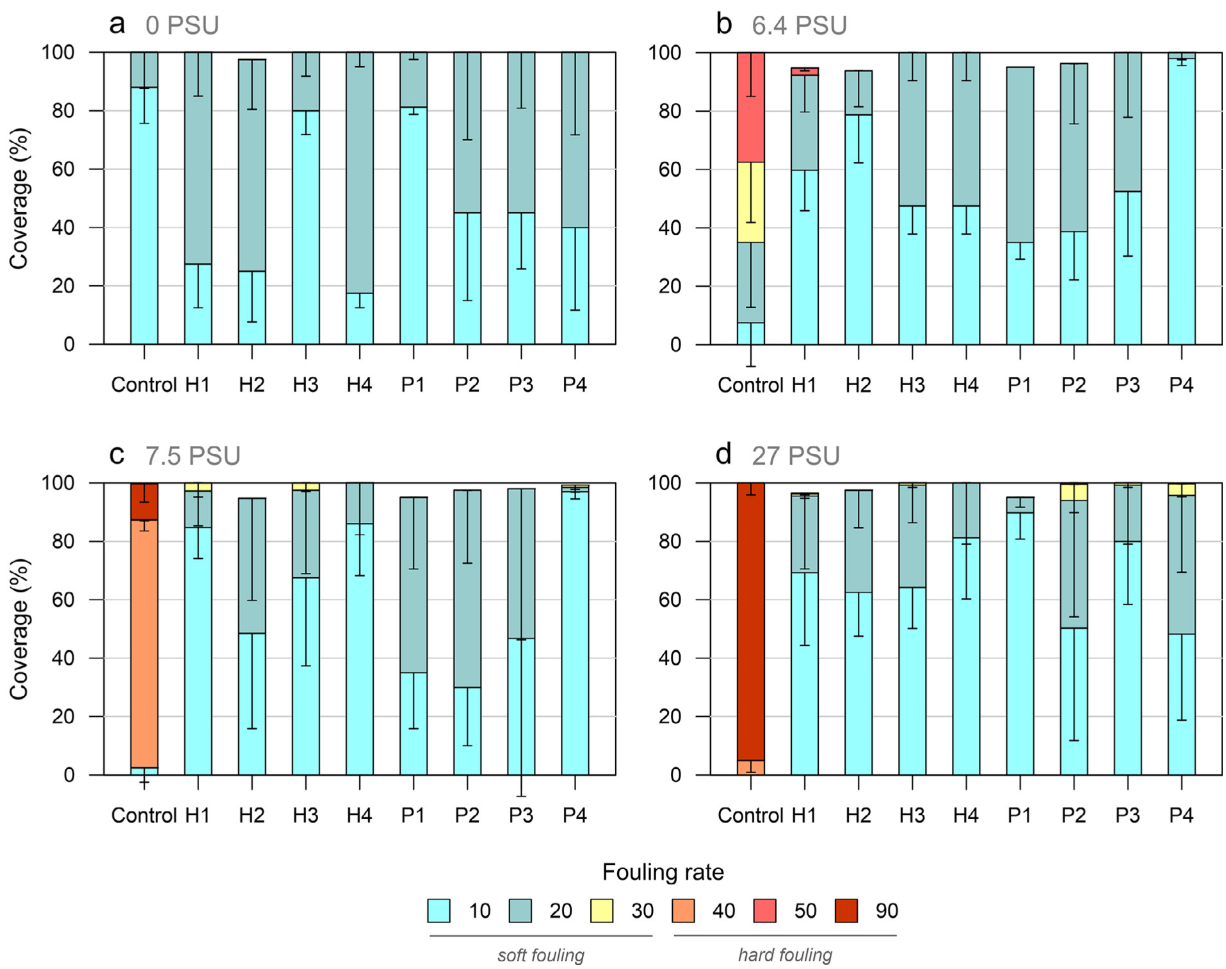

Fig. 3. Average coverage and type of fouling (shown here as fouling rate) on controls and painted panels with antifouling coatings exposed for 5 months at Site 1, 0 PSU (a), Site 2, 6.4 PSU (b), Site 3, 7.5 PSU (c) and Site 4, 27 PSU (d). Error bars show the standard deviation of replicates (n = 4) and are only displayed here in the negative direction. Note that only observed fouling rate classes are shown here.

3. Results & discussion

3.1. Efficacy

The fouling rates recorded for the control panels coated only with primer reflect the local fouling pressure at the study sites after five months exposure in different salinities. The control panels at all four sites were completely fouled (99 – 100% of panel surface covered with fouling), but the type of fouling varied from only soft fouling in fresh water to several sorts of hard fouling at the most saline site (Fig. 2 and Fig. 3). At the saline sites 2 – 4 (Fig. 3b-d), hard fouling (FR ≥ 40) was observed, but in varying amounts, seemingly as a function of salinity. A study of the fouling pressure at various locations in the Baltic Sea shows however that yearly variations may be greater than those due to variations in salinity (Wrange et al., 2020a). In the present study, the average panel surface ± 1 standard deviation colonized by hard fouling increases with increased salinity as follows: 0.0 ± 0.0% (0 PSU), 38 ± 15% (6.4 PSU), 97 ± 5% (7.5 PSU), 100 ± 0.0% (27 PSU). With increased salinities, fouling prevention methods will thus be presented with greater challenges and the performance demand on the antifouling coating increases.

The antifouling coatings were found to be efficient in preventing the colonization of calcareous organisms, with very low surface coverage (≤ 3%) of hard fouling (FR ≥ 40). The only minor recordings of hard fouling were for the paints H1 (Site 2, 6.4 PSU, 2.5 ± 1.0% coverage and Site 4, 27 PSU, 0.3 ± 0.5% coverage) and P2 (Site 4, 27 PSU, 0.5 ± 0.6% coverage). Hence, although the panels coated with antifouling paints were more or less completely fouled at all sites, with > 90% of the panel surface covered, the majority (≥ 92%) of this fouling was soft (FR ≤ 30). The presence of soft fouling on the antifouling coatings is not unexpected as several microalgal species are known to be tolerant to copper (Barranguet et al., 2000; Finnie and Williams, 2010; Zargiel et al., 2011). Co-biocides, also known as booster biocides, are therefore typically added to antifouling paints to complement the biocidal activity of copper (Howell and Behrends, 2010).

At the time of this field study, new guidelines within the EU for the evaluation of antifouling paint efficacy were established (European Chemical Agency, 2018). According to these, static raft testing should generally be carried out over a minimum of six months and cover the full fouling season. The guidelines further state that test location(s) be representative and that three replicate plates be used. Hence, the efficacy evaluation of the present study complies with the new guidelines, apart from the exposure time which was one month shorter than recommended. In the present study, an exposure time of 5 months was chosen as this is the typical length of the yachting season in Scandinavian waters and as amateur antifouling paints normally claim to last for one yachting season. According to the new guidelines, the performance of a product tested in marine waters is acceptable if the coverage of macrofouling on the panels is below 25% (European Chemical Agency, 2018). The guidelines define “macrofouling” as large organisms visible to the human eye such as barnacles, tubeworms, algae > 5 mm. This would correspond to hard fouling on the NSTM fouling rate scale, i.e. FR ≥ 40. Hence, all antifouling products tested in this study fulfill the EU’s efficacy requirement.

Although all antifouling paints investigated in the present study meet the requirements for efficacy, differences in performance between the products merits further investigation through comparison of their weighted fouling rates, FR_W (see Eq. (1)). The average FR_W for all treatments including the controls are shown in Fig. 4 along with the results from the ANOVA testing. At the freshwater site, site 1 (Fig. 4a), the control panels (coated only with primer) had the significantly least severe fouling out of all treatments with an average FR_W ± 1 standard deviation of 11 ± 1. The statistical testing also shows that the antifouling paints H3 ($FR_W = 12 \pm 1$) and P1 ($FR_W = 12 \pm 0$) were not significantly different compared to the control. The remaining six copper paints, equally of hard and polishing types, displayed however a lower antifouling performance and had significantly higher weighted fouling rates ($16 \leq FR_W \leq 18$) compared to the control. Although a primer paint would not be solely applied to vessels which are coated with biocidal antifouling paint, most hulls would nevertheless likely hold some type of biocide-free top-coating (e.g. epoxy or silicone). The result of the biocide-free coating in this study, albeit a primer, suggests that applying a copper coating on a vessel berthed in freshwater is unnecessary and could, in some cases, even be counterproductive. It can however not be ruled out that differences in surface characteristics and paint color, which can be factors of importance for settlement and growth of fouling organisms (Scardino et al., 2008), can explain the observed superiority of the primer paint. Nonetheless, the use of biocidal paints in freshwater have been restricted in Sweden since 1992, following a risk/benefit analysis (Swedish Chemicals Agency, 1993). According to a Swedish national survey, 85% of respondent boat owners stated that they do not perceive hull fouling as an issue (The Swedish Transport Agency, 2015). Nonetheless, 12% stated that they were using an illegal coating. Apart from Sweden, there are only two other countries in the EU with total restriction on biocidal coatings in freshwater bodies: Denmark (Danish Ministry of the Environment, 2014) and Finland (Tukes, 2018). As for freshwater bodies in other EU member states, biocides such as Tolylfluanid and Dichlofluanid have been banned from use in freshwater according to ECHA (European Chemical Agency, 2014, 2016) while the other approved biocides including copper and copper compounds are still allowed. As the results here suggest the release of copper from antifouling paints to constitute an unnecessary load of biocides to the environment, the potential for restriction should be investigated in other EU member states. Germany, for example, has an estimated yearly consumption of 141 tons of Cu from the use of antifouling paint on leisure boats and 71% of recreational berths are located in freshwater (Daehne et al., 2017). Restrictions on the use of copper paints in freshwater could thus lead to significant reductions in the environmental load of copper for this member state.

For the (saline) sites 2, 3 and 4 (Fig. 4b-d), the statistical testing showed identical results: a significant difference in FR_W between controls ($33 \leq FR_W \leq 88$, depending on site) and antifouling paints ($10 \leq FR_W \leq 17$, depending on paint and site) and no significant difference between the latter. In addition, most antifouling paints show no or only small differences in FR_W between the three saline sites. Overall, all antifouling paints thus performed similarly in brackish and marine waters regardless of type (hard or polishing), biocidal content and fouling pressure.

3.2. Release rates

3.2.1. Copper

The average release rates estimated between days 14 and 56 of exposure are shown in Fig. 5 (all release rates can also be found in table S1 in the Supporting Information). For Cu (Fig. 5a), it is evident that two parameters affect the release rate: salinity and Cu content. The statistical regression analyses of the study sites’ salinities against the Cu release rates reveals significant linear relationships for all but paint P2 (see fig. S1a of the Supporting Information), with increased release rates at higher salinity. This confirms the findings of previous XRF release rate studies with both polishing and self-polishing paints (Ytreberg et al., 2017; Lagerström et al., 2018). Increased salinity has been shown to increase both the dissolution rate Cu_2O particles as well as the solubility and polishing rates of both polishing and self-polishing paint matrices, resulting in an increased release of copper from the paint surface (Ferry and Carritt, 1946; Rascio et al., 1988; Kiil et al., 2002). In Lagerström et al., 2018, a ~2-fold increase in Cu release was observed between 5 and 14 PSU for four polishing paints. A 3-fold increase was however observed for a self-polishing paint that was also included in the study. This result suggested that the magnitude of the effect of salinity could be dependent on paint type. To evaluate the effect of paint type, the slopes of the linear regressions established between salinity and the paints’ Cu release rates can be compared. The greater the effect of increased salinity on a specific the paint, the higher the slope of the regression will be. Comparison of the slopes of the hard paints (slopes of 0.15 – 0.54) to those of the polishing paints (slopes of 0.24 – 0.88) using a *t*-test revealed however no significant differences.

In Lagerström et al., 2018, no correlation between Cu content and Cu release could be established for five studied paints. Significant linear regressions could however be established here at all four sites (fig. S2a). A recent study found that an increased concentration of ZnO, albeit when added to the same rosin-based paint formulation, increased the release of copper (Lindgren et al., 2018). The effect of Zn content on the Cu release was therefore also investigated. However, no significant relationship between the paints’ Zn content and the release of Cu could be established at any of the salinities for the paints studied here ($p > 0.005$, data not shown), regardless of whether all or just the hard or polishing coatings were included in the analysis.

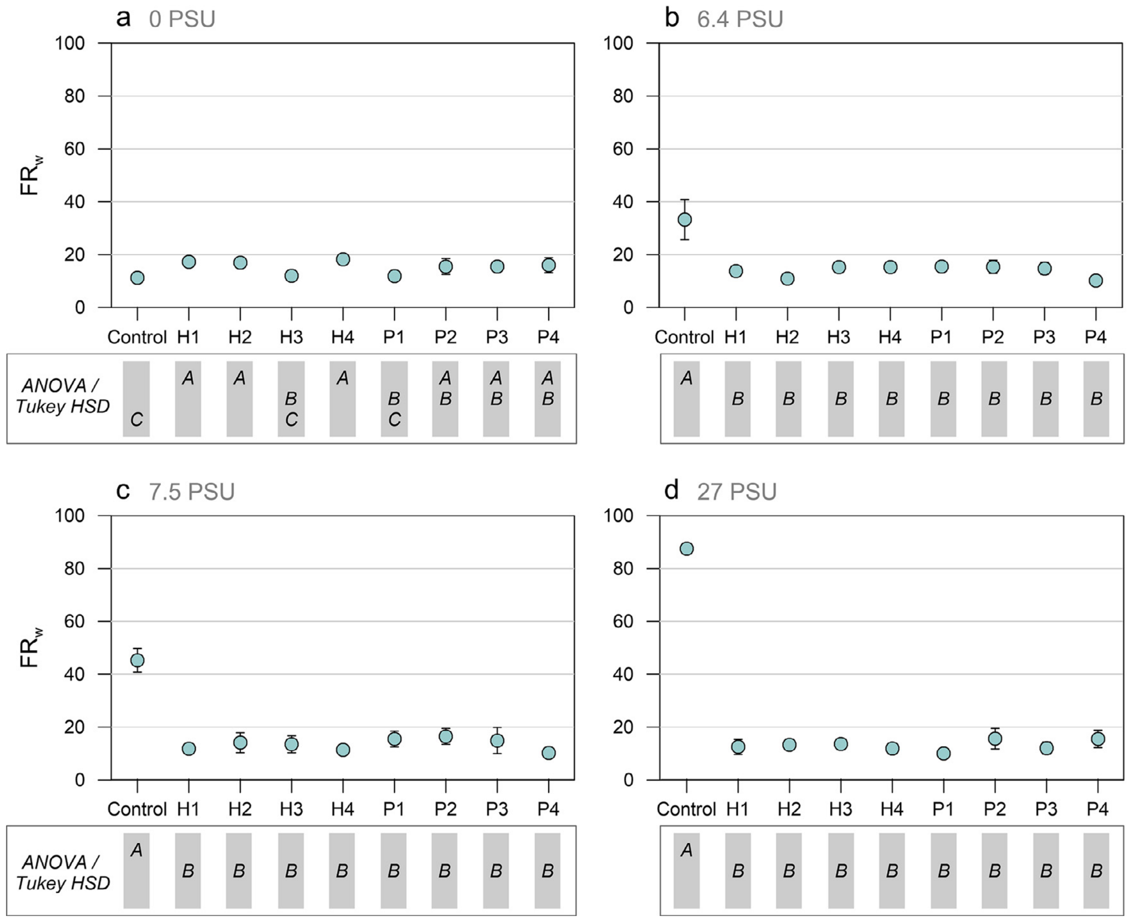

Fig. 4. Weighted fouling rate on controls and antifouling paints at Site 1, 0 PSU (a), Site 2, 6.4 PSU (b), Site 3, 7.5 PSU (c) and Site 4, 27 PSU (d). Error bars show the standard deviation of replicates ($n = 4$). The results from the ANOVA are shown below each graph. Treatments not connected by the same letter are significantly different ($\alpha = 0.05$).

Five parameters (salinity, Cu content, Zn content, temperature and paint type) were tested for significance on the release rate of Cu through stepwise regression in order to obtain a single explanatory model. Only two parameters, salinity and Cu content, were found to be significant with the resulting model able to account for 74% of the observed variation ($r^2 = 0.738$) (fig. S3a). This suggests that knowledge of salinity and Cu content can be used for a rough estimate of the Cu release rate at temperatures comparable to those of this study. A considerate part of the variation (26%) is however caused by other parameters. Both the solubility of the active Cu substance in the paint (Cu_2O or copper powder here) and its particle size, as well as the properties of the paint resin (e.g. erodibility of the binder and content of other soluble pigments) will affect the release rate of Cu from a paint (Yebra and Weinell, 2009). Differences in paint matrix between the eight studied paints could therefore account for the unexplained variability.

3.2.2. Zinc

The effect of salinity on the Zn release rates is not as clear-cut as for Cu (Fig. 5b). Although the highest release rates are obtained at the highest salinity for some paints (H1, P2 and P3), no significant linear regressions between salinity and Zn release rates could be established for any of the paints (fig. S1b). For most (all but P1), the highest or second to highest release rates instead occur in freshwater, suggesting perhaps water parameters other than salinity may be influencing the release rate of Zn. Zn content as an explanatory variable was also not significant at any of the studied sites when considered separately (fig. S2b). Out of the five parameters tested for significance in a multiple regression model, three were found to be significant on the Zn release rate: paint type, Cu content and Zn content. The overall fit of the model is however poor with $r^2 = 0.540$ (fig. S3b). The prediction model of the Zn release rate is thus more uncertain than that of Cu, suggesting that unknown parameters have a greater influence on the release of Zn than that of Cu. These are most likely related to the specific composition of the paints and go beyond the simple distinction between hard or polishing.

3.3. Critical and minimum leaching rate of copper in marine waters

As no large differences in FR_w were detected between paints or sites (Fig. 4) despite large differences in Cu and Zn release rate (Fig. 5), no significant linear regressions could be established between release rates and FR_w for either of the two metals (data not shown). It is thus more relevant to discuss the paints' performance and Cu release rates in relation to threshold values such as the critical release rate and the minimum leaching rate.

As mentioned previously, an indicative Cu release rate of 10 µg/cm^2/d has been determined as the critical limit to deter attachment of macrofouling (Barnes, 1948; WHOI, 1952). The presence of macrofouling, i.e. FR $\geq$ 40, on the panels treated with antifouling paints, albeit rare, can give some idea of the critical release rates specifically for the Baltic Sea and Kattegat area. To carry out this assessment, the effect of the release of Zn on the performance of the paints must be assumed to be limited. Poor long-term antifouling performance of zinc oxide by itself has been demonstrated in another study, supporting this assumption

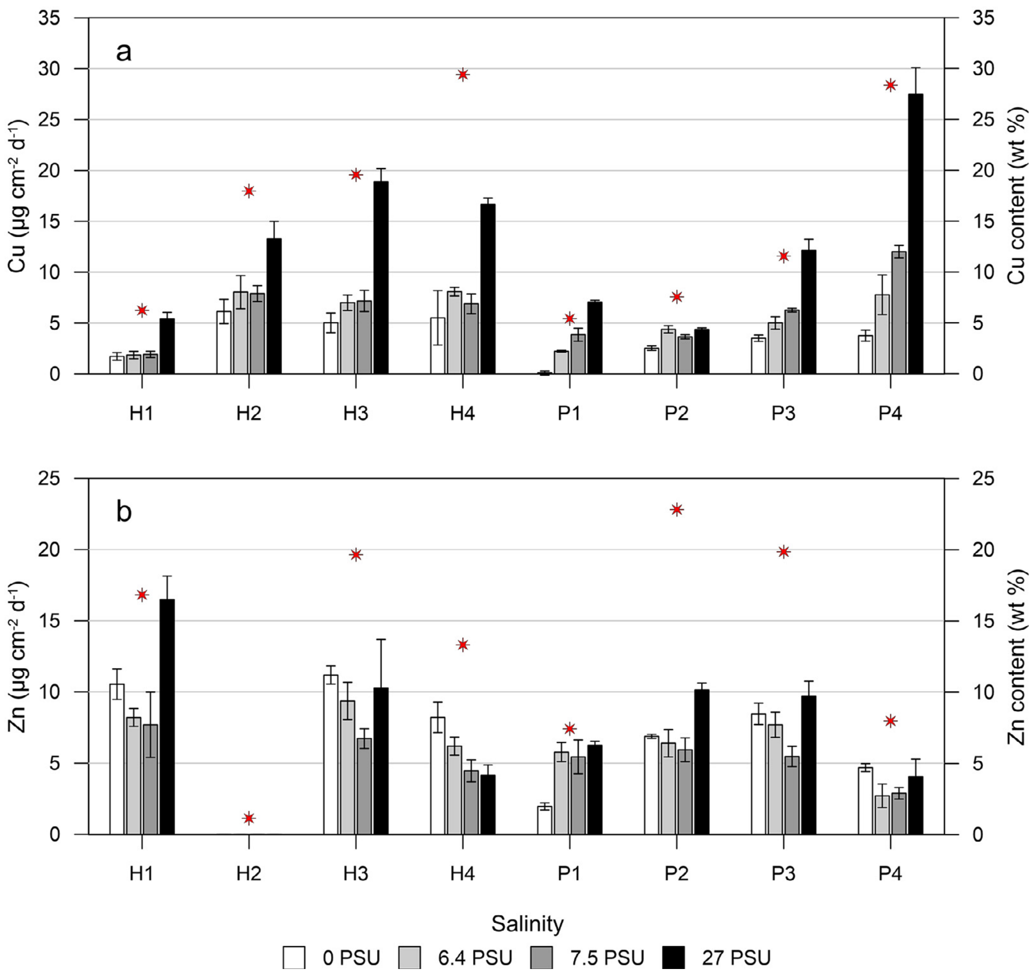

Fig. 5. Average Cu (a) and Zn (b) release rates from the four hard (H) and four polishing (P) paints between days 14 and 56 of immersion at the four study sites. Error bars show the propagated standard deviation ($n = 3$ panels). The red star symbols show the paints' Cu and Zn content (in wt%, ww). Note that the Zn release rates for H2 were very low (< 0.01 µg/cm^2/d) as no ZnO was included in its formulation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Lindgren et al., 2018). In this study, macrofouling was detected in small amounts at sites 2 and 4. At site 2, paint P2 (2.5 ± 1.0% surface coverage of macrofouling) was the paint with the slowest release (1.9 µg/cm^2/d). At the same site, no macrofouling was present on the paint with the second to lowest release rate (P1, 2.2 µg/cm^2/d). At site 4, two paints were observed to hold macrofouling: P2 (0.5 ± 0.6%) and H1 (0.3 ± 0.5%). These coatings also held the lowest Cu release rates of 4.4 and 5.4 µg/cm^2/d, respectively, at this site. Paints with release rates of at least 7.1 µg/cm^2/d were however free of macrofouling. At site 3, no macrofouling was observed on any of the treated panels, suggesting the critical release is below or equal to the lowest measured release rate. In summary, one can thus deduce that the critical release rate is between 1.9 and 2.2 µg/cm^2/d at site 2 (Baltic Sea, 6.4 PSU), $\leq$ 1.9 µg/cm^2/d at site 3 (Baltic Sea, 7.5 PSU) and between 5.4 and 7.1 µg/cm^2/d at site 4 (Kattegat, 27 PSU). Previous studies of the efficacy and release rates of antifouling paints have also indicated that the critical release rate is $<$ 10 µg/cm^2/d in the Baltic Sea and Kattegat. Lindgren et al., 2018 assessed the efficacies of different paint formulations with Cu release rates ranging from 4.7 to 10.6 µg/cm^2/d after five months static exposure in a marina outside Gothenburg, Sweden (~15 PSU). The study found that the lowest release rate of 4.7 µg/cm^2/d was sufficient to deter macrofouling at that location. In Lagerström et al., 2018, the release rates of five commercial antifouling paints for recreational vessels were measured in two marinas and found to range between 2.1 – 4.6 (Stockholm, Sweden, 5 PSU) and 4.2 – 8.9 (Gothenburg, Sweden, 14 PSU) µg/cm^2/d. The same paints were found to have no or $<$ 1% macrofouling when the efficacy under static conditions was evaluated after 5 months exposure in the same marinas (Wrange et al., 2020b). The critical Cu release can therefore be deduced as $\leq$ 2.1 µg/cm^2/d in the Stockholm area and $\leq$ 4.2 µg/cm^2/d in the Gothenburg area. The latter is comparable to the findings of Lindgren et al., 2018. The geographical variation in the critical release rate for macrofouling in the Baltic Sea and Kattegat area is shown in Fig. 6.

The leaching rates of the tested products are almost all above the indicative critical leaching rates. The minimum leaching rate is therefore, by definition, also exceeded (Fig. 1). At the three saline sites, the efficacy evaluation showed all paints to be effective according to the EU guidelines. Additionally, no significant differences in FR_W could be established between the eight studied paints, suggesting overall similar performances. The paints' Cu release rates, on the other hand, vary greatly. Depending on the site, the paint with the highest release rate (H4 or P4) leached copper at a rate 4 – 6 times that of the slowest leaching paint (H1 or P1) over the first ~ 2 months of the paints lifetime studied here. Calculated differently, the slowest leaching paints thus had release rates corresponding to 16 – 23% of those of the highest leaching paints. This result suggests there is potential for a ~ 80% reduction in Cu release rates from the highest leaching antifouling products

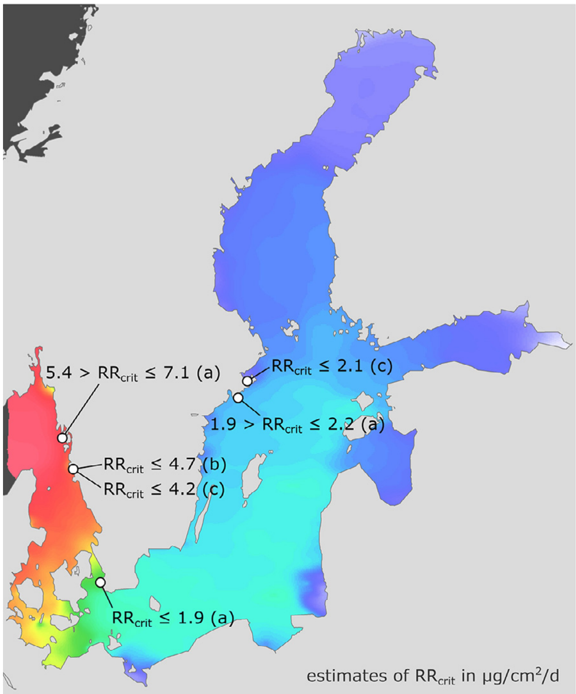

Fig. 6. Salinity map of the Baltic Sea showing estimates of the critical Cu release rates (RR_{crit}) at five locations along the Swedish coast from this study (a), Lindgren et al., 2018 (b) and Lagerström et al., 2018 (c). The salinity data originates from Institute Of Marine Research et al., 2012. The map was produced in Ocean Data View (Schlitzer, 2018).

for recreational vessels in the Baltic Sea and Kattegat area without any efficiency loss.

4. Conclusions

In this study, the application of copper-containing antifouling paint in freshwater was concluded to be redundant as the products contributed no antifouling effect. Any release of copper in such environments thus only pauses a risk to the environment without any beneficial gain for the boat owner. Although there is a ban in Swedish freshwater for the use of biocidal antifouling paints, that is not the case for most EU countries. These member states may gain from performing risk/benefit analysis to assess whether the continued use of biocidal antifouling paints in freshwater is indeed necessary. For marine waters, the mapping of the critical Cu release rate revealed variations in the sensitivity of the fouling community in the Baltic Sea/Kattegat, with higher release rates required to deter macrofouling at higher salinities. However, as the release rate of Cu from antifouling paints also increases with increased salinity, all the eight tested paints were found to be efficient regardless of location along the salinity gradient. In fact, the Cu release rates of a majority of the paints greatly exceeded the critical release rate. For some products, a reduction of up to 80% in the release rate of Cu would be possible without any loss in efficiency. The properties of these products are thus not in alignment with the principles of the BPR which requires the release of active substances to be the minimum necessary.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2020.116383.

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