Copper release rate needed to inhibit fouling on the west coast of Sweden and control of copper release using zinc oxide

J. Fredrik Lindgren, Erik Ytreberg, Albin Holmqvist, Magnus Dahlström, Peter Dahl, Mattias Berglin, Anna-Lisa Wrage & Mia Dahlström

To cite this article: J. Fredrik Lindgren, Erik Ytreberg, Albin Holmqvist, Magnus Dahlström, Peter Dahl, Mattias Berglin, Anna-Lisa Wrage & Mia Dahlström (2018): Copper release rate needed to inhibit fouling on the west coast of Sweden and control of copper release using zinc oxide, Biofouling, DOI: 10.1080/08927014.2018.1463523

To link to this article: https://doi.org/10.1080/08927014.2018.1463523
Copper release rate needed to inhibit fouling on the west coast of Sweden and control of copper release using zinc oxide

J. Fredrik Lindgren\textsuperscript{a}, Erik Ytreberg\textsuperscript{b}, Albin Holmqvist\textsuperscript{a}, Magnus Dahlström\textsuperscript{b}, Peter Dahl\textsuperscript{c}, Mattias Berglin\textsuperscript{a}, Anna-Lisa Wränge\textsuperscript{a} and Mia Dahlström\textsuperscript{a}

\textsuperscript{a}Unit for Chemistry, Materials and Surfaces, RISE Research Institutes of Sweden, Borås, Sweden; \textsuperscript{b}Department of Mechanics and Maritime Sciences, Chalmers University of Technology, Gothenburg, Sweden; \textsuperscript{c}Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

ABSTRACT

How zinc oxide influences copper release has been tested and the lowest release rate of copper from various combinations of copper and zinc in a paint matrix evaluated, whilst still deterring macrofouling, including barnacles and bryozoans. Copper (I) oxide was added to a generic AF paint in 0, 8.5, 11.7 or 16.3 wt% copper oxide in combination with 0, 10 or 20 wt% zinc oxide and applied on PMMA panels. The results show that zinc influences the release rate of copper. When 10 and 20 wt% zinc was added, the total amount of copper released significantly increased by on average 32 and 47% respectively. All treatments that included copper were successful in deterring macrofouling, including the treatment with the lowest average Cu release rate, ie 4.68 $\mu$g cm$^{-2}$ day$^{-1}$.

Introduction

Biofouling on man-made structures is a well-known problem that has been combated by various techniques since humans started to use sea transport (Yebra et al. 2004). The effects of biofouling on ships and other man-made structures have been thoroughly examined. Fouling causes increased weight, increased frictional resistance, decreased maneuverability, increased costs for hull maintenance and fuel consumption, as well as contributing to the introduction of alien species (Almeida et al. 2007). The most commonly used technique to combat biological fouling is adding toxic compounds to paint matrices which then are applied to boat hulls and various static structures. Following the coming into force of the International Maritime Organization's (IMO) International Convention on the Control of Harmful Antifouling Systems on Ships, which stated that ships are not allowed to reapply the widely used biocide tri-butyl-tin (TBT) from 2003 and then, from 2008 the introduction of a global ban on TBT in antifouling (AF) coatings (IMO 2001), the use of copper as an AF biocide in marine paints was revisited. Copper is today the most commonly used AF biocide. It exerts its AF effect on eg barnacles, tubeworms and algae through toxic mechanisms (Voulvoulis et al. 1999). However, some species of algae tolerate high concentrations of copper, rendering it necessary to include additional biocides in the paint that target photosynthesizing organisms, so called ‘booster biocides’ (Manzo et al. 2008). The copper used in AF paints is usually in the form of metallic copper, copper thiocyanate or copper (I) oxide (Cu$_2$O) and the copper content can vary between ~7 to 75 wt% (wet), depending on the fouling pressure at the intended geographical location of use. The release rate of copper from the paint depends on several factors including water temperature, pH, copper content, paint formulation, salinity and age of the paint (Woods Hole 1952; Srinivasan and Swain 2007; Ytreberg et al. 2017; Lagerström et al. 2018).

Copper is an essential micronutrient used in various metabolic processes, hence low concentrations of it are needed. However, higher concentrations of copper are toxic to organisms. For example, cyanobacteria and embryos/larvae of mussels, oysters and sea urchins are known to be highly sensitive (Voulvoulis et al. 1999; Hellio and Yebra 2009). High concentrations of dissolved copper are commonly found in shallow, near-coastal marine areas due to leisure boating or commercial shipping. For example, Biggs and D’Anna (2012) reported 22 $\mu$g l$^{-1}$ of dissolved Cu in a marina located in San Diego Bay.
the UK, dissolved copper concentrations up to 4.8 and 6.7 μg l⁻¹ have been reported from harbors and marinas, respectively (Jones and Bolam 2007), which is above the EU PNEC (predicted no effect concentration) in marine environments (2.6 μg l⁻¹) (Copper 2008). Copper also adsorbs to particulate matter in the water column, and settles and accumulates in sediments (Thomas and Brooks 2010). These shallow coastal areas are used as spawning, nursery and feeding grounds by numerous marine organisms, and the potential impact of AF compounds on non-target species is therefore substantial, especially at the launch of freshly painted AF pleasure crafts in spring (eg in Northern Europe and Canada) that commonly coincides with the reproduction cycles in marine organisms.

To date, there is not a sufficiently effective and environmentally safe AF biocide on the market with no negative environmental effects on non-target organisms. Nowadays, copper-based AF paints are still the preferred alternative for leisure boaters (Karlsson et al. 2010). However, to minimize the copper leakage from AF paints, without compromising the AF efficacy, controlling the release rate of copper is of great importance. Furthermore, to be able to successfully minimize the release rate of the active biocide, paint manufacturers and researchers need to be able to efficiently measure the release under field conditions, in order to determine the required release rate to deter macrofouling in different geographical areas where environmental conditions may vary. Determination of the concentration of primarily metal elements, ie copper and zinc, in a paint layer or their release rates from the layer to the water over time has until now been a time-consuming and costly process.

It has involved advanced chemical analytical techniques, for example inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) of scraped off paint flakes and release into ambient water from painted surfaces in laboratory experiments (Ytreberg et al. 2015). AF paints are regulated within the EU through the Biocidal Products Regulation (BPR). Within the BPR, products need to pass an environmental risk assessment to obtain authorization to be made available on the market. The release rates of the AF products are generated through two standardized methods, a rotating cylinder method (ASTM D6442-06/ISO 15181:2007) and a mass balance calculation method (ISO 10890:2010) (ISO 2007, 2010). However, it has been shown that the laboratory ISO/ASTM methods to measure the release rate overestimate the actual in situ release (Finnie 2006). Another method that is generally regarded as the best method to measure in situ release rates, is the US Navy Dome method that was developed by the Space and Naval Surface Warfare Center in San Diego (SSCSD). It allows measurements of in situ release rates using a closed recirculating system, where a dome is attached to an underwater hull or panel. However, the costs involved and issues of practicality using the method during operation has led to it not being standardized (Valkirs et al. 2003; Schiff et al. 2004). A method able to measure the actual release during operation in a cost-efficient way would make estimations regarding service life of the AF coating more realistic and could ultimately prolong the interval between dry-dock. To overcome these shortcomings, Ytreberg et al. (2017) developed a novel release rate method using a handheld X-ray fluorescence spectroscopy (XRF) analyser calibrated for measuring copper and zinc (μg cm⁻²) release from AF paints. In brief, measurements on a surface coated with a zinc and copper containing paint are performed prior to being submerged into the sea (t₀), and again measured after retrieval (t₁). The loss of Cu and Zn (t₀ – t₁) is then calculated as the released amount of zinc and copper over time (Ytreberg et al. 2017).

Zinc oxide (ZnO) is a component in AF paints that can be included as an extender or pigment, can improve coating performance and work as an erosion facilitator. It has been suggested to also increase the release rate of the biocide included in the paint (French et al. 1984; Hellio and Yebra 2009; Karlsson et al. 2010; Jessop and Turner 2011; Bellotti and Romagnoli 2014). It is not considered to be a biocide in relation to AF paints (EU 1998). However, to what extent zinc affects the release rate of copper is still not fully clarified. Hitherto, what release rate of copper in situ is needed to inhibit macrofouling (eg barnacles and bryozoans) on the Swedish west coast has not been investigated, nor to what extent zinc oxide is involved in influencing the release rate of copper under field conditions.

The purpose of this study was to investigate these two parameters. Specific concentrations of copper oxide and zinc oxide were added to a generic rosin-based paint and the release rates of copper and zinc were measured during an 84-day period, while simultaneously monitoring the establishment of macrofouling. The test site was selected based on the fouling community (deemed as high fouling pressure dominated by hard macrofoulers such as barnacles, and secondary macrofouling of ascidians and bryozoans), water temperature and salinity, which are representative of southern Skagerrak and Kattegat. It is of particular interest to study how release rates of copper and zinc could be minimized without compromising paint AF efficacy in these areas, since the Baltic Sea and transition water bodies such as the Kattegat are classified as being a Particular Sensitive Sea Area (PSSA) (IMO 2005; Andersson et al. 2016) and minimizing the supply of substances of environmental concern such as copper and zinc is a high priority. In addition, leisure boating in the Kattegat and Skagerrak areas is very popular; these
areas host some 100,000 leisure boats, of which a substantial proportion are painted with high copper containing paints (Lagerqvist and Andersson 2016).

**Materials and methods**

**Preparation of generic paint and dosing of copper and zinc**

An experimental generic paint was obtained from the paint manufacturer Boero Group (www.boerogroup.com). Its formulation is based on hydrogenated rosin as binder together with an acrylate as film former and erosion retarder. It is prepared by dissolving rosin in xylene to a final concentration of 50% (w:w⁻¹) using a Cowles mixer and then adding an acrylic retarder and red pigment (Fe₂O₃). Then the plasticizer is added followed by the extenders, barium sulfate (BaSO₄) and anhydrous talc, and then the anti-sagging agent, SiO₂. Finally, the viscosity of the formulation is controlled by adding once again xylene solvent. The paint is thoroughly mixed throughout this process. The dispersion of the paint components was analyzed with a grindometer.

To this generic paint copper oxide (Cu₂O, Alfa Aesar, Karlsruhe, Germany 99% purity, particle size < 74 μm) and zinc oxide (ZnO, Alfa Aesar, 99.0% purity, particle size < 44 μm) were then added and thoroughly mixed using a T25 ultra-turrax disperser equipped with a R50 high speed stirring shaft. The added copper oxide concentrations were 8.5, 11.7 and 16.3 wt% with 0, 10 or 20 wt% zinc oxide. Copper oxide and zinc oxide is hereafter referred to as copper (Cu) and zinc (Zn), eg wt% Cu refers to wt% copper oxide. PMMA panels (11 × 11 cm) were sanded and painted with controlled thickness (100 μm, wet surface) using a Quadruplex paint applicator (VF2170, TQC). Dry film thickness (DFT) was measured on two of the paints tested, the generic paint and the generic paint with 16% Cu₂O and 20% ZnO added. A wet film of 100 μm was coated on a 75 μm thick Mylar A © film (Pütz GmbH+Co, Folien KG, Tannstein, Germany). DFT measurements were performed (n = 10) on each film with a film thickness gage (Defelsko Positector 6000, Ogdensburg, NY, USA). Certified coating thickness standards were measured to ensure accurate readings. The results showed the DFT to be 29.2 ± 2.7 (generic paint), 32.0 ± 3.3 (generic paint with 16.3% Cu₂O and 20% ZnO added); the variation is expressed as SD.

Particle size of Cu₂O and ZnO was measured by scanning electron microscopy (SEM) using a Supra 40VP microscope (Zeiss, Oberkochen, Germany) equipped with a Gemini electron source. The microscope was operated at 2 kV and secondary electrons were detected by using the SE2 detector at a working distance of 3.1–3.2 mm. Particle powder was placed on an aluminum foil and transferred to the sample holder via double sided adhesive carbon tape and analyzed directly. Particle diameter was assessed by taking the average of two particle diameters (d₁ and d₂) measured perpendicular to each other at the longest and shortest distance. The presented diameter of the particle was the average of the two (d₁ and d₂). The shape of the particles was indicated by calculating the aspect ratio (aspect ratio = d₁/d₂). For the analysis, at least 150 particles of Cu₂O and ZnO was measured.

In total, nine treatments and three control treatments using 0 wt% copper and 0, 10 or 20 wt% zinc were prepared. Each treatment was replicated 24 times. After the painting dried, the panels were divided into six batches with four replicates in each. Each batch of panels was attached to a line (six in total) and placed in the sea during the most intense fouling period from mid-July, at ~1.5 m depth in a marina outside Gothenburg, on the Swedish west coast (57.647°N, 11.853°E, ~15 PSU). After four, seven, 14, 28, 56 and 84 days a batch of panels were retrieved from the sea and dry-stored until analysis.

**Inspection of fouling and XRF analysis**

In the laboratory, the panels were inspected using a stereomicroscope for recruitment of barnacles, ie *Amphibalanus improvisus*, as well as other fouling organisms, eg bryozoans, ascidians and algae. In addition to evaluating AF efficacy through recruitment of fouling species, release of copper and zinc from the different paint treatments was measured using a handheld X-ray fluorescence (XRF) analyser (DELTA-50, Innov-XD, Olympus, Hamburg, Germany), powered with a 4 W, 50 kVX-ray tube. Each sample, in the present case, an AF paint of a known thickness, is irradiated with X-rays resulting in electrons from an inner orbital (K or L) being ejected, causing electrons from higher energy levels to fill the positions. Excess energy is then ejected in the form of X-ray photons, whose wavelengths are characteristic of the elements present in the sample (Turner et al. 2015). The instrument calibration curve for calculation of copper and zinc concentrations in the paint was retrieved from Lagerström et al. (2018) and Ytreberg et al. (2017), and used together with Compton normalization.

Measurements of copper and zinc concentrations on the painted panels were performed at day 0 (t₀) and subsequently when the panels where retrieved from the sea (t₁), after a drying period of at least 12 h. A very thin layer of microfouling (slime) was present on some panels that theoretically could affect the XRF measurement. However, this disturbance has been shown to be insignificant and not to affect the measurements more than a
Results

AF efficacy of the generic paint treatments

All of the treatments that included copper significantly deterred macrofouling successfully during the study (84 days), compared to the control panels with no copper or zinc (Kruskal–Wallis, \( p < 0.05 \)). Control panels including no copper and zinc had 222 ± 12, 0 wt% Cu and 10 wt% Zn had 127 ± 86 and 0 wt% Cu and 20 wt% Zn had 92 ± 98 (95% conf. inter.) barnacles attached at day 84 (Figure 1). Furthermore, the treatments with no copper (and 0, 10 and 20 wt% zinc) had on average a bryozoan coverage (%) of 98 ± 2, 68 ± 13 and 68 ± 32 (95% conf. inter.) respectively. This shows that zinc, in itself, did not have an effective level of biocidal activity against barnacles and bryozoans after 84 days.

A very low average bryozoan coverage (<2%) was found on all treatments which included copper. The treatments including copper significantly differed compared to the treatments without copper (Kruskal–Wallis, \( p < 0.001 \)), with respect to bryozoan coverage. The abundance of barnacles on the control panels with no Cu and Zn peaked at day 28, with a decrease in abundance of 42 and 34% at day

the day-to-day differences in the instrument performance (Lagerström et al. 2018). The release of copper and zinc was calculated as differences in concentrations between \( t_0 \) and \( t_1 \). Release rates in \( \mu \text{g cm}^{-2} \text{ day}^{-1} \) of copper and zinc were calculated using varying start times (\( d_0, 4, 7, 14 \) and \( 28 \)) and \( d_{56} \).

Statistical analysis

Differences in release rate of copper and zinc between treatments and time points, and slopes of the release rate trend lines were analyzed with one-way ANOVA using the software SPSS (IBM Corporation, Armonk, NY, USA). Tukey’s post hoc test was used to detect differences between treatments and control. Homogeneity of variances was tested with the Levene’s test (Levene 1960). Non-homogenous variances (ie abundances of barnacles and bryozoans) were analyzed with the non-parametric Kruskal–Wallis test (Kruskal and Wallis 1952). Regressions of the dose–response relationship between copper concentrations and zinc release were performed using the Analysis ToolPak in Microsoft Excel (Microsoft, Redmond, WA, USA).

Figure 1. Abundance (±1SD) of barnacles (\( A. \ improvisus \)) on the panels after four, seven, 14, 28, 56, and 84 days (\( n = 4 \)). The legend displays the treatments as wt% Cu, wt% Zn and Control as no included copper or zinc. (a) Treatments without Zn; (b) treatments with 10 wt% Zn; (c) treatments with 20 wt% Zn, and (d) treatments without Cu. (*) indicates that the abundance was multiplied by a factor of 10 to facilitate visual inspection.
56 and 84, respectively. This decrease was due to growth of the individual barnacles (thus outcompeting each other), as the abundance was limited to the area of the Plexiglas panel. Furthermore, a delayed settlement on control panels is common, as barnacle larvae prefer to settle on older biofilms, with a higher cell density. For example, cyprid larvae have been shown to prefer six day-old biofilms over three day-old or no biofilm at all (Hugget et al. 2009; Hung et al. 2008).

The treatment with lowest copper and zinc content, i.e. 8.5 wt% copper with 0 wt% zinc that still more or less completely deterred fouling, had 0–3 (average 1.0) barnacles attached after 84 days, indicating that the copper release from this treatment was sufficient to have an AF effect on the Swedish west coast (even without zinc). The control treatments with 10 and 20 wt% of zinc had an AF effect of their own at day 4, 7, 14 and 28, compared to the control treatment with no Cu and Zn (Kruskal–Wallis, \( p < 0.05 \)). At day 56 the control treatments including Zn did not deter fouling any longer, compared to the control without Cu and Zn (Figure 1).

**Copper release and average release rates**

Overall, the release of copper followed a similar pattern over time in all the copper treatments, with or without zinc added, showing a higher released amount with an increased concentration of copper in the paint (Figure 2). The total released copper during the course of the experiment (84 days) for the treatments were 285–474 μg cm\(^{-2}\) for the 8.5 wt% copper treatments, 401–492 μg cm\(^{-2}\) for the 11.7 wt% treatments and 576–826 μg cm\(^{-2}\) for the 16.3 wt% treatments (Table 1). The differences in total released copper over the 84 days were on average 21% between 8.5 and 11.7 wt% Cu; and 77% between 8.5 and 16.3 wt% Cu. Furthermore, the copper release increased significantly with the incorporation of zinc in the paint (ANOV A, \( F = 19.03, p < 0.0001 \)). The average increase, compared over all Cu concentrations, when 10 wt% Zn was included was 32% and 47% when 20 wt% Zn was included. This increase in copper release was significant in the 8.5 wt% Cu treatments (\( p < 0.027 \) [10 wt% Zn], \( p < 0.004 \) [20 wt% Zn]) and 16.3 wt% Cu treatment with 20 wt% Zn (\( p < 0.011 \)), compared to the same treatments with no zinc.

This relationship was further investigated when comparing slopes of the release rate trend line from the respective treatment; the trend line being the most linear approximation of the released copper over time. Slopes were calculated between day 0 and day 56 as the release rate decreased between day 56 and 84, which was reflected in linearity, and, hence the average \( r^2 \)-values of the slopes. However, the slopes increased significantly
The abundance of barnacles was highest on the control panels exposed for 28 days followed by a slight decrease after 56 days (Figure 1). Therefore, an average release rate of copper and zinc during d14–d56 was calculated to assess the impact of copper and zinc release on fouling deterrence.

A decrease in the linearity of the copper release between day 56 and 84 indicated a non-steady state release rate. This was further evaluated when analyzing the average release rate with the incorporation of zinc in the paint (ANOVA, $F = 5.89$, $p < 0.0001$). In the 8.5 wt% Cu treatment with 10 and 20 wt% Zn, the slope increased on average 54 and 51%, respectively, which was significant in the treatment with 20 wt% Zn ($p < 0.009$). It increased with 10 and 37% respectively in the 11.7 wt% Cu treatment, and 11 and 14% in the 16.3 wt% copper treatment (significant difference at the $p < 0.1$ level in the 20 wt% Zn treatment [$p < 0.057$]) (Figure 2).

The abundance of barnacles was highest on the control panels exposed for 28 days followed by a slight decrease after 56 days (Figure 1). Therefore, an average release rate of copper and zinc during d14–d56 was calculated to assess the impact of copper and zinc release on fouling deterrence.

A decrease in the linearity of the copper release between day 56 and 84 indicated a non-steady state release rate. This was further evaluated when analyzing the average release rates between the different measurement points (d0–4, d4–7, d7–14, d14–28, d28–56 and d56–84) ± 95% confidence interval. Diamonds = 0, triangles = 10, and squares = 20 wt% zinc. Diagram (a) shows treatments with 8.5% Cu; (b) treatments with 11.7% Cu and (c) treatments with 16.3 wt% Cu.

Table 1. Average release rates of copper as $\mu g \text{ cm}^{-2} \text{ day}^{-1} \pm 95\%$ confidence interval (days 14–56, $n = 4$) by the tested treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cu release rate (d14–56, $\mu g \text{ cm}^{-2} \text{ day}^{-1}$)</th>
<th>Zn release rate (d14–56, $\mu g \text{ cm}^{-2} \text{ day}^{-1}$)</th>
<th>Total released Cu (d0–84, $\mu g \text{ cm}^{-2}$)</th>
<th>Total released Zn (d0–84, $\mu g \text{ cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>4.68 ± 0.48</td>
<td>0.24 ± 0.04</td>
<td>284.6 ± 12.30</td>
<td>10.4 ± 4.24</td>
</tr>
<tr>
<td>11.7</td>
<td>6.09 ± 1.04</td>
<td>0.18 ± 0.08</td>
<td>400.6 ± 15.82</td>
<td>5.2 ± 5.23</td>
</tr>
<tr>
<td>16.3</td>
<td>9.42 ± 1.94</td>
<td>0.17 ± 0.10</td>
<td>576.0 ± 82.54</td>
<td>5.2 ± 4.30</td>
</tr>
<tr>
<td>8.5</td>
<td>6.94 ± 0.48</td>
<td>6.92 ± 0.25</td>
<td>643.5 ± 21.18</td>
<td>434.9 ± 31.72</td>
</tr>
<tr>
<td>11.7</td>
<td>10.60 ± 1.94</td>
<td>3.95 ± 0.53</td>
<td>680.5 ± 74.10</td>
<td>306.4 ± 38.72</td>
</tr>
<tr>
<td>16.3</td>
<td>10.01 ± 1.58</td>
<td>4.03 ± 0.58</td>
<td>825.7 ± 116.97</td>
<td>513.2 ± 115.27</td>
</tr>
</tbody>
</table>

Notes: The total amount of copper and zinc released during the 84 day study is displayed as $\mu g \text{ cm}^{-2} \pm 95\%$ confidence interval ($n = 4$). The amounts of Cu and Zn in the treatments are weight/weight.
The 20 wt% Zn treatments released on average 1.8 times more zinc compared to the treatments with 10 wt% Zn (Figure 4). Furthermore, the release rate of zinc was always lower, in a significant dose dependent manner (regression, \( F = 20.1, p < 0.045 \), \( F = 303.3, p < 0.003 \) respectively), with the increase in copper concentration. This lower release rate in the 10 wt% Zn treatments was 10–36% and in the 20 wt% Zn treatments 29–51% (Figure 4).

**Particle size Cu\(_2\)O and ZnO**

The average diameter of the Cu\(_2\)O particles was 1.77 ± 0.15 μm, which can be compared with the average diameter of the ZnO particles that were 0.20 ± 0.01 μm. The distribution was rather narrow but particles with a maximum diameter of about five times the average diameter could be found. Although not totally spherical this difference in diameter results roughly in a 78-fold increase in the relative surface area for the ZnO particles compared with the Cu\(_2\)O particles. This large surface area increases the speed of erosion of the ZnO particles, compared to the Cu\(_2\)O particles. The ZnO particles were generally more rod-shaped than the more spherical Cu\(_2\)O particles as release rate between the studied time-points, d0–4, d4–7, d7–14, d14–28, d28–56, and d56–84 (Figure 3). The variation in release rates were in general high prior to day 14. Between d14 and d56, the release rate was more constant followed by a substantial reduction between d56–86. Therefore, to compare copper and zinc release between paint formulations, the average release rate between days 14 and 56 was used. Highest average release rates of copper were found in the 16.3 wt% Cu treatments with 10 and 20 wt% zinc; 10.6 ± 1.94 and 10.01 ± 1.58 μg cm\(^{-2}\) day\(^{-1}\), respectively. The lowest average release rate of copper to still deter macrofouling during this time period was 4.68 ± 0.48 μg cm\(^{-2}\) day\(^{-1}\), in the 8.5 wt% Cu with no zinc treatment (Table 1).

**Release rates of zinc**

Release rates of zinc increased with the amount zinc included in the generic paint, while in the control treatments without zinc only background levels were recorded. The treatments with 10 wt% Zn released 306–435 μg cm\(^{-2}\) of zinc and the treatments with 20 wt% Zn released 513–746 μg cm\(^{-2}\) of zinc during the experiment (84 days, Table 1). The 20 wt% Zn treatments released on average 1.8 times more zinc compared to the treatments with 10 wt% Zn (Figure 4). Furthermore, the release rate of zinc was always lower, in a significant dose dependent manner (regression, \( F = 20.1, p < 0.045 \), \( F = 303.3, p < 0.003 \) respectively), with the increase in copper concentration. This lower release rate in the 10 wt% Zn treatments was 10–36% and in the 20 wt% Zn treatments 29–51% (Figure 4).
reflected in a slightly higher average aspect ratio, 1.9 ± 0.1 and 1.5 ± 0.1, respectively.

Discussion

The purpose of the study was to investigate how the release rates of copper from a generic AF paint vary, when copper and zinc were added in different concentrations. Furthermore, the minimum release rate of copper needed to deter fouling of barnacles and bryozoans during an 84-day period was investigated.

Firstly, as expected, the released amount of copper during the field study increased with the concentration of copper added to the paint, representing a 21% increase in the released amount between 8.5 and 11.7 wt% treatments and a 77% difference between 8.5 and 16.3 wt% treatments, when copper alone was added to the paint. Moreover, the released amount of copper was significantly influenced by the zinc concentration present in the paint, as seen in the total amount of released copper and the slopes of the release rate trend line from the respective treatment. Furthermore, the presence of zinc, 10 and 20 wt%, increased the day 14 to day 56 average release rate of copper on average 20 and 33%, respectively, significantly so in three out of six treatments. This is the first time that the influence of zinc on the copper release from an AF paint in an in situ study has been presented. However, additional research is needed to confirm this relationship due to the sometimes large variations between replicates.

All of the tested treatments were successful in deterring fouling; hence a total copper concentration of 8.5% and an average release rate of 4.68 μg cm⁻² day⁻¹ had sufficient AF efficacy for the Swedish west coast. Extrapolating the release rate and average 10 data, ie the amount of copper included in the treatment from the start, this treatment would hypothetically be able to have an AF effect for 146 days (approximately five months), which is equivalent to a boating season on the Swedish west coast. In addition, the paint was applied using a controlled paint thickness of 100 μm, which results in 30–40 μm of dry paint. If the paint were to be applied using a roller or a brush and in two layers, which is often recommended by the manufacturer, the dry paint thickness would increase to ~ 75 μm (data not shown). This would probably increase the period of AF efficacy of the treatment considerably, provided that the erosion rate of this rosin based AF paint was constant over time. This fact is contradicted by a decreasing linearity in the cumulative released copper between days 56 and 84. However, since these are static panels this can be the result of the prevailing hydrodynamic regime not being able to remove the built-up erosion layer, resulting in a decreased release of copper. Speed through water might be needed to remove this erosion layer. Seasonal cooling (days 56–84 were in October) of the ambient water at the study area could also be a factor contributing to this drop off in the copper release rate. This was also seen in the average release rates in Lagerström et al. (2018), a study performed in the same area at the same time-period. The water temperature dropped 4.2–6.4°C in the area at the end of the experimental period, from the maximum water temperatures of 19.1°C in July and 16.9 in September (data from SMHI – sharkweb, https://www.smhi.se/klimatdata/oceanografi/havsmiljodata/marina-miljovervakningsdata).

All treatments studied (except the controls) were successful in deterring fouling and thus the cut-off release rate value of copper for AF efficacy could not be determined. However, it can be assumed that the AF cut-off for the release of copper is lower than 4.68 μg cm⁻² day⁻¹. Not taking into account the probable non-steady state during day 56 release to 84, the lowest release rate (day 14–84) of the treatment with 8.5% Cu and 0% Zn that still deterred fouling was 3.04 μg cm⁻² day⁻¹ (Schiff et al. 2004; Hellio and Yebra 2009). The fouling pressure on the Swedish west coast is generally somewhat lower compared to many other parts of the world and is mainly comprised of the barnacle A. improvisus, which is overgrown by bryozoans and algae. In addition, the average release rates of copper in this study were found to be similar or lower than found by eg Valkirs et al. 2003 (5–20 Cu μg cm⁻² day⁻¹ after 30 days) using the same exposure conditions, ie a static harbor exposure with established biofilms on the panel surfaces. The average temperature and salinity conditions were higher in that study, probably contributing to the higher release rate (Valkirs et al. 2003). Hence, the lowest release rate to deter fouling in this study is probably beneath the cut-off release rate in waters with higher fouling pressure, but is probably too high for eg brackish waters where the fouling pressure is often lower (eg in the Baltic Sea). In future, a streamlined version of this type of field study could therefore be executed to determine the release rate of copper needed to prevent macrofouling in various geographical areas. By performing XRF measurements after 0, 14, and 56 days, data could easily be generated of the copper release rate needed to prevent macrofouling in an area. On this basis, AF paints for leisure boats could theoretically be manufactured to match a specific needed cut-off release rate required for certain regions with large differences in
fouling pressure, eg the Baltic Sea and the Mediterranean, reducing costs for the manufacturer and avoiding excess input of copper and zinc into the marine environment.

In the present study, the average release rates were calculated for the time period d14–56 and used to assess differences between coatings. Release rates were also calculated using day 0, 4, 7, 14, and 28 as starting values (Table S2). On average the release rates varied no more than 9.8% when using another starting day than day 14. This supports the validity of the calculated release rates presented here (Table 1).

Using data from the marina where the field study was performed, which holds roughly 700 leisure boats, it was calculated that the leisure boats spent most of the time at berth in the marina between the period May to October: the time at berth was 85% ± 1.0 (n = 53); the average number of days deployed in the sea was 150 days ± 4.2 (n = 53) out of which the boat was used for on average 23 days ± 2.6 (n = 53) (Dahlstrom et al. 2014). These results agree with what has been reported in other previous studies (Lagerqvist and Andersson 2016). Hence, passive leaching (no hull cleaning activities) is often the largest source of biocides, up of 95% of the total copper load (Schiff et al. 2004). This strengthens the usefulness of results from field tests of AF efficacy and release rates using static deployed panels.

In the present study, all the treatments deterred fouling for 84 days. However, the treatments with 10 and 20 wt% Zn released 32–47% more copper compared to the treatments without zinc. The majority of the copper released together with zinc was released unnecessarily, since it did not add to the AF efficacy during the time period studied. This excess amount of copper, not needed for AF efficacy, contributes to additional costs for manufacturers and consumers and failure of member states to reach the target limits for copper which is set within the national implementation of the Water Framework Directive and an overall negative impact on the marine environment (EU 2000). Furthermore, it is shown here that zinc is an important component in AF paints that acts to enhance the release rate of copper if a higher Cu release rate is needed, for example in areas with high fouling pressure. Zinc in itself alone in the paint matrix had an AF effect for approximately a month in the study performed. However, that one metal, toxic to aquatic organisms, is added to act as a pigment, and a stabilizer to govern the release rate of another toxic metal is surely a trade-off in environmental performance. Even though zinc has a higher aquatic PNEC in EU (7.8 µg l−1) (Zinc EU RAR 2010) compared to copper (2.6 µg l−1) in marine environments (Copper EU RAR 2008), a more favorable solution would be to replace zinc with another component, which is as effective in controlling copper leakage rates, but without having toxic effects in the marine environment. This could be a constituent, such as salts, sugars or proteins, with suitable water solubility to facilitate a proper paint polishing rate, eg calcium carbonate (Kiil et al. 2002). Further studies are required to investigate the possibility of replacing zinc with another water-soluble extender that can work in the same fashion as zinc, by increasing the release rate of copper.

Adjusting the release of copper from antifouling paints is important when for example meeting new regulations or optimizing antifouling efficacy. In this study, the release of copper showed a linear correlation with copper load when the data from coatings with no zinc oxide was analysed. With this load, one can expect the copper particles to be fully dispersed and no interconnectivity between particles is expected. The dissolution of copper occurs by a diffusion mechanism. When adding zinc oxide to the coating, the release rate of copper increases but no simple linear relationship between copper load and release is now applicable. Understanding the interplay between copper and zinc loading including other paint components could facilitate future coating development. In this study, we have shown that the use of a handheld XRF instrument could rapidly provide this information in an in-situ situation. To investigate the chemical and material interactions behind zinc’s influence on the copper release rates was not within the scope of this study. However, when zinc is included in the paint it most likely increases the erosion rate compared to the rosin alone without zinc, as the AF paint used is designed to erode at slow rate. The zinc oxide (ZnO) particles will quickly react with the chloride ions in the sea water and leave the paint matrix. The absence of zinc particles in the rosin paint will leave behind pores and spaces in the paint matrix, which will increase the total wetted area that is able to react with the copper particles. As a consequence, the release rate of copper increases (Hellio and Yebra 2009). Furthermore, particle size distribution also affects the rate of polishing, for example the polishing rate in TBT-based coatings has been shown to increase by decreasing particle sizes (Olsen et al. 2010). The particle size of copper and zinc that was used in this study was on average 0.20 µm for the ZnO and 1.77 µm for the Cu2O. The smaller particle sizes of ZnO, and therefore a relative large surface particle area, could also contribute to an increased polishing rate and hence an increase in copper release rate (Yebra et al. 2006). Together these factors could explain the increased release of copper in the treatments including zinc. However, further research is needed to elucidate the chemical and material interactions underlying the increased release of copper in the presence of zinc in AF paints. The release of zinc...
was largest in the treatments which included the lowest amounts of copper and was lowest in the treatments which had the highest amount of copper. This can be explained with copper having a lower eroding rate compared to the rosin. Hence, there will then be a smaller wetted area for the zinc to react with the water, compared to if the paint is containing lower amounts or no copper.

The generic AF paint used in the present study was not designed specifically to include the concentrations of copper and zinc used herein, so there might be differences in the impact of copper release by zinc in a commercial AF paint designed specifically to release and contain a certain amount of copper and zinc. The generic paint used here was a hard, rosin-based paint, designed to erode at low speeds. However, comparing the release rate data obtained in the present study with release rate data from a field study performed at the same location, with the same XRF-technique, and with the same general conditions using commercial paints, shows that the release rates of copper in the generic AF paint was in the same range, albeit lower, ie 2.1 in the 8.5%, 1.6 in the 11.7% and 1.5 times lower in the 16.3% treatments compared to the average release rate from the commercial paints (Lagerström et al. 2018). This demonstrates that the generic AF paint performed successfully as an experimental AF paint to study release rates of copper and zinc under field conditions.

To conclude, an average release rate of copper of 4.68 μg cm⁻² day⁻¹ is sufficient to deter settlement of barnacles in the Kattegat area, which is a lower rate than previously suggested in the existing literature, and it is also lower than the copper released by some commercial AF paints available on the market for this area today. Furthermore, incorporating zinc in the generic AF paint increases the average release rate and total amount of released copper. Consequently, it is shown that zinc can be used to increase the release rate of copper when needed to provide sufficient AF performance. The results presented here can be used to strive towards tailor-made AF paints regarding the release rate of copper to the specific fouling conditions in the geographical area which the paint will be used in. This will save costs for manufacturers and consumers while at the same time avoiding unnecessary environmental impact on non-target species.

Acknowledgements
The authors would like to thank the Boero group for supplying the generic paint, and Johan Nordberg, RISE for technical help in preparing the field panels.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This work resulted from the BONUS CHANGE project and was supported by BONUS (Art 185), funded jointly by the EU and Naturvårdsverket (Swedish Environmental Protection Agency).

References


