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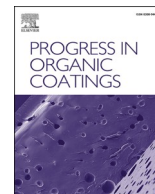
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## Investigation of critical copper release rates for dose optimization of antifouling coatings

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### ABSTRACT

Antifouling coatings are applied to ship and boat hulls to prevent the unwanted attachment of marine organisms known as biofouling. Most antifouling coatings do so through toxic means by continuously releasing copper from the paint film to the surrounding water and are thus of environmental concern. Few studies have investigated the minimum dose of copper from an antifouling coating required to inhibit biofouling, commonly referred to as the critical release rate. This study presents a comprehensive investigation into the critical release rates of copper from commercial antifouling coatings in European coastal waters, with study sites in the Atlantic (Arcachon, France), Kattegat (Hundested, Denmark) and Skagerrak (Tjärnö, Sweden). Employing a combination of X-ray Fluorescence (XRF) analysis and visual inspection, this six-month field study has evaluated the efficacy of various antifouling coatings with differing copper contents. The findings of this study indicate that a release rate of  $7 \mu\text{g cm}^{-2} \text{d}^{-1}$  was sufficient to inhibit macrofoulers at all three sites during static conditions. Results also indicate that the critical release rate is a parameter that coating manufacturers can optimize, as the performance of the coatings was not solely dependent on the copper release rates. The general critical release rate of  $7 \mu\text{g cm}^{-2} \text{d}^{-1}$  could serve as a benchmark for dose optimization of coatings for both the yacht and ship sectors in the studied waters to reduce their environmental impact. It can also be used as support for decision-makers to phase out coatings with unnecessarily high copper release rates from the market.

### 1. Introduction

Coastal zones provide vital ecosystems services of environmental, economic, social, cultural and recreational value and are currently globally under threat from chemical pollution and climate change [1]. The emission of biocides from antifouling (AF) coatings constitutes one of these threats. While these products are applied to hulls for biofouling prevention, thus reducing a vessel's consumption of fuel and its consequent atmospheric emissions, they do so through the release of one or more active substances meant to repel or poison settling organisms [2]. A review by de Campos et al. [3] showed some AF biocides to be up to 400 times more toxic to non-target organisms than target ones. The emission of biocides directly into coastal marine environments which affect marine species, whether they be the intended targets or not, is

therefore of environmental concern. As exemplified here through numerous studies published only in the last few years, the emission of biocides from AF coatings has been shown to deteriorate environmental water quality and negatively affect non-target organisms worldwide [4–18].

The efficacy of an antifouling coating is, besides the surface properties, dependent on (1) the identity of its contained biocide(s), as this will determine the product's biological target spectrum, and (2) on the delivered dose when the coating is in use, i.e. the biocide release rate(s) from the paint surface, typically expressed in  $\mu\text{g cm}^{-2}$  per day [19]. A given AF biocide will only be effective against its target(s) so long as its release rate does not fall below the minimum required to prevent their settlement or recruitment, also known as the *critical* release rate [20]. Cuprous (I) oxide ( $\text{Cu}_2\text{O}$ ) is the most frequently employed biocide in AF

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coatings today and acts to inhibit fouling through the release of copper [21]. Copper (Cu) is a broad spectrum antifoulant, active against many different fouling organisms such as barnacles, tubeworms, bivalves and many algal fouling species with the exception of some algae (e.g. *Enteromorpha* spp., *Ectocarpus* spp., *Achnanthes* spp.) that have been found to exhibit a high copper tolerance [22]. Despite its widespread use as an AF biocide, very few studies examining the critical release rate of copper were found in a recent literature review [23]. A critical release rate of  $10 \mu\text{g cm}^{-2} \text{day}^{-1}$  is often referenced in the scientific literature, but this result has been derived from a study in Atlantic waters carried out some 75 years ago [24].

The lack of methods to easily determine the biocide release rate from AF coatings in the field is likely an explanation for the absence of more recent field studies coupling efficacy and dose of copper. A method for the measurement of field release rates has however been introduced in recent years which can be used to remedy this knowledge gap [25]. The method, which is based on elemental X-ray Fluorescence (XRF) analysis, enables the quantification in  $\mu\text{g cm}^{-2}$  of total copper and zinc in a dry paint film applied on a panel. As the method is non-destructive, the concentration of an element in the same measurement point can be determined before and after water exposure in the field, enabling the derivation of the release rate by calculating the difference in concentration between the two time points divided by the number of exposure days [23,25]. The XRF method has thus far mainly been applied to measure the short-term release of copper from leisure boat paints at locations along the Swedish coast [23,26,27]. Although the aims of these previous studies were not per se to determine the critical release rate, their results suggest that it may vary between different coastal waters and be well below  $10 \mu\text{g cm}^{-2} \text{d}^{-1}$  in some areas, particularly in the Baltic Sea [23]. This suggests that environmental savings without function loss can be achieved by optimizing the dose of copper delivered from AF coatings.

The focus of this study was to determine the critical release rate of copper for modern-day antifouling paints for the prevention of macrofouling organisms in European waters. To this aim, commercially available copper coatings were exposed at three sites in different European bodies of water (Kattegat, Skagerrak and the Atlantic) with varying seawater salinities, temperatures and fouling challenges during a 6-months long field study. Coatings were chosen to provide a range of copper release rates, from low to high, to estimate the minimum necessary release to inhibit macrofouling. Panels were coated with the selected paints and exposed statically in the field. At multiple timepoints (2 weeks, 2 months, 4 months and 6 months), coupled measurements of copper release rates by XRF and assessments of coating performance through visual inspection were carried out on the panels. The aim of the study was to both determine the critical release rate of copper to deter macrofoulers at each site, and to investigate whether it differs depending on the composition of the local fouling community. We also discuss how the findings of this study may be used to ensure compliance with the European Union's Biocidal Product Regulation (BPR), which stipulates that the dose from a biocidal product should be the minimum necessary to achieve the desired effect [28].

## 2. Materials & methods

### 2.1. Coating selection and panel preparation

Five copper coatings labeled C1-C5 of the same color (black) were exposed for 6 months at three selected sites. The coatings, available commercially for the recreational sector in Sweden, were selected with the aim to cover a wide range of copper release rates and thus held varying amounts of cuprous oxide (6–32 wt%, ww) as their sole biocide (Table 1). All coatings also contained zinc oxide, as is common in the vast majority of current commercial coatings [27]. The coatings were marketed as either self-polishing (C1), polishing (C2, C5) or hard (C3, C4), thus covering the different commercially available paint

**Table 1**

Copper coatings C1-C5 used to assess the critical copper release rates to deter macrofoulers. The content of the sole active substance (cuprous oxide) was extracted from the Swedish Chemicals Agency public pesticide register [29]. The zinc oxide content range was obtained from the coatings' safety data sheets. Further details about the coatings can be found in Table S11 in the Supporting Information.

Coating	Cuprous oxide (wt%, ww)	Zinc oxide (wt%, ww)
C1	6.1	$\geq 10 - < 25$
C2	8.5	$\geq 10 - < 25$
C3	13	7–10
C4	22.02	$\geq 10 - < 25$
C5	31.93	$\geq 2.5 - < 25$
Control	0	0

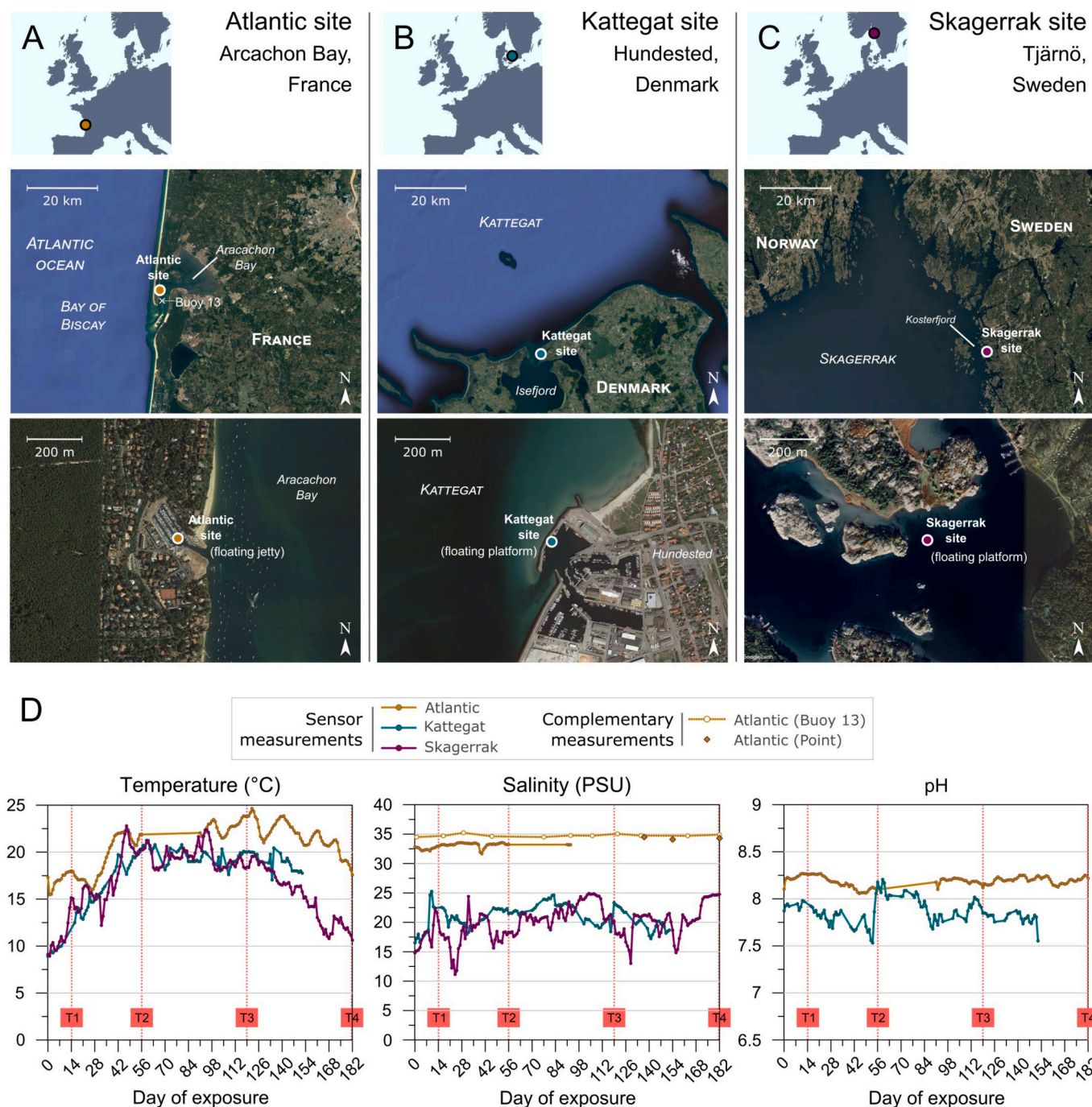
technologies of the current market. Regardless of paint technology, the lifetime of any coating is deemed to be spent when its release rate of active substance(s) drops below the minimum effective level [19,20,30]. To monitor the changes in release rate over time through XRF analysis, four parallel sets of panels, with three replicates of each of the five coating treatments (C1-C5), were prepared for the respective exposure sites.

PVC (Poly Vinyl Chloride) panels ( $10 \times 10$  or  $10 \times 20$  cm, and 2 mm thick) were lightly sanded, then coated with a first layer of primer (Hempel's Underwater Primer 26,030) with a wet film thickness (WFT) of  $100 \mu\text{m}$ . This was followed by the application of the top coating containing copper with a WFT of  $300$  or  $400 \mu\text{m}$ , to obtain dry film thicknesses (DFT) in the  $80$ – $120 \mu\text{m}$  range. Such thicknesses matched or exceeded those recommended by the coatings' manufacturers for one boating season, thus avoiding the risk of copper depletion before the end of the 6-month field study. An automatic, motorized film applicator (TQC AB3120) was used for all coatings to obtain smooth films. Control panels covered only with the primer coating were also prepared in triplicate for the fourth set of panels which was immersed for the full length of the field study. No copper nor zinc were detected through XRF analysis on control panels covered only with the primer coating.

### 2.2. Exposure sites and immersion times

The sites were selected to cover different ranges of seawater salinity, temperature and fouling challenge. The exposure sites and conditions were also selected to obtain conditions favorable for fouling colonization. All sites were therefore located in near-coastal waters and panels were exposed statically. The panels were attached randomly to frames and deployed in the coastal waters of three European countries: France (in Arcachon Bay in the Bay of Biscay by the Atlantic Ocean;  $44.6744^\circ\text{N}$ ,  $-1.2400^\circ\text{E}$ ), Denmark (in Hundested at the CoaST Maritime Test Center by Kattegat;  $55.9661^\circ\text{N}$ ,  $11.8427^\circ\text{E}$ ) and Sweden (at Tjärnö Marine Laboratory by Skagerrak;  $58.8818^\circ\text{N}$ ,  $11.1340^\circ\text{E}$ ) (Fig. 1A-C). At the Atlantic site, the frames were attached to a floating pier inside the enclosed marina of Port de La Vigne in Arcachon Bay. A floating platform, located at the outlet of the Isefjord, was used at the Kattegat site, with the frames attached to its more sheltered, inner walls. Finally, a floating platform located some 900 m away from Tjärnö Marine Laboratory by boat was used at the Skagerrak site. Sensors, point measurements and/or monitoring data from near-by buoys were used to monitor environmental parameters (temperature, salinity and pH, if available) at each site (Fig. 1D).

Panels were exposed between 35 and 95 cm below the surface, with the exact exposure depth of a panel depending on its vertical (randomized) position on the frame. The four parallel sets of panels were immersed at all three sites within a week of each other at the end of April/beginning of May in 2023 (T0). One set of panels was then retrieved at 4 pre-defined time points: 14 days (T1), 56 days (T2), 119 days (T3) and 182 days (T4). The only exception to this time schedule



**Fig. 1.** Location and satellite photos at two different scales of the Atlantic (A), Kattegat (B) and Skagerrak (C) exposure sites for coated panels. Graphs (D) show the average daily water temperature, salinity and pH, as recorded by sensors. For the Skagerrak site, only salinity and temperature data was recorded by sensors ~350 m south from the floating platform [31]. For the Atlantic site, salinity sensor data is missing for the second half of the field study. To complement this data set, salinity measurements from near-by monitoring buoy 13 (for location see figure panel A) and on-site point measurements (shown as diamonds). Red dotted lines show the 4 time points of the field study (T1-T4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was at the Atlantic site where T1 occurred after 15 days.

### 2.3. Fouling assessment

To enable the determination of critical release rates, the presence of macrofouling organisms on copper coatings and controls was closely assessed. Here, the European Chemical Agency's (ECHA) definition of macrofouling organisms was used which states that: "Macro-fouling is defined as large, distinct multicellular organisms visible to the human eye such as barnacles, tubeworms, or fronds of algae. Algae shorter than 5 mm

should be regarded as micro-fouling, together with slimes." [32].

At each checkpoint in time (T1-T4), photographs were taken of the individual panels belonging to the fourth and last set, which was immersed for the entirety of the season (i.e. the full 6 months). A visual inspection was then carried out to qualitatively determine if macrofouling was detected, the type of organism(s) present and the identity of the species. Any biofouling attached or with point of growth located within 15 mm from all edges of the coated surface was disregarded in the assessment of the copper coatings to avoid characterizing biofouling growing on the unprotected panel edge, obscuring the main panel area.

Two macrofouling species were not found on the control panels but detected on some of the copper coatings and also commonly found on the frames holding the panels. For these species, the timing of their settlement on the frames was included in the results to aid result interpretation.

## 2.4. Release rate determination by XRF

### 2.4.1. XRF principle and thickness considerations

In this study, release rate determinations were carried out through XRF analysis. The principles behind this method have been described in detail in e.g. Lagerström and Ytreberg [23] and, are thus only described briefly here. XRF is a widely employed technique for elemental detection and quantification in a range of applications, typically involving solid samples. During analysis, the instrument's X-ray tube emits primary X-rays onto the sample, causing excitation of its atoms and their consequent emission of photons, also known as secondary X-rays. The secondary X-rays are counted by the instrument's detector and recorded in the form of a spectra. The intensity of the signal in the spectra (typically measured as peak area) at the characteristic energy of a given element, is proportional to the concentration of that element in the sample [33]. XRF calibrations to quantify copper (Cu) and zinc (Zn) in AF coatings (in  $\mu\text{g cm}^{-2}$ ) have recently been utilized to enable the derivation of release rates through integration of their  $K\alpha$  peaks in the recorded spectra, as first described in Ytreberg et al. [25]. More specifically, release rate determination by XRF is carried out by measuring the area concentration of the metal before and after exposure. The average release rate (in  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ) during the exposure time is then inferred as the difference in concentration between the two time points, divided by the exposure time.

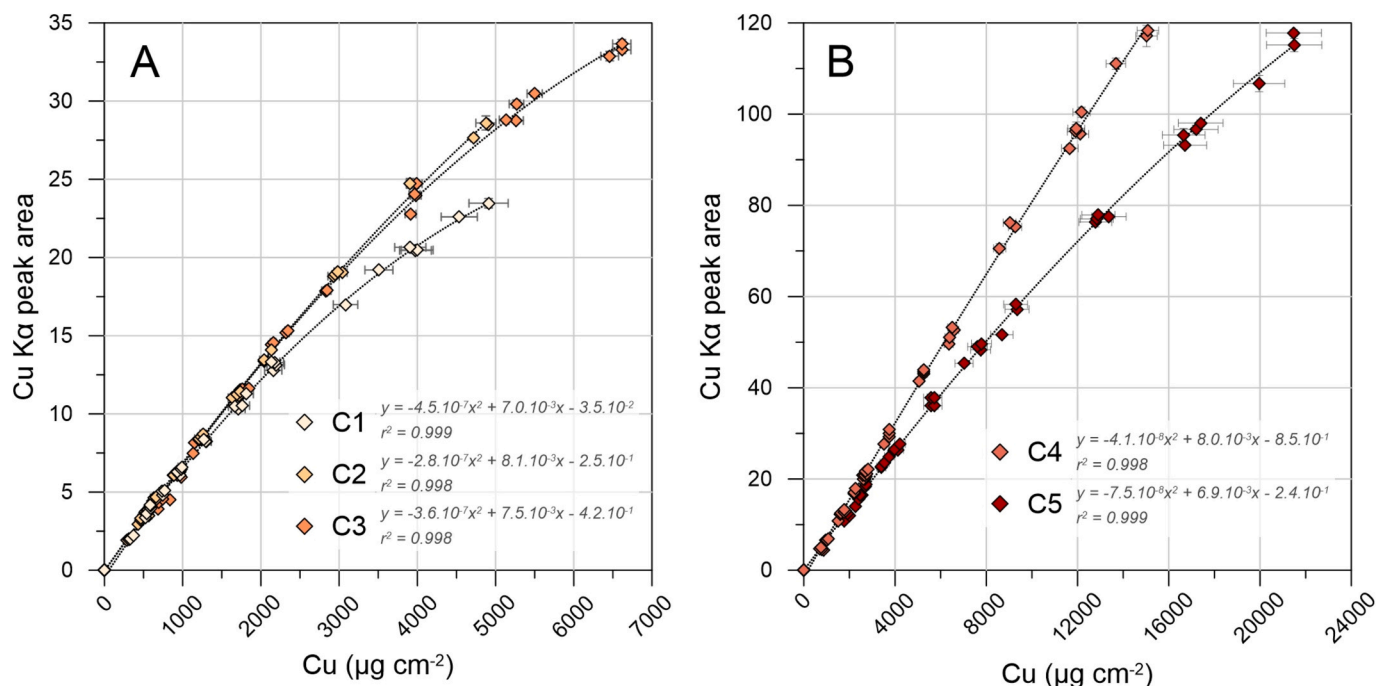
In previous studies where XRF analysis has been used to measure Cu release rates, a low DFT of around 30–40  $\mu\text{m}$  has been used to enable measurements of AF coatings within the linear response range of the instrument [23,26]. At such low DFTs, matrix effects caused by absorption of the secondary X-rays by the sample itself are negligible and a

“universal”, linear calibration curve may be applied. Yet, using such thin coatings puts time constraints on the experimental design [23]. In this study, higher DFTs were required to ensure coatings would not be depleted of copper before the end of the 6 months study. However, at DFTs outside the linear range, absorption effects of the secondary X-rays by the sample are no longer negligible and result in a decrease of the detected copper signal (i.e. the Cu  $K\alpha$  peak area). If such matrix effects are not accounted for, the total amount of copper in the film may be underestimated [25]. The degree of absorption by a sample will depend on its overall chemical composition and thus, in the case of paint, the specific formulation of the coating. Hence, individual calibration curves (Fig. 2) were established for all the coatings in this study, as described in the supporting information.

### 2.4.2. Panel measurements and release rate derivation

All coated panels were analyzed by XRF (Delta-50, Innov-X, Olympus) in triplicate in the same 4 measurement points before and after deployment. Measurements were made in dry conditions and any obstructing fouling present on panels retrieved from the field was removed as gently as possible to avoid damaging the underlying coating. In case of barnacles, their base plates were deliberately not detached to avoid paint removal as these can be firmly attached to the coating surface. When barnacles or other strongly adhering organisms were removed, the underlying surface of the coating was carefully inspected for damage overlapping with XRF measurement points. Such occasions were noted for 6 out of 720 points and the data from these points were excluded. Coincidence of remnant barnacle base plates with XRF measurement points were only noted for some of the replicate panels of coating C2 at the Skagerrak site at T3 and T4. No significant differences in the derived copper loss could however be determined between replicates with and without such coinciding barnacle base plates (one-way ANOVA,  $\alpha = 0.05$ ), suggesting XRF measurements were not impacted by the presence of base plates.

The area concentrations of the two metals for all measurements were derived using the integrated Cu and Zn  $K\alpha$  peak areas and the previously



**Fig. 2.** Calibration curves showing the relationship between copper area concentration ( $\mu\text{g cm}^{-2}$ ) and Cu  $K\alpha$  peak area derived from XRF spectra for coatings C1-C3 (A) and C4-C5 (B). Horizontal error bars show the propagated standard deviation from the chemical analysis of the coating (each analyzed in triplicate). Vertical error bars show the standard deviation of triplicate XRF measurements (note that these are often smaller than the symbol size and therefore not visible). Dashed and full lines show fitted polynomial and linear curves, respectively. Curve equations and  $r^2$ -values are shown next to each coating in the legend. The calibration curves for Zn can be found in Figure S11 in the supporting information.

established calibration curve equations (Fig. 2). The average area concentration in each measurement point was calculated ( $n = 3$  measurements). Three in-house coating standards holding concentrations of copper and zinc from  $\sim 200$  to  $2000 \mu\text{g cm}^{-2}$  were measured every 12th sample to determine measurement precision. The variation within one measurement day ( $\text{RSD} \leq 1.8 \%$ ) was comparable to the day-to-day variation ( $\text{RSD} \leq 1.1 \%$ ).

The cumulative release (in  $\mu\text{g cm}^{-2}$ ) was determined by calculating the difference in total area concentration before and after exposure for each measurement point. The results per panel were first averaged ( $n = 4$  points), before the average of triplicate panels was calculated. To assess for statistical differences in cumulative release among the three study sites, one-way ANOVAs with post hoc testing (Tukey HSD) were performed on the coating's cumulative releases.

Linear regressions were fitted between consecutive time points to interpolate the cumulative release. The slope of the fitted linear regression, represents the average release rate per day. The 95 % confidence interval of the slope of the fitted regression between two consecutive time points  $t_1$  ( $n = 3$  panels) and  $t_2$  ( $n = 3$  panels) was used to investigate significant differences in release rate between coatings. All statistical analyses were carried out in JMP® Pro (version 17.0.0) at a significance level of  $\alpha = 0.05$ .

#### 2.4.3. Accuracy of XRF-determined concentrations

Once immersed, the distribution of copper and zinc pigments in the coating's films will be altered due to the establishment of a depleted leached layer at the surface of the coating. Biofilm was also observed to settle on the surface of all the panels. To evaluate whether these changes to the coating condition could have affected the XRF-derived concentrations determined for the panels post-exposure, confirmatory chemical analysis was performed on a subset of exposed panels. Namely, panels from each of the four exposure periods (T1 – T4) were randomly selected from the Hundested set for both a coating with a lower (C2) and higher (C4) copper content. Squares of roughly  $1.9 \times 1.9 \text{ cm}$  were outlined on each panel and four XRF measurements were performed, one in each quarter of the square, to adequately cover the whole outlined area given the roughly 10 mm spot size of the XRF analysis. For the subsequent chemical analysis, all the paint contained within each outlined square was carefully chiseled off, gathered and subjected to total acid digestion according to the same procedure described previously (see 2.4.2). Each sample was weighed prior to analysis and the surface area of the scraped-off paint determined by processing scanned images of the panels in a graphic software (Inkscape v.1.3.2.), enabling the calculation of the area concentrations.

The comparison showed overall good agreement between the average area concentrations derived from the XRF measurements ( $n = 4$ ) and those calculated from the chemical analysis of the scraped-off paint samples ( $n = 1$ ). The average recovery ( $\pm 1$  standard deviation) for the XRF analysis of copper in comparison to the chemical analysis was 100 % ( $\pm 6 \%$ ) for coating C2 and 116 % ( $\pm 2 \%$ ) for coating C4. Similarly for zinc, the recoveries were 106 % ( $\pm 5 \%$ ) and 117 % ( $\pm 5 \%$ ), for C2 and C4 respectively. No statistically significant increasing or decreasing trends in the recovery over time could be detected ( $p > 0.05$ ), suggesting that neither the establishment of a leached layer or biofilm settlement on the surface of the coating had a discernible effect on the XRF-derived concentrations.

#### 2.5. Critical copper release rate range

An exact determination of the critical release rate for copper-based antifouling coatings would have required a more extensive study, with more coatings and more frequent release rate measurements. Upper and lower boundaries were instead derived to indicate a range within which the true critical copper release rate of each macrofouling organism likely lies. To ensure that the inhibition of macrofoulers was due to the effect of the coatings and not low natural abundance, critical release rate ranges

were only determined for commonly occurring macrofoulers, defined here as organisms settled on all three control replicates or found in ubiquitous numbers on the frames holding the panels. Macrofoulers only identified on e.g. one out of three control replicates were thus not considered.

The upper boundary was defined as the lowest derived copper release rate at which no presence of the specific macrofouling species was observed. Conversely, the lower boundary was the highest copper release rate that failed to prevent organism settlement. The detailed decision-making process for upper and lower boundaries is presented in the Results & Discussion section.

### 3. Results & discussion

#### 3.1. Fouling assessment

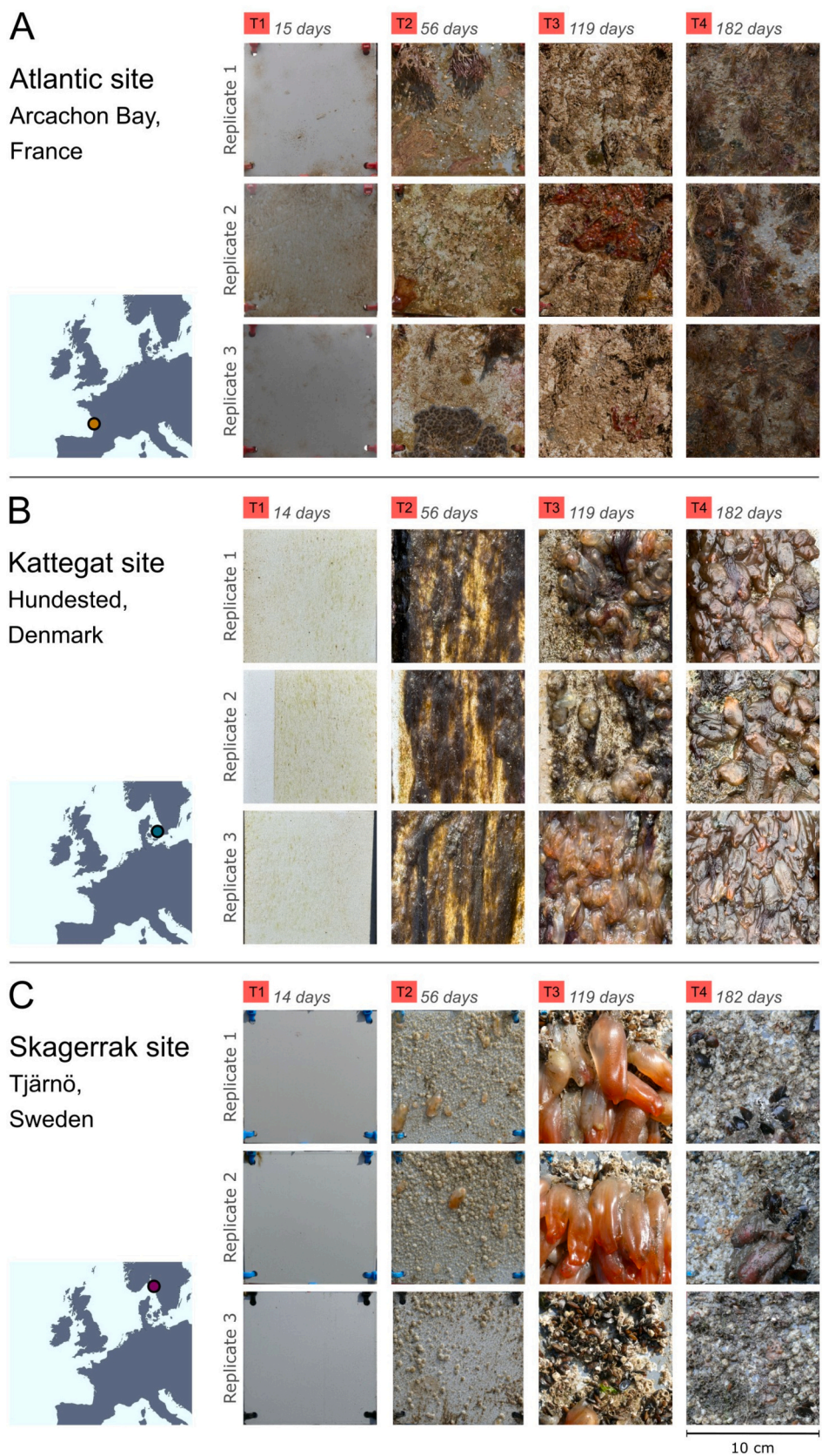
##### 3.1.1. Local macrofouling communities

Visual assessment of the control panels at the four timepoints (T1–T4) was performed to identify macrofouling organisms present in each panel and at each site, i.e. the target organisms, and their approximate settling time (Fig. 3). Distinct variations in biofouling were observed across the three European sites. These differences were notable both in terms of the species composition and the timing of colonization. The results from the qualitative fouling assessment, i.e. the identified species and the number of replicates panels on which they were observed, have been compiled in Table 2. Fifteen different species, categorized into 7 different types of macrofouling organisms, namely macroalgae, tunicates, bryozoans, tubeworms, barnacles, mussels and oysters, were identified across the three sites. All 7 types of macrofouling organisms were however not observed at all sites.

The Atlantic site's fouling community was distinguished by the presence of tubeworms (*Spirorbis dibrantatus*), which appeared already at the two-month checkpoint (T2). The other hard-shelled organism observed at the Atlantic site were oysters (*Magallana gigas*), which were also observed on the panel frames at Skagerrak (Table 2). At both sites, oysters were only observed at the final 6-month timepoint (T4) and thus settled quite late in the season. However, the most dominant macrofoulers in terms of surface coverage at the Atlantic site were branching (*Bugula neritina*, *Tricellaria inopinata*) and encrusting (*Schizoporella* spp.) bryozoans, and tunicates (mainly *Botrylloides* spp.), which started to settle between T1 and T2 (Fig. 3A). The Kattegat site was unique in its substantial growth of brown algae (*Pylaiella littoralis*), observed after two months (T2). At this time point, the geographically closest site in Skagerrak was instead characterized by a high number of barnacles (*Amphibalanus improvisus*). Barnacles were also present on the controls at the Kattegat site from T2 and onward, albeit to a lower extent. For both sites however, the surface became predominantly covered by tunicates (mainly *Ciona intestinalis*) after T2 (Fig. 3B and C). Apart from oysters and barnacles, mussels (*Mytilus Edulis*) were the third form of hard-shelled organisms observed at the Skagerrak site. Mussels were also present at the Kattegat site, although they were predominantly found not on the control panels, but on the frames used to mount the panels.

##### 3.1.2. Macrofouling on copper coatings

Most copper coatings were successful in preventing the attachment or development of a majority of the macrofoulers observed on the controls, as highlighted by the color coding in Table 2. At the Atlantic site, failure to inhibit colonization by bryozoans was observed for three coatings (C1, C2 and C3) and tubeworms for one coating (C2). At Kattegat, only single coatings were unable to prevent settling of barnacles (C2) and mussels (C1). For both the Atlantic and Kattegat sites, the observed failures rarely befell all coating replicates and the number of observed macrofouling individuals was also low, as illustrated by panel photographs (Fig. 4B and C). After 6 months of exposure (T4), the photographs reveal little visual differences between the 5 copper coatings at these two sites. Although not classified as macrofouling, the



**Fig. 3.** Photos of control panels (10 × 10 cm) deployed at the turn of the month April/May 2023 and retrieved at 4 time points (T1-T4) at each immersion site. Panel photos prior to exposure can be viewed for comparison in figure SI2 of the supporting information.

**Table 2**

Qualitative fouling assessment: number of replicate panels with macrofouling are indicated in each cell, complemented by a color code that visually represents fouling prevalence - ranging from red (identified on all three replicates) to green (not identified on any). (\*) Although not observed on the control panels, mussels were readily observed on the frames holding the panels at Kattegat and likewise for oysters at the Skagerrak site. Also shown are the average copper release rates in  $\mu\text{g cm}^{-2}$  ( $\pm 95\%$  C.I.) for the time interval preceding each timepoint.

Location	Organism	Species	Coatings and time checkpoints																											
			Control				C1				C2				C3				C4				C5							
			T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4				
Atlantic (Arcachon Bay, France)	Macroalgae	<i>Ulva spp. (green)</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Botrylloides spp.</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Tunicate	<i>Styela clava</i>	0	0	1	1	0	0	2	2	0	0	2	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Bugula neritina</i>	0	3	3	3	0	0	2	2	0	0	2	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
	Bryozoan	<i>Tricellaria inopinata</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Schizoporella spp.</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Tubeworm	<i>Spirorbis dibrantatus</i>	0	3	3	3	0	0	0	0	0	0	1	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Oyster	<i>Magallana gigas</i>	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Copper release rate ( $\mu\text{g cm}^{-2} \text{d}^{-1}$ )	Time interval	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4
		Average ( $\pm 95\%$ C.I.)	0	0	0	0	5.6 (±0.8)	6.3 (±0.8)	5.0 (±2.2)	3.2 (±3.1)	8.0 (±1.0)	8.7 (±3.1)	5.7 (±2.7)	0.2 (±2.8)	8.6 (±0.6)	10.7 (±2.3)	9.5 (±2.3)	1.4 (±3.2)	25.1 (±5.3)	24.8 (±4.9)	24.4 (±5.8)	10.3 (±10.2)	6.5 (±6.1)	34.1 (±11.2)	15.2 (±7.5)	20.5 (±5.5)				
Kattegat (Hundested, Denmark)	Macroalgae	<i>Ulva spp. (green)</i>	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Ceramium sp. (Red)</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Pylaiella littoralis (Brown)</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Tunicate	<i>Ciona intestinalis</i>	0	0	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		<i>Botryllus schlosseri</i>	0	0	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Barnacle	<i>Amphibalanus improvisus</i>	0	3	3	3	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Mussel	<i>Mytilus Edulis</i>	0	0*	0*	0*	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Copper release rate ( $\mu\text{g cm}^{-2} \text{d}^{-1}$ )	Time interval	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4
		Average ( $\pm 95\%$ C.I.)	0	0	0	0	1.4 (±0.1)	5.5 (±1.0)	3.9 (±1.0)	1.6 (±0.9)	3.6 (±1.2)	5.5 (±0.5)	5.5 (±0.7)	0.2 (±0.8)	4.0 (±1.0)	5.9 (±1.2)	6.2 (±1.7)	1.3 (±2.2)	6.6 (±1.8)	22.7 (±1.7)	14.3 (±2.3)	8.4 (±3.6)	0.0 (±0.0)	14.1 (±4.7)	21.9 (±3.5)	13.4 (±1.8)				
	Skagerrak (Tjärnö, Sweden)	Macroalgae	<i>Ulva spp. (green)</i>	0	0	3	3	0	0	0	0	0	0	0	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
Tunicate		<i>Ciona intestinalis</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Bryozoan		<i>Membranipora membranacea</i>	0	3	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacle		<i>Amphibalanus improvisus</i>	0	3	3	3	0	3	3	3	0	3	3	3	0	3	3	3	0	3	0	0	0	3	0	0	3	0	0	0
Mussel		<i>Mytilus Edulis</i>	0	0	3	3	0	0	0	1	0	0	3	3	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0
Oyster		<i>Magallana gigas</i>	0	0	0	0*	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Copper release rate ( $\mu\text{g cm}^{-2} \text{d}^{-1}$ )		Time interval	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4	T0-T1	T1-T2	T2-T3	T3-T4
	Average ( $\pm 95\%$ C.I.)	0	0	0	0	2.6 (±0.7)	3.7 (±1.3)	4.6 (±1.4)	3.2 (±1.2)	3.7 (±2.4)	5.6 (±1.0)	5.6 (±1.4)	1.0 (±4.3)	6.3 (±0.6)	5.2 (±1.1)	4.6 (±1.3)	2.3 (±2.1)	9.4 (±6.8)	19.6 (±5.0)	14.6 (±3.4)	3.9 (±2.9)	0.0 (±0.0)	3.3 (±3.8)	15.8 (±4.7)	15.7 (±6.7)					

presence of slime on the copper coatings at the Atlantic site is noteworthy in comparison to the other two sites. Any difference in copper release rate between coatings does not seem to have impacted its extent, which is not surprising as copper is not an effective biocide against slime [34].

The highest number of failures were detected for the Skagerrak site. These instances mostly involved the settlement of hard fouling, i.e. barnacles, mussels and oysters (Table 2), typically affecting all replicates of the failing coating(s). Interestingly, all five coatings were unable to inhibit settlement of barnacles by the two months checkpoint T2. Here, small barnacles (approximately  $\phi$  1 mm) were detected on all replicates of all panels (Fig. 4C). The individuals were however much smaller than those observed on the controls at the same timepoint (Fig. 3C) and most appeared to have died whilst still in the cyprid stage (no base plate formation was observed) or soon after metamorphosis. During T2-T3, barnacles were only encountered on the three coatings with the lowest copper content, i.e. C1, C2 and C3. As illustrated by the panel photos, it is however clear that there are large differences in performance among the three lowest coatings: whereas all panels with coating C2 were highly colonized by barnacles already at T3, the observed degree of coverage on coatings C1 and C3 was generally lower at both T3 and T4. Mussels were also observed on C1-C3, whereas oysters were only detected on C2.

### 3.2. Copper release

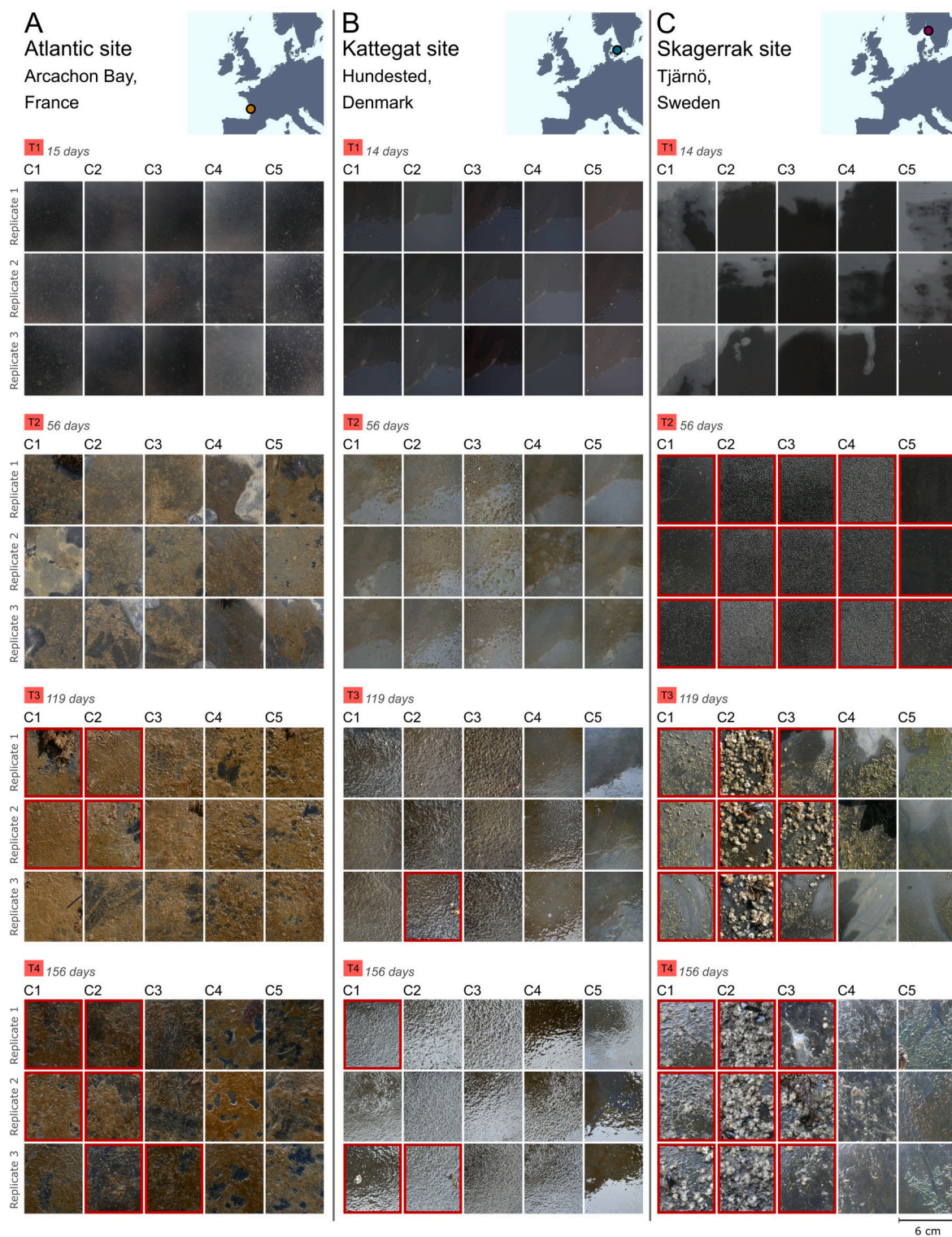
#### 3.2.1. Cumulative release

The cumulative releases (in  $\mu\text{g cm}^{-2}$ ), i.e. the total copper and zinc losses, from the coated panels were derived for all coatings at the three

respective sites. Only the results for copper are shown here, but results for zinc (Figure SI3), as well as the raw data (Table SI2), can be found in the Supporting Information. Based on the cumulative release of copper (Fig. 5), the five studied coatings can roughly be divided into two categories as either low (C1, C2 and C3) or high (C4 and C5) leaching. These results reflect in part but not entirely the coatings' copper contents. Despite its higher copper content, C5 (32 wt% Cu<sub>2</sub>O) did not always have a significantly higher release compared to C4 (22 wt%). Similarly, even though the other three coatings both held lower amounts of copper and had lower releases, the release of C3 (13 wt%) was not always significantly higher than those of C1 (6 wt%) and C2 (8.5 wt%). Although copper content is an important factor controlling the copper release rate from a coating, it is by far not the only one, as already demonstrated in previous field studies (e.g. [26]). Other paint parameters such as the size of the cuprous oxide particles and the chemical properties of the rest of the paint matrix, i.e. the composition of the binder and the amount of other sea-soluble pigments added such as zinc oxide, also play an important role [27,35,36].

Statistical testing showed a significantly higher cumulative release of copper at the Atlantic site for all coatings at all time points with one mere exception (coating C2 at T4 = 182 days, for  $p$ -values see Table SI3). Both salinity and temperature were higher at the Atlantic site (on average 33 PSU and 21 °C) compared to the Kattegat (21 PSU, 18 °C) and Skagerrak sites (20 PSU, 17 °C) (Fig. 1D), which could explain the higher release rates observed here. An increased copper release at higher salinity has been documented in other field and laboratory studies [25,26,37–39]. Higher temperatures and salinities both act to enhance the dissolution rate of cuprous oxide particles [35] and may also increase the solubility of certain paint binders [40,41]. Few significant



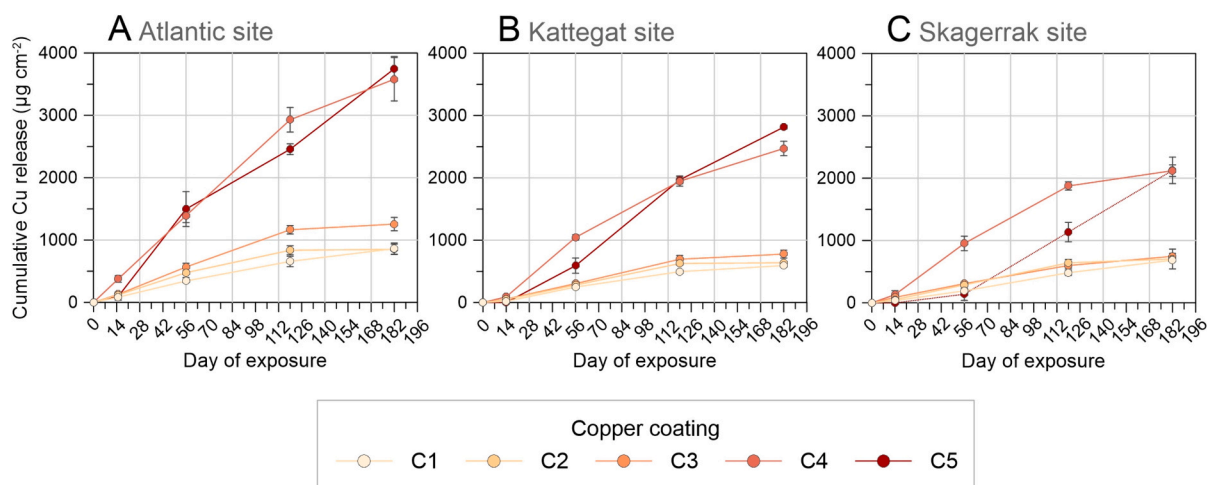


**Fig. 4.** Photos of evaluated area ( $6 \times 7$  cm) of panels coated with copper coatings C1-C5 deployed at the turn of the month April/May 2023 and retrieved at 4 time points (T1-T4) at each location. Macrofouling was observed on panels with red frames. Panel photos prior to exposure can be viewed for comparison in figure SI2 of the supporting information. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

differences in cumulative copper release from the coatings were detected between the Kattegat and Skagerrak sites (Fig. 5B and C), likely due to the similar seawater salinity and temperatures during the field experiment.

### 3.2.2. Release rates

Assuming a linear relationship between the cumulative release and the time of exposure, the average release rates (in  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ) between consecutive timepoints were derived as the slope of these linear regressions. The results can be found below the fouling assessment at each site in Table 2. Given the changing water parameters over the course of



**Fig. 5.** Average cumulative release of copper (in  $\mu\text{g cm}^{-2}$ ) over time for the five copper coatings C1–C5 at the three study locations, as determined by XRF. Error bars show the standard deviation ( $n = 3$  panels). Lines show the linear regression between time points.

the field experiment (Fig. 1D, e.g. temperature), variations in release rates over time might be expected. However, 10 out of 15 coating scenarios (five coatings  $\times$  three locations) had no significant differences in release rates, at least during the initial 4 months of exposure (compare Table 2). The remaining 5 scenarios (C1 and C4 in Kattegat and C5 at all sites), are characterized by an increase in release rates over the first 2–4 months. Such a behavior was also observed in other studies [26,42] and is likely attributed to hydration processes [43].

For some of the coatings, the copper release rates drop to significantly lower levels in the last time interval (Table 2). For coatings C1 (in Kattegat), C2 (all sites) and C3 (Atlantic and Kattegat) specifically, the final rates were so low that they were not significantly different from zero. As more than half of the copper contained in their paint films remained at the end of the field study, the observed decrease cannot be attributed to copper depletion, but more likely a result of the extended static conditions. Upon initial immersion of a coating, the copper nearest the surface will leach out, leaving a porous polymer structure without cuprous oxide particles, known as the leached layer, through which the subsequently released copper ions will diffuse [20]. Polishing action by moving seawater is typically required to maintain a stable leached layer thickness and prevent early coating failure [44,45]. The lack of dynamic conditions in the current study may have resulted in an increased leached layer thickness and thus longer diffusion paths for the dissolved copper ions over time, eventually halting the release of copper altogether for some coatings. The decrease in seawater temperature during the final time interval (Fig. 1D) may have been an additional contributing factor.

### 3.3. Coupling of performance and dose

#### 3.3.1. Defining the critical release rate range

The presence and absence of macrofoulers on the different coatings in combination with their derived release rates of copper was used to indicate a range for the critical release rate. As discussed previously, all copper coatings were successful in deterring a majority of the macrofoulers identified on the controls. In these cases, the critical release rate range was easily determined: the lower boundary is the release of the control (i.e.  $0 \mu\text{g cm}^{-2} \text{d}^{-1}$ ), while the upper boundary is the lowest copper release rate at the time point when settlement first appeared on the control panels. For all other cases, i.e. when one or several copper coatings failed to prevent settlement of a given species, the lower boundary was instead the highest release rate at which settlement was not prevented, while the upper boundary was defined as the lowest copper release rate at which no colonization of the specific macrofouling

species was observed. For these latter cases, the specific considerations made to determine the upper and lower boundaries are discussed below. The defined critical release rate ranges based on these considerations have been summarized in Table 3.

**3.3.1.1. Atlantic site.** At the Atlantic site, the settlement of branching bryozoans (*B. neritina* and *T. inopinata*) and tubeworms (*S. ditrantatus*) was not prevented by some of the copper coatings (Table 2). The settlement of both species of bryozoans was observed at the two-month checkpoint (T2) on the controls but not on any of the copper coatings. The lowest release rate of copper in the preceding time interval (T1–T2) of  $6.3 \pm 0.8 \mu\text{g cm}^{-2} \text{d}^{-1}$  (coating C1) was thus able to inhibit settlement. At the next timepoint T3, coatings C1 and C2 were both unable to prevent the settlement of bryozoans on two of their replicates. Their release rates preceding these observed instances of failure were  $\leq 5.7 \pm 2.7 \mu\text{g cm}^{-2} \text{d}^{-1}$ . Hence a narrow range for the critical release rate of copper can be given for bryozoans at this site, with a lower boundary of 5.7 and an upper boundary of  $6.3 \mu\text{g cm}^{-2} \text{d}^{-1}$ .

Settlement of tubeworms was only observed on coating C2. The initial instance was recorded after four months (T3), but it involved only a single tubeworm on one of the replicates. Therefore, this occurrence was not considered significant enough for the critical release rate determination. By the next timepoint (T4) however, tubeworms were present on all three replicates, albeit in low numbers ( $\leq 10$  individuals per panel). The average release rate for C2 between T3–T4 was  $0.2 \pm 2.8 \mu\text{g cm}^{-2} \text{d}^{-1}$ . Although this release rate was not significantly different from those of C1 and C3, it is the lowest on average of the three and no tubeworms were present on the other two coatings. It was therefore set as the lower boundary. Meanwhile, the next higher release rate that successfully prevented settlement during this time interval ( $1.4 \pm 3.2 \mu\text{g cm}^{-2} \text{d}^{-1}$ , coating C3) was designated as the upper boundary.

**3.3.1.2. Kattegat site.** At Kattegat, the observed instances of failure involved barnacles (coating C2 at T3) and mussels (coating C1 at T4). For barnacles, the failure involved only three individuals settled on one of the replicate panels of coating C2. The average copper release rate of  $5.5 \pm 0.7 \mu\text{g cm}^{-2} \text{d}^{-1}$  determined for coating C2 between T2–T3 (when settlement of barnacles occurred) is therefore likely very close to the critical release rate. During this time interval, the release rates of the three low-leaching coatings were not significantly different from one another, but no barnacles were observed to settle on C1 ( $3.9 \pm 1.0 \mu\text{g cm}^{-2} \text{d}^{-1}$ ) or C3 ( $6.2 \pm 1.7 \mu\text{g cm}^{-2} \text{d}^{-1}$ ). Following the pre-determined evaluation criteria, estimates of the lower and upper boundaries of the critical release rate were set to 5.5 and  $6.2 \mu\text{g cm}^{-2} \text{d}^{-1}$ , respectively.

**Table 3**

Estimated lower and upper boundaries of the critical copper release rates to prevent the prevalently occurring macrofouling species at the three investigated sites. The coatings and time intervals from which the critical release rate boundaries were derived are also provided.

Location	Organism	Species	Source of estimated boundary		Critical copper release rate range ( $\mu\text{g cm}^{-2} \text{d}^{-1}$ )	
			Lower boundary	Upper boundary	Lower boundary	Upper boundary
Atlantic (Arcachon Bay)	Macroalgae	<i>Ulva</i> spp.	Control, T1-T2	C1, T1-T2	> 0	$\leq 6.3 (\pm 0.8)$
	Tunicate	<i>Botrylloides</i> spp.	Control, T1-T2	C1, T1-T2	> 0	$\leq 6.3 (\pm 0.8)$
	Bryozoan	<i>Bugula neritina</i>	C2, T2-T3	C1, T1-T2	> 5.7 ( $\pm 2.7$ )	$\leq 6.3 (\pm 0.8)$
		<i>Tricellaria inopinata</i>	C2, T2-T3	C1, T1-T2	> 5.7 ( $\pm 2.7$ )	$\leq 6.3 (\pm 0.8)$
	Tubeworm	<i>Schizoporella</i> spp.	Control, T1-T2	C1, T1-T2	> 0	$\leq 6.3 (\pm 0.8)$
		<i>Spirorbis ditrantatus</i>	C2, T3-T4	C3, T3-T4	> 0.2 ( $\pm 2.8$ )	$\leq 1.4 (\pm 3.2)$
	Oyster	<i>Magallana gigas</i>	Control, T3-T4	C2, T3-T4	> 0	$\leq 0.2 (\pm 2.8)$
		<i>Ulva</i> spp.	Control, T1-T2	C1, T1-T2	> 0	$\leq 5.5 (\pm 1.0)$
Kattegat (Hundested)	Macroalgae	<i>Ceramium</i> sp.	Control, T1-T2	C1, T1-T2	> 0	$\leq 5.5 (\pm 1.0)$
	Tunicate	<i>Pylaiella littoralis</i>	Control, T1-T2	C1, T1-T2	> 0	$\leq 5.5 (\pm 1.0)$
		<i>Ciona intestinalis</i>	Control, T2-T3	C1, T2-T3	> 0	$\leq 3.9 (\pm 1.0)$
	Barnacle	<i>Botryllus schlosseri</i>	Control, T2-T3	C1, T2-T3	> 0	$\leq 3.9 (\pm 1.0)$
		<i>Amphibalanus improvisus</i>	C2, T2-T3	C3, T2-T3	> 5.5 ( $\pm 0.7$ )	$\leq 6.2 (\pm 1.7)$
	Mussel	<i>Mytilus Edulis</i>	C1, T3-T4	C1, T2-T3	> 1.6 ( $\pm 0.9$ )	$\leq 3.9 (\pm 1.0)$
	Macroalgae	<i>Ulva</i> spp.	C3, T3-T4	C1, T3-T4	> 2.3 ( $\pm 2.1$ )	$\leq 3.2 (\pm 1.2)$
	Tunicate	<i>Ciona intestinalis</i>	Control, T1-T2	C1, T1-T2	> 0	$\leq 3.7 (\pm 1.3)$
Skagerrak (Tjörnö)	Bryozoan	<i>Membranipora membranacea</i>	Control, T1-T2	C1, T1-T2	> 0	$\leq 3.7 (\pm 1.3)$
	Barnacle	<i>Amphibalanus improvisus</i>	C2, T2-T3	C4, T2-T3	> 5.6 ( $\pm 1.4$ )	$\leq 14.6 (\pm 3.4)$
	Mussel	<i>Mytilus Edulis</i>	C1, T3-T4	C4, T3-T4	> 3.2 ( $\pm 1.2$ )	$\leq 3.9 (\pm 2.9)$
	Oyster	<i>Magallana gigas</i>	C2, T3-T4	C3, T3-T4	> 1.0 ( $\pm 4.3$ )	$\leq 2.3 (\pm 2.1)$

Previous studies in Kattegat have found that copper release rates  $\leq 4.2 \pm 0.2$  [26] and  $\leq 4.7 \pm 0.5 \mu\text{g cm}^{-2} \text{d}^{-1}$  [27] have been sufficient to inhibit barnacle settlement. The estimated range for the critical release rate here may thus be somewhat conservative.

Similar observations as for barnacles were also made for the settlement of mussels at this site. Mussels were only observed on one coating (C1 at T4), with a single individual detected on two replicate panels. During the preceding interval (T3-T4), the release rate of C1 ( $1.6 \pm 0.9$ ) was not significantly different from those of C2 ( $0.2 \pm 0.8$ ) or C3 ( $1.3 \pm 2.2 \mu\text{g cm}^{-2} \text{d}^{-1}$ ). Nonetheless, the most conservative value for the lower boundary is  $1.6 \mu\text{g cm}^{-2} \text{d}^{-1}$ . In the preceding time intervals, when mussels were observed on the panel frames but not yet on any of the copper coatings, the lowest derived release rate able to prevent its settlement was  $3.9 \pm 1.0 \mu\text{g cm}^{-2} \text{d}^{-1}$  (C1 during T2-T3), which was therefore set as the upper boundary. But again, it might be possible to develop coatings with releases that fall below these values and are still effective.

**3.3.1.3. Skagerrak site.** The settlement of green macroalgae (*Ulva* spp.) on two of the copper coatings indicate that release rates of 1.0 (C2) and 2.3 (C3)  $\mu\text{g cm}^{-2} \text{d}^{-1}$  were not sufficient to deter this species. The latter was thus set as the lower boundary. The lowest successful release rate was  $3.2 \pm 1.2$ , delivered by coating C1 during T3-T4, and set as the upper boundary for this species.

As discussed previously (see 3.1.2), all five copper coatings failed to deter barnacles at the Skagerrak site that settled prior to T2. However, during the following time interval, barnacles only persisted on the lowest leaching coatings C1-C3. These findings suggest that, as opposed to those of C1-C3 ( $4.6$ – $5.6 \mu\text{g cm}^{-2} \text{d}^{-1}$ ), the release rates by C4 and C5 ( $14.6$ – $15.8 \mu\text{g cm}^{-2} \text{d}^{-1}$ ) were sufficient to prevent continued development of settled barnacles. The degree of barnacle survival on the low-leaching coatings varies however notably (Fig. 4C). While coating C2 was highly colonized by barnacles by T3, only a few small individuals had settled on two replicates of coating C1. For coating C3, only one replicate panel had a substantial number of settled barnacles, whereas few individuals were observed on the other two. The comparatively superior performances of coatings C1 and C3 are noteworthy given that no significant differences in copper release rate was detected between the three coatings during T2-T3 (or even at any point during T1 and T4). It is possible that other parameters could have aided in enhancing their performance. Zinc has, for example, been argued to increase the toxicity of copper [46], but coating C2 had significantly higher zinc release rates

during T2-T3 ( $11.4 \pm 4.1$ ) as compared to both C1 ( $3.0 \pm 0.6$ ) and C3 ( $1.8 \pm 1.4$ ) (see Table SI 4). Other properties of the coatings not evaluated here such as binder properties, surface smoothness and coating hardness could also have resulted in performance differences despite similar dose deliveries [47]. Variations in release rate over time that were not captured in the current study could also have been of importance. As the estimated copper release rates are mere averages over 2 months long time interval, they provide no information regarding possible daily or even weekly variations, which could have been the differentiating factor. As opposed to C1 and C3, the release rates of C2 during the last evaluated time period T3-T4 were not significantly different from zero. It is thus possible that the copper release from C2 had already slowed substantially towards the end of time interval T2-T3, explaining its comparatively poorer performance. Overall, the results from the three coatings reflect that their delivered copper doses at T2-T3 ( $4.6$ – $5.6 \mu\text{g cm}^{-2} \text{d}^{-1}$ ) were below but probably quite near the critical release rate for barnacles. The lower boundary was therefore set to  $5.6 \mu\text{g cm}^{-2} \text{d}^{-1}$ . Following the pre-defined evaluation criteria, an upper boundary of  $14.6 \mu\text{g cm}^{-2} \text{d}^{-1}$  was set, reflecting the successful prevention of barnacles by coating C4 during T2-T3. At three times that of the lower boundary, this is however a conservative estimate, i.e. likely in great excess of the critical release. This is supported by results from a previous study at a site on the border between Kattegat and Skagerrak which estimated that release rates  $> 5.4 \pm 0.6$  but  $\leq 7.1 \pm 0.2 \mu\text{g cm}^{-2} \text{d}^{-1}$  were sufficient to deter barnacles in this area. Nonetheless, due to a lack of coatings with intermediate release rates (e.g.  $7$ – $10 \mu\text{g cm}^{-2} \text{d}^{-1}$ ), the upper boundary cannot be set lower.

Mussels were also found to settle on the three lowest leaching coatings at this site. The first observed settlement was at T3 on coatings C2 (all replicates) and C3 (one replicate). However, the attachment occurred on top of already adhered barnacles and not on the coating surface itself. Of more relevance is thus the observed settlement that occurred directly on the surface of C1 during the subsequent time interval. Only a single replicate was affected for this coating whose average copper release rate was  $3.2 \pm 1.2 \mu\text{g cm}^{-2} \text{d}^{-1}$ . A lower boundary of  $3.2 \mu\text{g cm}^{-2} \text{d}^{-1}$  was therefore chosen, while the release rate of successful coating C4 at  $3.9 \mu\text{g cm}^{-2} \text{d}^{-1}$  during the same time interval was defined as the upper boundary. Finally, the occurrence of oysters on coating C2 at T4 suggested lower and upper boundaries of  $1.0$  and  $2.3 \mu\text{g cm}^{-2} \text{d}^{-1}$ , respectively.

### 3.3.2. Critical copper release rates for macrofouling organisms

An overview of the established critical release rate ranges from Table 3 is represented in Fig. 6, by order of organism.

The figure shows that most organisms were deterred with release rates of approximately 2–6  $\mu\text{g cm}^{-2} \text{d}^{-1}$ . The only exception were barnacles at the Skagerrak site, where the upper boundary had to be set to 14.6  $\mu\text{g cm}^{-2} \text{d}^{-1}$ , as discussed previously. However, as highlighted in Fig. 6, much lower release rates have been shown to effectively deter barnacles both in this (Kattegat site) and previous studies. Overall, release rates  $\leq 7 \mu\text{g cm}^{-2} \text{d}^{-1}$  from a modern-day copper coating are likely sufficient in preventing macrofouling organisms, regardless of coastal water. This is lower, but nonetheless comparable to that derived in the study by Barnes [24] carried out in 1945 at Millport, located by the Atlantic on the Great Cumbrae Island (off the Scottish coast). Barnes

concluded that a release rate of 10  $\mu\text{g cm}^{-2} \text{d}^{-1}$  seemed to prevent the settlement of all animal species observed, namely: *Didemnum* sp. (tunicate; 2  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ), *Pomatoceros triqueter* (tubeworm; 3–3.5  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ), *Obelia longissimi* (hydroid; 4  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ), *Balanus* sp. (barnacle; 9  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ) and *Tubularia coronate* (hydroid; 10  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ). The comparatively higher sensitivity of tubeworms to copper was also noted in this study, where average rates  $\leq 1.4 \mu\text{g cm}^{-2} \text{d}^{-1}$  were sufficient for its prevention. The suggested critical release rate to prevent barnacles derived by Barnes (9  $\mu\text{g cm}^{-2} \text{d}^{-1}$ ) is slightly higher than that determined here for the Kattegat site and previous field studies (with upper boundaries of 4.2–7.1  $\mu\text{g cm}^{-2} \text{d}^{-1}$ , as seen in Fig. 6). The discrepancy could be explained by differences in species sensitivity, in case a different barnacle species was included in the study by Barnes, but also by differences in release rate determination. Barnes determined the

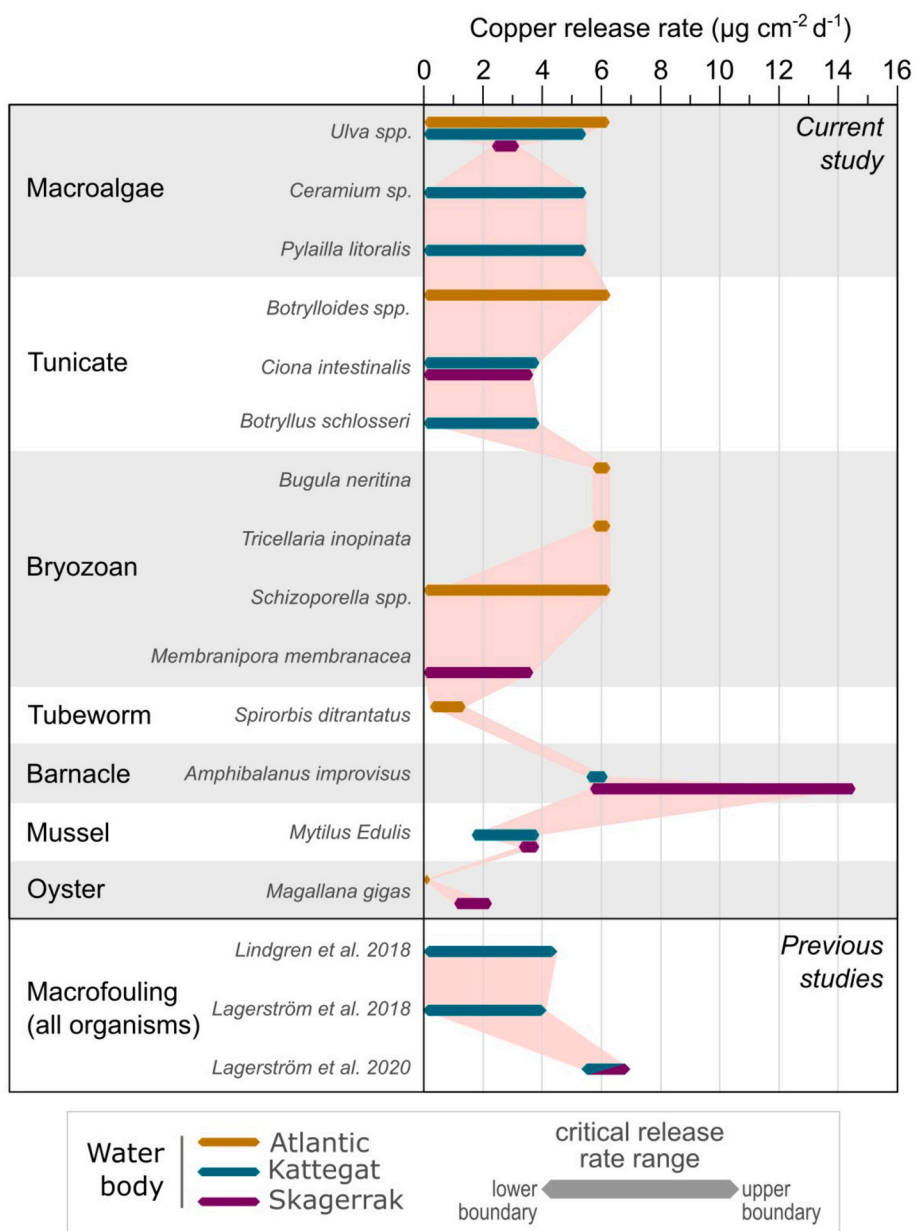


Fig. 6. Critical release rate ranges of copper for the macrofouling organisms at the three different sites (i.e. the true critical release rate lies somewhere on the colored bars). Upper and lower ends of bars have been connected by a colored (light pink) field to highlight the overall range of effective release rates across the different organisms. Also shown at the bottom of the graph are results from previous studies where the ranges were estimated for all macrofouling organisms as a group [26,27,48], all determined from coatings containing both  $\text{Cu}_2\text{O}$  and  $\text{ZnO}$ . In the study by Lagerström et al. 2020, the study site was located on the border between Kattegat and Skagerrak, hence the dual color of the bar in the graph. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

release rates by scraping off the paint from each test slide for subsequent analysis of its copper content. The release rate was then derived through comparison with the copper content of the original coating, an approach that may result in higher uncertainties.

### 3.4. Implication of findings for regulation and coating development

Investigations into dose optimization are highly relevant to reduce the environmental impact of antifouling coatings. Although increasingly efficient biocide-free silicone-based coatings have been developed over the past 30 years, they hold a relatively small market share when it comes to both the professional (ship) and recreational (yacht) markets, mainly due to conservative end-users skeptical towards non-biocidal options [49,50]. According to the EU BPR, which regulates the placing of biocidal products on the European market, the dose from a biocidal product should be “the minimum necessary to achieve the desired effect” [28]. However, as demonstrated in a previous study, many products marketed for the leisure boat sector in Sweden were found to release copper in large excess of the effective dose [23]. This is due to a current lack of guidance on how to evaluate whether the dose of an antifouling coating may be considered excessive or not. As paint compositions do not necessarily differ between countries, this is likely not an issue solely confined to the Swedish market or even the recreational sector.

A wide range of different copper coatings also containing zinc oxide were evaluated in this study to cover the plethora of coatings available on the current market. The findings indicate that copper release rates of approximately  $2\text{--}6\ \mu\text{g cm}^{-2}\ \text{d}^{-1}$  were sufficient to inhibit the settlement of macrofoulers in three different European coastal waters, depending on the species. To account for the variation in the derived release rates (Table 3), a release rate of  $7\ \mu\text{g cm}^{-2}\ \text{d}^{-1}$  is suggested to serve as a benchmark for both yacht and shipping sectors. This estimate represents a reduction of 30 % on the previously determined critical release rate of  $10\ \mu\text{g cm}^{-2}\ \text{d}^{-1}$ , derived for Atlantic waters [24]. Previous studies have shown that copper release rates can be even further reduced to around  $2\ \mu\text{g cm}^{-2}\ \text{d}^{-1}$  in less saline waters (0–8 PSU), such as the Baltic Sea, where fouling species appear to have a lower tolerance for copper [23]. It should therefore be noted that the overall critical release rate for copper established in this study is likely only applicable for waters of similar salinities as the studied locations (20–33 PSU). Additionally, although release rates of Zn were not found to be an explanatory variable for any performance differences here or in previous studies [23], it should be noted that these critical release rates were derived from (and for) modern-day antifouling coatings that also contain ZnO.

Ideally, a set of coatings formulated to deliver a gradient in copper release rates without any other differing variable between them would have been used to isolate the effect of copper. However, designing such coatings is practically challenging. Biocidal pigments of  $\text{Cu}_2\text{O}$  are a major component of copper-based antifouling paints, with mean weight percentages as high as 36 % (w/w) [21]. As the pigment volume concentration of a coating is optimized for a given formulation, the concentration of  $\text{Cu}_2\text{O}$  cannot simply be reduced without affecting essential coating properties [36]. Coatings with lower amounts of  $\text{Cu}_2\text{O}$  therefore typically contain higher amounts of ZnO (Lagerström, Ferreira, et al. 2020). However, increased amounts of ZnO may affect the coating's polishing rate and/or release rates of copper and zinc [27]. Apart from the practical challenge of designing experimental coatings, this study was performed on commercial coatings to increase the relevancy of the results as most copper-containing coatings today both contain and release zinc during use.

The use of commercial coatings also enabled this study to show that the release rate is not the only factor that determines a coating's antifouling performance. Especially at the Skagerrak site, differences in performance between coatings C1–C3 were visible even though their release rates were not significantly different. This knowledge enables coating suppliers to refine their formulations, recognizing the critical release rate as a specific coating property that can be further optimized.

Such fine-tuning not only enhances performance but also minimizes the environmental footprint of antifouling paints. Coating C1 (containing only 6.1 wt%  $\text{Cu}_2\text{O}$ ) of this study is mainly marketed for boats moored in the main Baltic Sea but was found to be quite effective in all three tested waters. Such low-leaching products should also be made available to boaters in other European countries, where typically coatings with higher copper contents (such as C4 and C5 of this study, whose release rates were on occasion as high as  $34\ \mu\text{g cm}^{-2}\ \text{d}^{-1}$ ) may otherwise be the only alternative. Through better application of the current regulation of the BPR and consequent phasing-out of unnecessarily high-leaching products, more environmentally friendly products could make their way onto the market and fill this niche.

Finally, this study can provide insights regarding exposure conditions during coating efficacy testing. Firstly, it has highlighted some limitations regarding long-term static conditions during raft testing. For several studied coatings, the copper release rates slowed or even halted after 4 months. This was likely due to a lack of polishing, a process which requires more dynamic conditions, resulting in an increased leached layer thickness. Performance evaluation based on long-term static testing for periods >4 months could therefore lead to wrongful conclusions of underperformance, especially for coatings designed to leach at levels close to that of the critical release rate. Additionally, extended static conditions may underestimate the coating's biocidal release and its consequent environmental impact. The efficacy evaluation of antifouling paints under the BPR according to the current guidance document requires static raft testing during at least 6 months across the full fouling season where exposed [51]. These recommendations may therefore need to be adjusted either by shortening the required static exposure time, or by allowing the inclusion of one or two short periods with dynamic conditions to refresh the coating surface, thereby better reflecting the exposure conditions during product use. Secondly, seawater salinity and temperature need to be considered during coating testing as these will impact the copper release rate. The average copper release rates across the first 4 months of the study period (T0–T3) for the same coating were up to 2.2 times higher when exposed at the warmer and more saline site in the Atlantic, as compared to the Kattegat and Skagerrak sites. To avoid unnecessary environmental release, the dose from yacht coatings could be optimized and ensured to not exceed the critical one at temperature and salinity conditions similar to those of intended use. Ships, on the other hand, are more likely to travel through waters of varying temperatures and salinities. To avoid releases falling below the effective threshold, the release of ship coatings should preferably be optimized for colder and/or less saline waters.

### CRediT authorship contribution statement

**Maria Lagerström:** Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Marcel Butschle:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation. **Ann I. Larsson:** Writing – review & editing, Methodology, Investigation. **Jérôme Cachot:** Writing – review & editing, Methodology. **Kim Dam-Johansen:** Writing – review & editing, Methodology, Funding acquisition. **Markus Schackmann:** Writing – review & editing. **Florane Le Bihanic:** Writing – review & editing, Methodology, Investigation.

### 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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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2024.108928>.

## Data availability

All raw data is provided in the supplementary material.

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