



DEPARTMENT OF MARINE SCIENCES

# RELEASE OF COPPER FROM ANTIFOULING PAINTS EXPOSED IN EUROPEAN WATERS

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## Populärvetenskaplig sammanfattning

Ett växande intresse för marinrelaterade frågor har uppstått och för att bevara en biologisk mångfald krävs det att vi uppmärksammar befintliga brister, problem och aktivt jobbar på nya lösningar för att hålla våra hav levande.

I havet är det en ständig kamp om yta för marina organismer att få plats och att kunna gro på. En populär yta att fästa på är båtbottnar. När alger och djur sätter sig på båtbottnen ökar friktionen mellan båtskrovet och vatten. Denna friktionsökning gör att båten går långsammare och för att hålla samma fart krävs en högre bränsleförbrukning. Det finns flera olika metoder för att undvika påväxt, där den vanligaste metoden är att måla skrovet med båtbottnfärger som innehåller olika gifter till havsmiljön. Problemet med dessa båtbottnfärger är att de fungerar genom att gifterna, även kallade biocider, läcker till havsmiljön där de kan orsaka oönskade effekter för vatten- och sedimentlevande organismer. De mest använda biociderna i båtbottnfärger är olika typer av kopparföreningar och deras läckage från färg till vatten har visat sig påverkas av vattnets salthalt och temperatur, där läckaget ökar med ökad salthalt och temperatur. Dessa studier har dock endast utförts i Östersjöregionen och det saknas studier på hur koppar läcker från båtbottnfärger exponerade i andra europeiska havsvatten.

Syftet med den här studien var därför att undersöka kopparläckaget från olika båtbottnfärger exponerade i Östersjöregionen, Skagerrak, Atlanten och Medelhavet. För att mäta läckaget av koppar användes en ny metod som bygger på röntgenfluorescens (XRF) där kopparmängden i båtbottnfärger mäts före och efter att de exponerats i olika hamnar. Projektet var ett samarbete med färgföretaget Jotun, vilka målade fem stora paneler (105 × 32 cm) med nio kopparbaserade båtbottnfärger med varierad kopparhalt. Färgerna mättes med XRF-instrumentet när de var färdigmålade, sedan exponerades dessa paneler på ungefär en meters djup, på fem olika exponeringslokaler i Europa; Stockholm, Göteborg, Stavern, Vigo och Girona. Dessa vattenområden har olika egenskaper gällande salthalt och temperatur. Efter 182-189 dagar hämtades panelerna och mättes ytterligare en gång med XRF-instrumentet och efter att läckaget av koppar beräknats så kunde det påvisas att det högsta kopparläckaget hade skett för panelen och färgerna som varit exponerade i Girona, där det var högst genomsnittsvärde på både salthalt och temperatur.



Eftersom samtliga färger exponerade i Stockholm var lika effektiva att motverka påväxt, trots att de innehöll och läckte olika mängd koppar, utfördes en beräkning för att undersöka hur stor minskningen av kopparläckaget i Östersjöregionen kunde ha varit genom att använda sig av färger med ett lägre kopparinnehåll. Under förutsättning att samtliga fritidsbåtar i Östersjöregionen var målade med den färg som hade högst läckage i studien så skulle fritidsbåtarna tillsammans läcka 77 ton koppar till Östersjön under en båtsäsong (180 dagar). Skulle istället samtliga båtar vara målade med den färg som läckte minst skulle endast 9,6 ton koppar tillföras Östersjön. Resultaten visar alltså på att det finns en väldigt stor möjlighet att minska tillförseln av koppar till Östersjön från båtbottnfärger utan att man behöver göra avkall på att färgerna ska vara effektiva i att motverka påväxt.

## Abstract

Copper release rates from antifouling paints are influenced by multiple physico-chemical factors including; salinity, temperature, pH, waterflow and biofilms. Since the highly toxic pollutant tributyltin was banned in antifouling coatings, cuprous oxide has been the most commonly used biocide. The overall aim of this study was to evaluate how environmental factors affect the release rate of copper from antifouling paints exposed at five different study sites, covering the Baltic Sea region, Skagerrak, Atlantic and Mediterranean Sea. Five panels measuring  $105 \times 32$  cm, painted with nine different antifouling paints, were prepared and immersed for 182-189 days, corresponding to a boating season.

An X-Ray Fluorescence (XRF) method has recently been developed allowing for determination of environmental release rates in the field of metallic or organometallic biocides. It has a short measurement time and is a cost-effective and non-destructive method. The release rates of copper were derived with the XRF method, including the development of a new calibration curve allowing the instrument to be used in handheld mode. Four copper based antifouling paints, provided by Jotun, were used in the study. The fouling pressure varied a lot between the exposure sites, with highest fouling at Gothenburg and Vigo, moderate fouling in Stockholm and Girona and lowest fouling in Stavern. The highest release rate of copper was found in Girona,  $10 \mu\text{g}/\text{cm}^2/\text{day}$  ( $\pm 0.4$ ). The study found that the two study sites (Vigo and Girona) with the highest mean temperature and salinity also had the highest copper release rates, for all paints analysed. The Stockholm study site had the lowest release rate of copper for three of the paints, possibly correlating to the low salinity and temperature, as well as high pH, at the study site.

Currently, antifouling paints are the most effective prevention against biofouling, therefore it is important to develop environmentally friendly alternative coatings with a low biocidal leaching rate. The coating specific release rates were used to calculate the yearly input of copper from all leisure boats in the Baltic Sea. The results showed a copper input of 77 tonnes if all boats were coated with the highest leaching antifouling paint during a time period of 180 days. The input could have been reduced to 9.6 tonnes if the boats were coated with the antifouling paint that showed the lowest release rate of copper.

The results indicate a possible reduction of anthropogenic input of copper from antifouling paints to the Baltic Sea if low leaching antifouling paints were to be used, since these were found to be as effective in deterring fouling as the higher leaching copper antifouling paints.

**Key words:** XRF, Antifouling, Copper, Release rate, Biocide

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## List of Abbreviations

AF	Antifouling
BPR	Biocidal Products Regulation
Cl <sup>-</sup>	Chloride ion
CO <sub>2</sub>	Carbon dioxide
Cu	Copper
Cu <sub>2</sub> O	Cuprous oxide
CuSCN	Copper thiocyanate
DFT	Dry film thickness
FRC	Foul-release coating
H <sup>+</sup>	Hydrogen ion
RR	Release rate
SO <sub>2</sub>	Sulfur dioxide
TBT	Tributyltin
XRF	X-ray Fluorescence
ZnO	Zinc oxide

# 1 Introduction

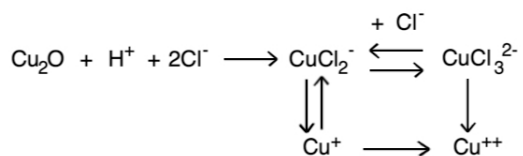
Marine biofouling is the accumulation of marine organisms on submerged structures in seawater. An immersed surface area without any protection will be fully fouled by primary colonizers (eg. bacteria and diatoms) within minutes to days (Hellio and Yebra, 2009). The fouling organisms can be divided into two groups, based on their size; microorganisms (biofilm, slime or microfouling) and macrofouling (largely consisting of hydroids, barnacles, mussels, bryozoans, tunicates or soft corals) (Azis et al., 2003; Selim et al., 2017). Biofouling is of concern since it increases the friction between hull and water, which can be translated into increased fuel consumption, increased carbon dioxide (CO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) released into the air, increased maintenance costs and the introduction of invasive species (Anisimov et al., 2019; Brooks and Waldock, 2009; Kiil et al., 2003; Selim et al., 2017; Yebra et al., 2004).

In the European Union, antifouling (AF) paints containing biocides are regulated under the Biocidal Products Regulation (BPR) (EU, 2006). BPR stresses the importance that the dose of biocidal products should be minimum necessary to achieve a desired effect. Hence, the products should not leach more biocides than what is

required to prevent biofouling. The AF paints are designed to dissolve all their biocidal compounds into the sea water during service life (Watermann and Eklund, 2019). The speed at which active substances are leached from the surface of the coating to the surrounding water is the biocidal release rate (RR), measured in  $\mu\text{g}/\text{cm}^2/\text{day}$  (Lagerström et al., 2020).

Since the extremely toxic pollutant tributyltin (TBT) was banned in AF coatings in 2008, cuprous oxide (Cu<sub>2</sub>O) is currently the most commonly used biocide (Almeida et al., 2007; Brooks and Waldock, 2009; Lagerström et al., 2020). Cu<sub>2</sub>O is widely used for both its low cost, bactericidal property and its moderating effect on erosion (Fay et al., 2005; Hellio and Yebra, 2009). Different copper (Cu) compounds are used as biocides in AF paints, Cu<sub>2</sub>O and copper thiocyanate (CuSCN) being two of them. CuSCN is mostly used for the pigment features, when a lighter color of hull coating is required (Hellio and Yebra, 2009). Cu is an essential element for all living organisms although it may also be toxic when physiologically required concentrations are exceeded (Ochoa-Herrera et al., 2011). The dissolution of Cu<sub>2</sub>O in seawater results in a sequence of reactions (Figure 1) and is proportional to the chloride ion (Cl<sup>-</sup>) and hydrogen ion (H<sup>+</sup>)

activity (Ferry and Carritt, 1946). The  $\text{Cl}^-$  and  $\text{H}^+$  ions react with the  $\text{Cu}_2\text{O}$  particles leading to production of chloro-copper complexes. The chloro-copper complexes are then oxidised to  $\text{Cu}^{2+}$  in the leach layer and released into the surrounding water as ionic Cu or labile Cu complexes (Ferry, 1952). Thus, an increase in  $\text{Cl}^-$ , i.e. an increase in salinity, increases the dissolution rate of  $\text{Cu}_2\text{O}$  (Ferry and Carritt, 1946).



**Figure 1:** Reactions involved in the dissolution of cuprous oxide in seawater.

Zinc oxide ( $\text{ZnO}$ ) is sometimes used as the principal biocidal pigment, even though it is relatively weak (Turner, 2010). Generally  $\text{ZnO}$  is used in combination with  $\text{Cu}_2\text{O}$  as a booster biocide, and the combination could, according to Watermann et al. (2005), increase the toxicity of Cu by 200 $\times$ . Furthermore  $\text{ZnO}$  can also act to impart the flexibility and facilitate the erosion process of the coating (Lindgren et al., 2018; Watermann et al., 2005). There are two main types of AF coatings; ablative (self-polishing) coatings and hard AF coatings. Chemically active AF coatings have a complex mechanism of action. This mechanism involve kinetics of dissolution of

biocidal pigments and fillers and furthermore water diffusion within the coating that results in controlled hydrolysis and solubilization of the polymer matrix (Marceaux et al., 2018; Watermann et al., 2005). The ablative AF coating slowly erodes so that a new layer of biocide is exposed, thereby maintaining a controlled release of biocides, so that growth can not accumulate (Takahashi, 2009). Hard AF coatings release biocides from the surface of the coating (Watermann and Eklund, 2019). When the biocide pigments are released from the AF paint, they dissolve faster than the polymer. This release causes two fronts; the polymer front at the surface of the coating and the pigment front. The distance between the polymer front and the pigment front is also known as the leach layer or the depleted layer (Howell and Behrends, 2006; Marceaux et al., 2018). When the leached layer is filled with sea-water the dissolved species can diffuse out from the coating (Marceaux et al., 2018). Since the matrix does not dissolve at the same speed as for the ablative coatings, this results in high leaching rate at start and then it gradually slows down (Takahashi, 2009). Ablative fouling paints have a controlled RR of biocides, while hard AF paints generally will get exhausted of biocides quicker (Yebra et al., 2004).

Cu pollution has become a worldwide

problem and especially in semi-enclosed marinas (Ytreberg et al., 2021b). The affected water quality through metal contamination has been shown to also affect biological systems, changing the abundance and composition of sessile and mobile organisms (Perrett et al., 2006). It has also been shown an increased metal content in organism tissue (Johnston et al., 2011). Annually the total natural and anthropogenic waterborne inputs of Cu to the Baltic Sea is 886 tons (Knuuttila et al., 2011), and in the Baltic and Baltic Transition regions, 57 tons annually of Cu has been reported from the leisure boat fleet (Johansson et al., 2020).

It has been discovered that salinity, temperature and pH affect the RR of Cu (Turner, 2010). Lagerström et al. (2020) studied how the salinity affected the RR of Cu in different AF paints that were exposed in Scandinavian waters. There have not been any similar studies performed for the North Sea, Atlantic or the Mediterranean. Currently there are only two standardized methods used to derive biocidal RRs from AF paints: a mass balance calculation method and a laboratory rotating cylinder method (IMO, 2009). The rotating cylinder method has been shown to overestimate the product leaching rate significantly (Finnie, 2006). To compensate for the overestimation

by laboratory test, a calculation method is used. However, RRs derived from both these methods have been shown to have poor correlation with field derived RRs in marinas (Lagerström and Ytreberg, 2021a).

Recently an X-ray fluorescence (XRF) method has been developed by Ytreberg et al. (2017) and further modified by Lagerström et al. (2018) and Lagerström and Ytreberg (2021b), allowing for determination of field RRs. Universal AF paint calibration curves for measurements of Cu in AF paints applied on plastic panels have been developed by Lagerström and Ytreberg (2021b), for the use of the instrument mounted in its test stand. Although, since the test panels might vary in size and when they are over a certain size they can not fit into the test stand, a calibration curve for the use of the XRF in handheld mode needs to be developed. Even though the XRF method requires an initial investment in the specific instrument and the calibration, this is only a one-time expense since the standards only need to be measured and derived once. The XRF is also very cost-effective due to the operating costs of the instrument being low (Lagerström and Ytreberg, 2021b).

### 1.1 Project aims

The specific aims of this study were to:

- evaluate how environmental factors affect the RR of Cu from AF paints exposed in European waters with varying salinity and temperatures;
- develop a new calibration curve for the Innov-X Delta-50 XRF instrument for use in hand held mode.

## 2 Theory

### 2.1 X-ray Fluorescence (XRF)

XRF is a non-destructive, multi-element technique and therefore suitable for liquids, solids and powders (Brouwer, 2006; Moens et al., 2000). Some of the advantages of XRF is that it has a short measurement time, it has become more commercially available and more affordable, especially handheld units (cost around \$30,000) (Higuera et al., 2012; Lindgren et al., 2018). The XRF measures the secondary X-rays, emitted from an inner energy orbital (K or L level) when excited by a primary X-ray source, leaving the atom in an ionized state (Brouwer, 2006; Lindgren et al., 2018; Ytreberg et al., 2016). When the electrons from a higher energy level fills the vacant position from the inner orbital, excess energy is ejected in the form of X-ray photons (Vo-Dinh et al., 2006). When the vacant position is in the K shell and it is filled with an electron from the L shell, the

characteristic energy of the emitted photon is called the K-alpha ( $K\alpha$ ) spectral line (Shackley, 2011). The wavelengths of the ejected X-ray photons are characteristic of the elements in the analysed sample (Lindgren et al., 2018; Turner et al., 2015). A spectra is generated by the instrument and the peak area is proportional to the concentration of a given element in the sample (Lagerström and Ytreberg, 2021b).

The penetration depth of X-rays is generally between a few micrometers down to several millimeters, depending on the sample matrix (Brouwer, 2006). Detection limits will generally be better for heavier elements, since more energetic X-rays are generated from heavier elements (eg, Cu, Ag, Au), these will be able to travel a longer distance within a sample contrary to lighter elements (eg. Mg, Al, Si) which will be harder to detect even at a lower depth in a sample. High concentrations of heavier elements which absorb X-rays strongly, also affects the possibility for the secondary X-rays to escape from deep within a sample and be detected by the instrument (Brouwer, 2006; Lagerström and Ytreberg, 2021b).

To be within the linear response of the XRF measurements, the AF paint film thickness ( $d_{thin}$ ) should preferably have a dry film thickness (DFT) below 40  $\mu\text{m}$  (Ytreberg et al., 2017). Greater thickness

may result in underestimated values due to absorption effects within the sample. However, the RR from the paint is not a function of the film thickness, it is the interaction between the seawater and paint that leads to the release of metals from the surface of the coating during immersion (Lagerström and Ytreberg, 2021b).

### 3 Materials & Methods

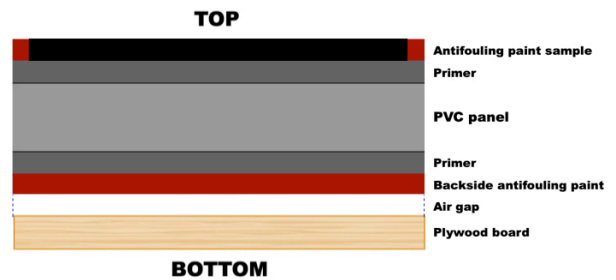
#### 3.1 Experimental setup

The experimental setup was prepared and provided by Jotun, one of the world’s leading manufacturers of paints and coatings. Jotun was founded in Norway in year 1926 and they manufacture decorative paints, protective coatings, powder coatings and marine coatings. They have a variety of AF paints, both for leisure boats and commercial shipping vessels (Jotun, 2022).

The prepared setup consisted of five metal frames, each with a mounted plastic panel (approximately  $105 \times 32$  cm) coated with different AF paints for the leisure boat market.

Each panel had a first layer with a vinyl primer paint manually spray painted in a thin layer on the front. On the backside of the panel an epoxi primer was manually spray painted. On top of the primer paint, i.e. on the front of the panel, there were nine

different AF paints spray painted as triplicate stripes, with the aim of a DFT of approximately  $40 \mu\text{m}$ . To divide each paint stripe into sections (eg. measurement locations for the XRF instrument) three white lines were painted on top of the AF paint. These lines would also work as a reference for the starting values of the DFT measured by Jotun. Figure 2 represents a cross section view of the panel (the white lines, non-polishing reference, were excluded in the figure).

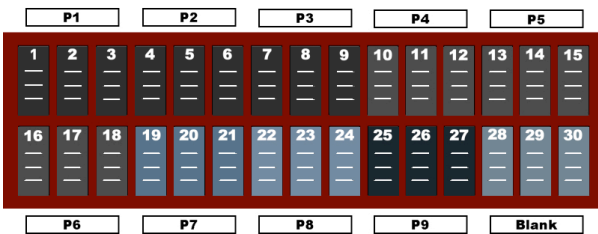


**Figure 2:** Cross section illustration of a small scale model of the setup of the panel when measuring with the XRF.

Unfortunately, the complete backside of the panel was spray painted with AF paint, to deter fouling on the back during the experiment. This was not taken into account before the start of the measurements, therefore additional steps were taken at the end measurements to evaluate possible Cu background effect. This was performed by placing a separate panel ( $10 \times 10$  cm), painted with an AF of known concentration of Cu, behind the experimental panel, and then conducting XRF measurements. The

XRF measurements were performed with and without the known Cu concentration panel behind the measurement spot of the experimental panel.

The nine different paints were provided by Jotun and were classified, therefore they will be labeled as P1, P2, P3, P4... P9, each number corresponding to the specific paint. Triplicate stripes of the primer paint was kept as the control, since the primer did not contain Cu. The control stripes were positioned to the bottom right of each panel and acted as a fouling pressure indicator for each study site. To separate each stripe, an AF paint was painted between, approximately 2-2.5 cm wide, leaving each stripe between 4-4.5 cm wide and 14.5 cm long. P1, P2, P3, P4, P5 and P6 contained Cu<sub>2</sub>O as an active biocide, while P7, P8 and P9 contained CuSCN. P4, P5, P8 and P9 were hard fouling paints while P1, P2, P3, P6 and P7 were ablative. Each panel had a total of 30 stripes (see Figure 3).



**Figure 3:** Illustration of one of the panels. P1 corresponds to AF paint color 1 and has triplicate paint stripes: 1, 2 and 3. A total of 9 different AF paints and the last stripe numbers: 28, 29 and 30 consisting of primer paint, regarded as the control.

Measurements of the five panels were

performed at the Division of Maritime Studies at Chalmers University of Technology, with a handheld XRF (Delta-50, Innov-X, Olympus), powered with a 4 W, 50 kV X-ray tube. The spectra were obtained from the 40 kV beam. The method of measurement were as described in Lagerström and Ytreberg (2021b). The XRF was carefully placed at the centre of each measurement spot on the stripes. The analytical time was set to 20s per measurement and triplicate measurements per spot was performed. In order to monitor for instrumental drift, three standards with low ( $\sim 200 \mu\text{g}/\text{cm}^2$ ), medium ( $\sim 800 \mu\text{g}/\text{cm}^2$ ) and high ( $\sim 2000 \mu\text{g}/\text{cm}^2$ ) concentrations of Cu and Zn were measured every 12th sample. The raw spectra were exported from the instrument and further processed in Matlab. To derive Cu concentrations the scatter normalized adjusted intensities of the K $\alpha$  signals were used.

The panels were obtained after six months exposure in their study locations (study locations are described in section 3.3), the panels were rinsed and then the same XRF measurement points were measured again to obtain total area concentrations of Cu. Data points with  $>90 \%$  depletion of Cu after exposure were excluded from the data set, since values above this indicate an

uncertainty of the amount of biocide content left in the paint (Lagerström et al., 2020). It could also not be certain when such a depletion would have occurred, if it had been depleted for a longer period, the final concentration results would have been biased. This was only the case for three points (all measurement spots on stripe 111 in Vigo). The average Cu RR for each paint stripe was calculated as the loss of metals in  $\mu\text{g}/\text{cm}^2$ , (i.e. the difference in concentration from start to end) and then divided per exposure days according to the equation:

$$RR = \frac{\text{Concentration}_{start} - \text{Concentration}_{end}}{\text{Exposure days}} \quad (1)$$

The final average Cu RR was calculated for each AF paint.

Reproducibility of measurement points between measurement analysts were performed to conclude if there was a significant difference. Two analysts performed XRF measurements on the same spot twice, at different times. The results were then compared in a paired t-test between the mean values for the first analyst versus the second analyst's mean values.

### 3.2 Dry Film Thickness

Jotun analysed the panels for DFT results. This was performed by cutting the panels and analysing the cross section with a light microscopy first and then with scanning electron microscopy (SEM). The AF painted underneath the non-polishing reference (three white lines painted on each stripe) was regarded as the starting values of the experiment, since this layer had not been in contact and therefore affected by "outer environment" e.g sea water. Six points were measured on each stripe and a mean value was obtained for each point.

### 3.3 Study sites

Marine EU waters are divided into four different regions, Baltic, Baltic Transition, Atlantic and Mediterranean. The panel mounted frames were immersed at five different sites (see Figure 4), one frame in each region and two frames in the Atlantic region (Stavern and Vigo). During the first three weeks of exposure, the Gothenburg panel was originally immersed in Kristineberg. It was then moved to a marina at Sjöstadens shipyard in Gothenburg.





**Figure 4:** Map representing the five study sites.

Four of the sites were marinas and the fifth site in Stockholm was at a private mooring.

After XRF start measurements of the panels, they were submerged over the summer of 2020, from the beginning of April until the beginning of October. The panels were kept in a static position at approximately one metre depth.

Salinity and temperature values for Stockholm, Gothenburg, Vigo and Girona were obtained from Copernicus (the EU Earth observation program), providing information services based on satellite earth observation- and field obtained data (non-space based). The salinity and

temperature values for the fifth study site (Stavern) was obtained from a local measurement spot. The pH values were obtained from Copernicus for all study sites (Copernicus, 2022). Table 1 shows the gathered information regarding the study sites.

### 3.4 XRF calibration curve

To generate calibration curves (XRF peak intensity versus concentration), calibration standards with known element concentrations were used. These curves were then used to calculate the concentrations from observed spectra. The handheld XRF analyzers are commonly used for measurements on e.g. soils and alloys, to measure elemental concentrations. Most commercial instruments are already equipped with calibrations for the measurements of those matrices. Currently there is no commercial method to analyse metals in AF paints, although Ytreberg et al. (2017) have developed an empirical method for analysing metals in AF paints and developed AF paint standards. For this

**Table 1:** Information about the study sites. Values for salinity, temperature and pH are average values with the minimum and maximum values at 1 m depth are shown in brackets.

Location	Latitude	Longitude	Salinity (‰)	Temperature (°C)	pH
Stockholm	59.638672°	18.684096°	3.5 (1.7-4.6)	13.2 (2.0-22.7)	8.2 (8.1-8.3)
Gothenburg	57.666559°	11.848590°	6.5 (0.2-18.8)	14.7 (4.9-22.5)	8.1 (8.0-8.2)
Stavern	59.000818°	10.042225°	22.6 (5.7-33.4)	14.1 (4.6-21.6)	8.1 (8.0-8.2)
Vigo	42.255900°	-8.705853°	33.7 (27.9-35.7)	17.2 (13.2-20.8)	8.1 (8.0-8.1)
Girona	42.116727°	3.147978°	37.7 (37.1-38.1)	20.2 (13.1-24.9)	8.0 (8.0-8.1)

project, a new calibration curve needed to be established, to replicate the handheld experimental setup. For the AF paints to pass the XRF criteria, it is important that the DFT does not exceed 40  $\mu\text{m}$  or the maximum Cu concentration, which was determined from previous existing standards of 3300  $\mu\text{g}/\text{cm}^2$ . A small scale model was built to resemble the setup of the XRF measurements. Above mentioned Figure 2 is a cross section illustration of the model, where the AF paint sample is at the top and the black rectangle represents the paint stripe.

To be able to conduct an accurate quantitative analysis, the primer piece chosen for use as the standard in the calibration curve, should be as similar as the unknown samples as possible. Since the Cu content on the backside of the panels varied (due to the variation in applied DFT), separate small scale calibration curves needed to be established. Hence, to further evaluate the impact of the Cu content in the AF paint on the backside of the panel, three measurement points were chosen from the total measurements of the primer stripes, corresponding to low, medium and high Cu content. The three chosen primer paint stripe locations were cut into  $2 \times 2$  cm squares, and fitted inside a measurement cup behind already established AF standards,

with a variety of film thicknesses and Cu concentrations (0 to 3426  $\mu\text{g}/\text{cm}^2$ ), ranging from low concentrations to high. Lagerström and Ytreberg (2021b) provide a more detailed explanation of the XRF calibration standards. A linear relationship was established for the three panel pieces for the Cu concentration ( $\mu\text{g}/\text{cm}^2$ ) versus the scatter corrected Cu area.

### 3.5 Cu RR model for the Baltic Sea

A calculation of the total leisure boat water surface area in the Baltic Sea and RR of Cu was performed for the AF paints. This was obtained from presented values of total boat water surface area in the Baltic Sea, a study performed by Johansson et al. (2020). The survey in the study presented the total amount of boats in the Baltic Sea region and a percentage was available for each boat size and each country. The water surface area modelled for the boats were 7  $\text{m}^2$ , 11  $\text{m}^2$ , 16  $\text{m}^2$  and 26  $\text{m}^2$ . In the calculation in this study, the sum of boats for each size were calculated and their total water surface area. For each AF paint (P3, P7, P8 and P9) the average RR in  $\mu\text{g}/\text{cm}^2/\text{day}$  was converted to  $\text{mg}/\text{m}^2/\text{day}$ . The total input of Cu from leisure boats from one boat season (180 days) were estimated by multiplying the coating specific RR with the total hull surface area of the Baltic leisure boat fleet.

## 4 Results

The XRF criteria was not met by five of the paints; P1, P2, P4, P5, P6, due to exceeded levels of DFT and Cu start concentrations, risking an underestimation of the actual Cu concentrations. The measured average DFT for the panels P3, P7, P8 and P9 were 53, 57, 47 and 53  $\mu\text{m}$  respectively. The four paints could successfully be measured with the XRF.

The background effect caused by the AF paint on the back of the panel was found negligible when a linear relationship between Cu concentration versus Cu area scatter corrected was established.

### 4.1 Fouling pressure

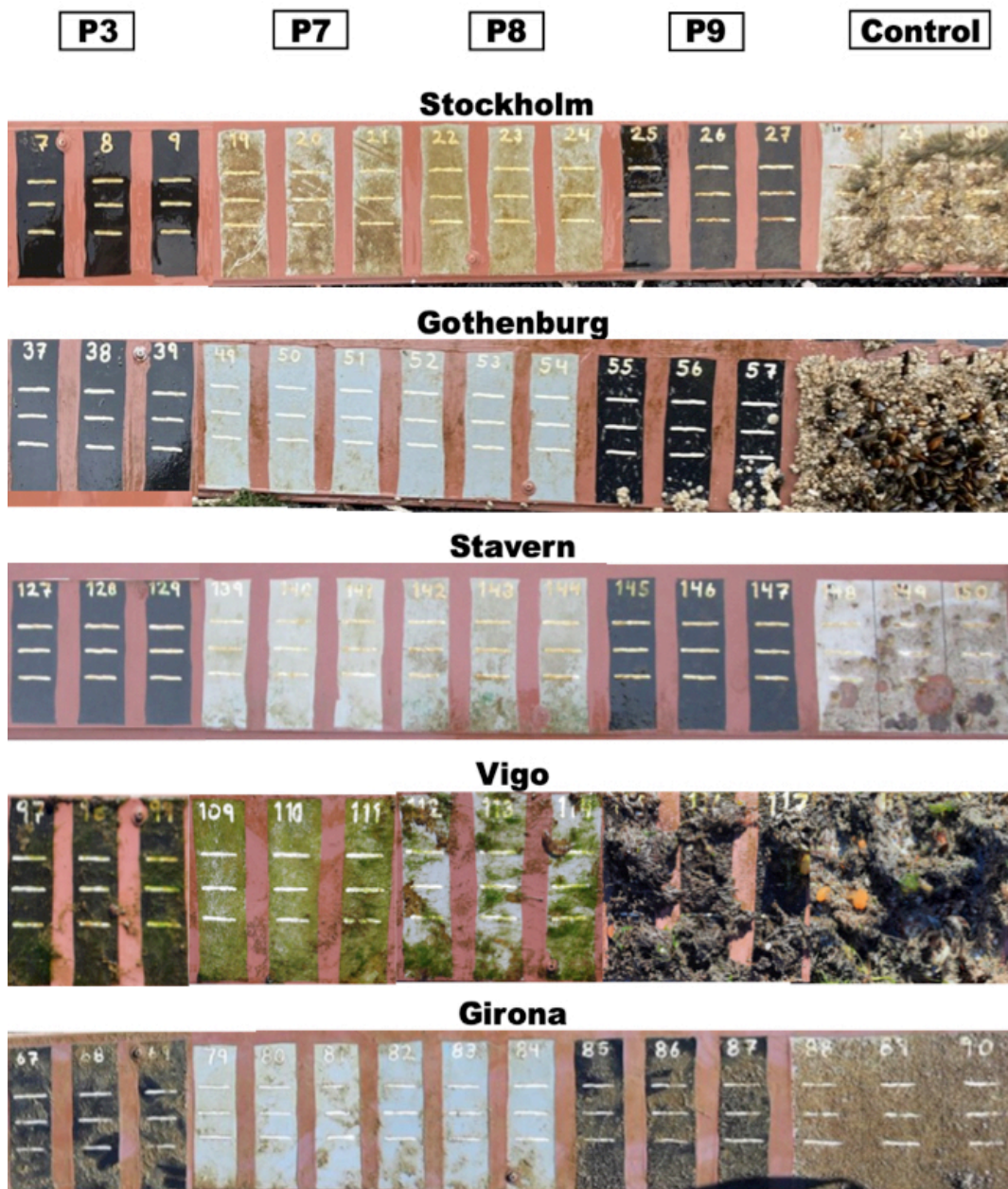
Figure 5 presents the control and the four paints that could be analysed; P3, P7, P8 and P9. The fouling on the control stripes represents the local fouling pressure at each study site. The control stripes exposed in Stockholm and Girona showed extensive amount of fouling, Stockholm was mainly fouled by barnacles and also algae, Girona was fouled by slime. The Gothenburg and Vigo control stripes were completely fouled by barnacles and algae and slime respectively. The Stavern control stripes had a small amount of growth of hydroids, bryozoa and slime.

Furthermore, the AF paints P3, P7, P8 and P9 in Stockholm did not show any hard fouling organisms, P7, P8 and P9 had a small amount of algae growth. In Gothenburg there was a small amount of hard fouling on the bottom of the AF stripes of P9. P3, P7 and P8 were not fouled. The AF paints exposed in Stavern showed a very low pressure of fouling, P8 and P9 had a small amount of algae growth. The panel in Vigo had the highest fouling pressure regarding the extensive algae and slime growth on the AF paint stripes. P9 was completely fouled and P3, P7 and P8 were extensively fouled.

The Girona panel showed an extensive amount of slime for P9. P3 was almost completely fouled by slime as well, while P7 and P8 only had a small amount of slime fouling.

### 4.2 Reproducibility of measurement points between measurement analyst

A paired t-test was performed (data not shown) to conclude the reproducibility and uncertainty between two analysts conducting the XRF measurements at different measurement dates. The results showed no significant difference with a p-value of 0.88 (significance level of 5%,  $\alpha = 0.05$ ).



**Figure 5:** Photographs of the retrieved panels after six months at the study sites. Paint three for all study sites is pictured furthest to the left, next to paint three is paint seven for all study sites, etc. The control is located furthest to the right and represents the local fouling pressure for each study site.

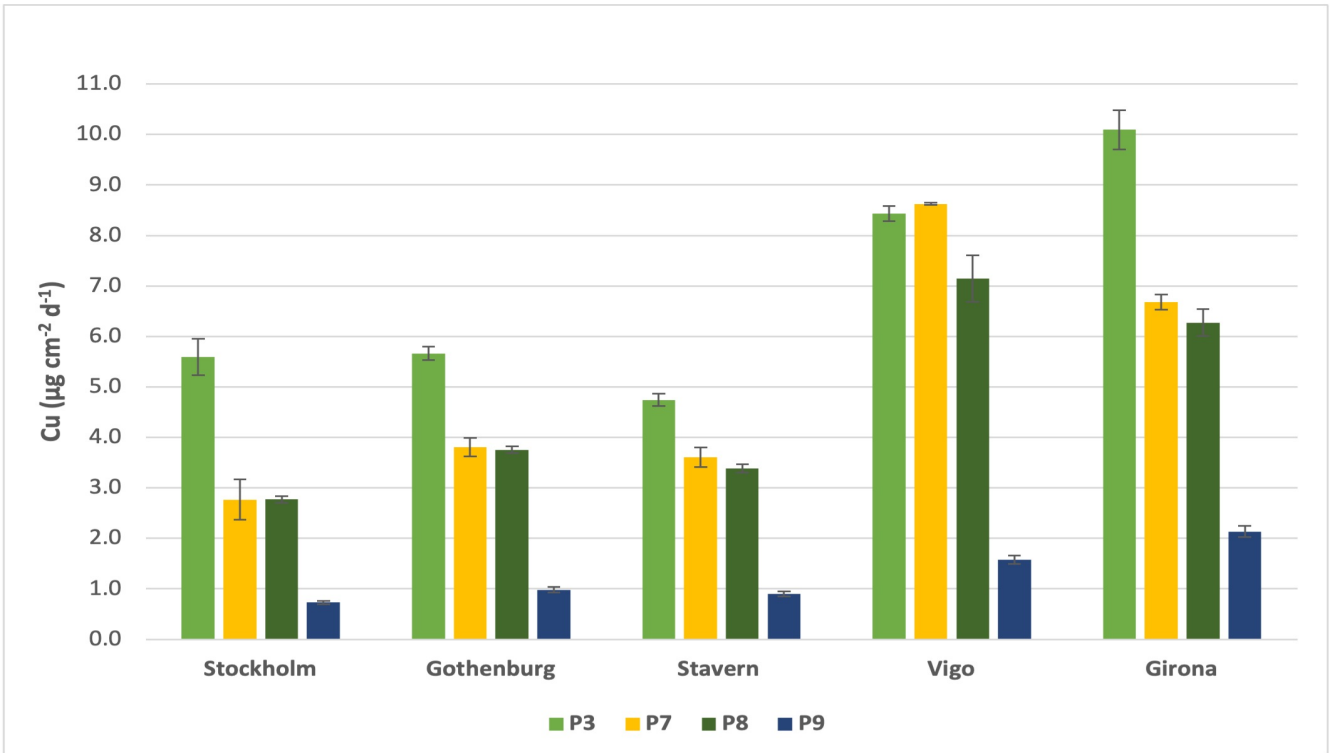
### 4.3 Copper release rates

Values for the average Cu RRs ( $\mu\text{g}/\text{cm}^2/\text{day}$ ) for each test site and paint can be found in Table 2, and the results are also shown as a graph in Figure 6. At each study site,

except in Vigo, P3 had the highest RR. P7 and P8 had similar RRs for all sites except in Vigo, where P7 had a RR of ( $8.6 \mu\text{g}/\text{cm}^2/\text{day}$ ,  $\pm 0.0$ ), P3 RR was ( $8.4 \mu\text{g}/\text{cm}^2/\text{day}$ ,  $\pm 0.2$ ) and P8 ( $7.1 \mu\text{g}/\text{cm}^2/\text{day}$ ,  $\pm 0.5$ ).

**Table 2:** Average release rates of copper ( $\mu\text{g}/\text{cm}^2/\text{day}$ ).

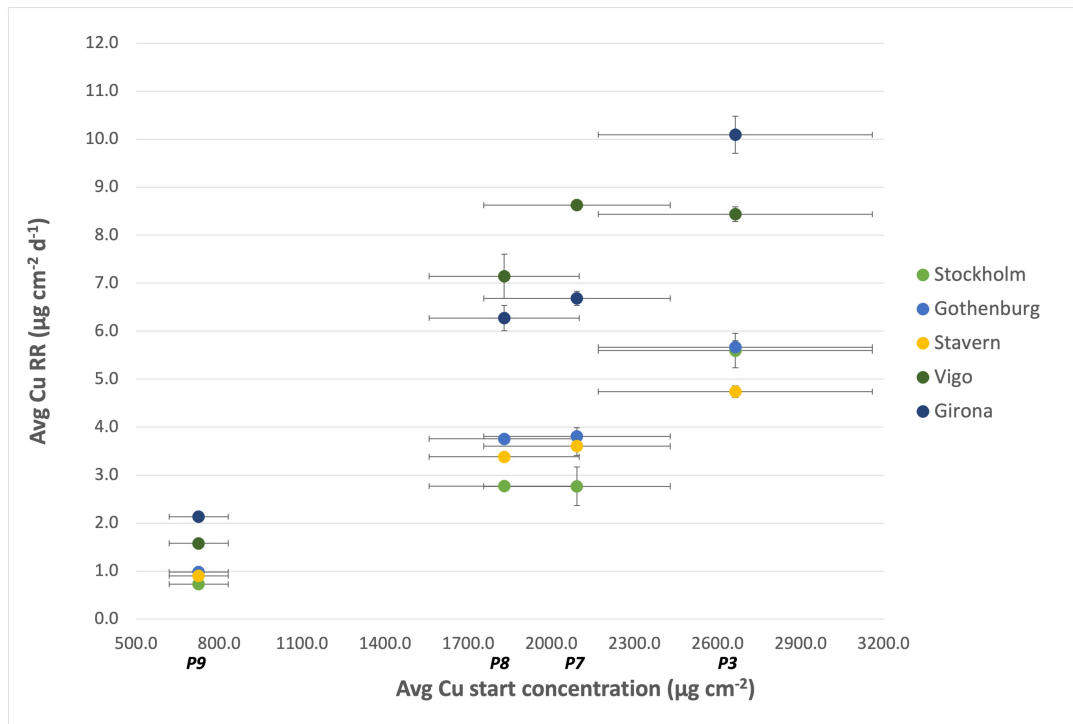
Study site	P3 (Cu <sub>2</sub> O / Ablative)	P7 (CuSCN / Ablative)	P8 (CuSCN / Hard AF)	P9 (CuSCN / Hard AF)
Stockholm	5.6 ( $\pm 0.4$ )	2.8 ( $\pm 0.4$ )	2.8 ( $\pm 0.1$ )	0.7 ( $\pm 0.0$ )
Gothenburg	5.7 ( $\pm 0.1$ )	3.8 ( $\pm 0.2$ )	3.8 ( $\pm 0.1$ )	1.0 ( $\pm 0.1$ )
Stavern	4.7 ( $\pm 0.1$ )	3.6 ( $\pm 0.2$ )	3.4 ( $\pm 0.1$ )	0.9 ( $\pm 0.0$ )
Vigo	8.4 ( $\pm 0.2$ )	8.6 ( $\pm 0.0$ )	7.1 ( $\pm 0.5$ )	1.6 ( $\pm 0.1$ )
Girona	10.1 ( $\pm 0.4$ )	6.7 ( $\pm 0.1$ )	6.3 ( $\pm 0.3$ )	2.1 ( $\pm 0.1$ )



**Figure 6:** Average release rate for copper in the study sites. Different colors of bars represent the paints P3, P7, P8 and P9. Copper release rates in  $\mu\text{g}/\text{cm}^2/\text{day}$  are shown on the y-axis. Error bars show standard deviations.

The average RR of Cu versus the average starting concentration of Cu for each paint and at each study site were plotted against each other in a graph and is presented in Figure 7. P3 is pictured to the right, with the highest Cu starting concentration (2664

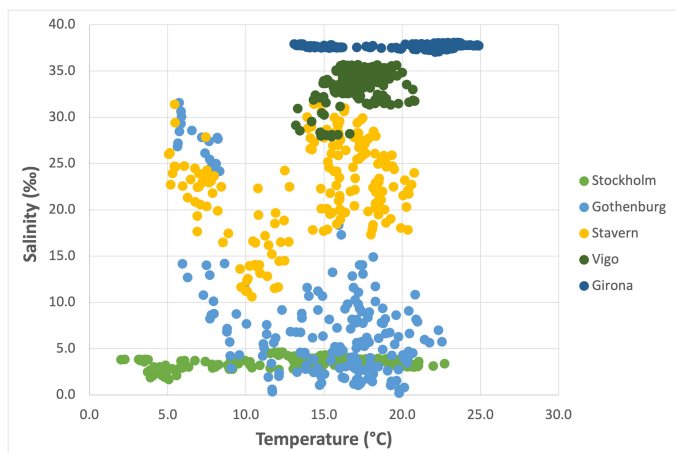
$\mu\text{g}/\text{cm}^2$ ,  $\pm 495$ ) and the highest Cu RR at study site Girona. P8 and P7 showed similar RR for Stockholm, Gothenburg and Stavern. P9 is pictured to the left and had the lowest Cu starting concentration and had the lowest Cu RR.



**Figure 7:** Illustration of average Cu start concentration versus average Cu RR for each paint and all study sites. Error bars show the standard deviation.

#### 4.4 Impact of salinity and temperature on copper release

Salinity and temperature values for each study site are presented in Figure 8.

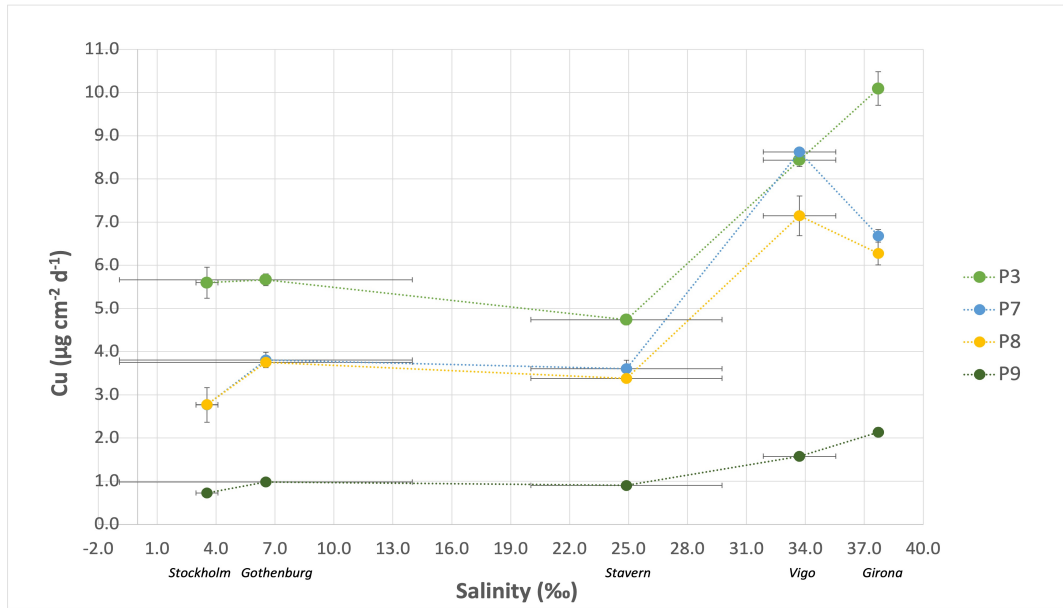


**Figure 8:** Illustration of daily average values for temperature (°C) and salinity (‰) at each study site during the study period.

The largest variation was found for Gothenburg and Stavern values. All values for both salinity and temperature overlapped between study sites, except for Girona's values. The salinity profile for Girona was the most stable, ranging between 37.1-38.1 with a mean of 37.7 (‰).

Figure 9 present the average Cu RR versus the different salinity values at the study sites. P7 and P8 show a similar trend at the lower salinity study sites, Stockholm and Gothenburg. P3 and P8 show a reduction in RR at Stavern as compared to the Gothenburg values, before increasing in Vigo. P3 and P9 further increase the RR in Girona while P7 and P8 decrease.

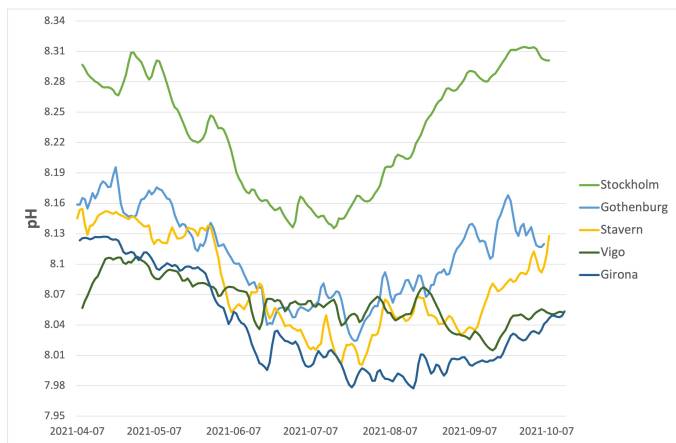




**Figure 9:** Graph illustrating the average release rate for copper ( $\mu\text{g}/\text{cm}^2/\text{day}$ ) versus different salinity ( $\text{‰}$ ) profiles for the different study sites. Different colors of markers represent the paints P3, P7, P8 and P9. Error bars show the standard deviation for x-axis and y-axis values for each marker.

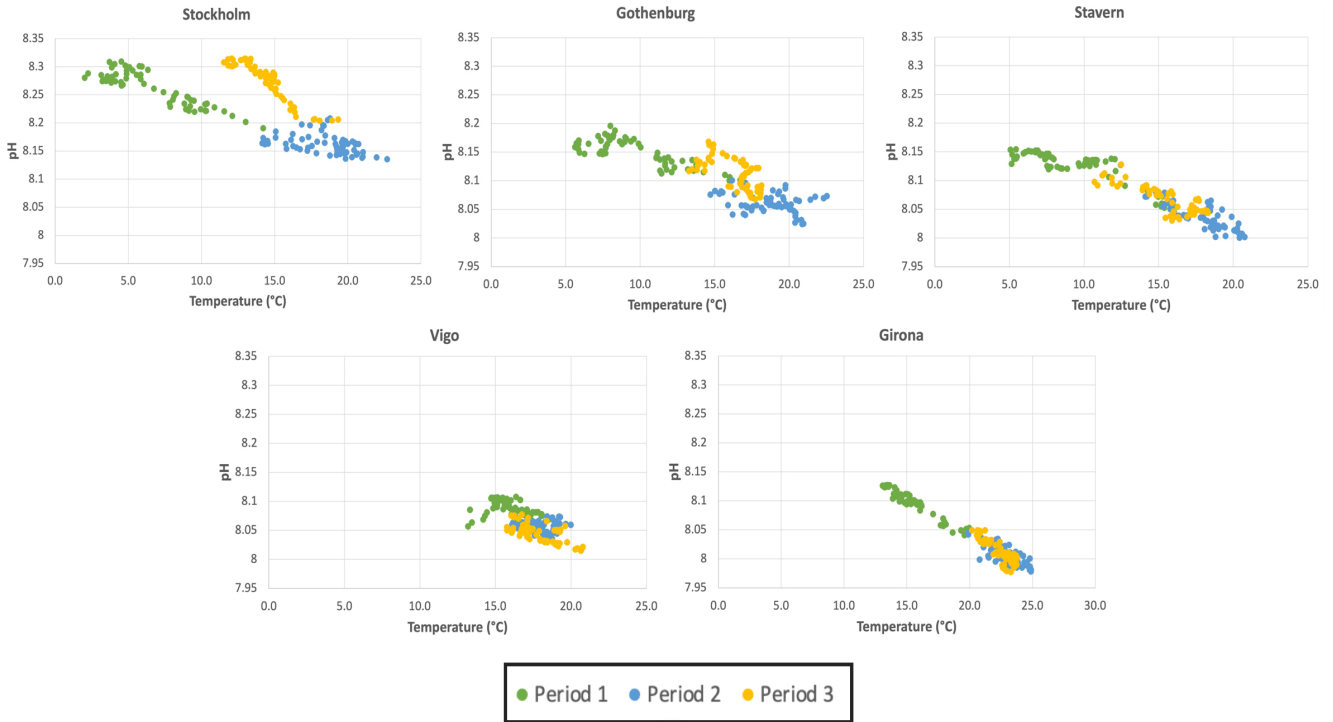
#### 4.5 Temperature versus pH

The obtained pH values are presented in Figure 10. A general trend during the summer months, June to August, was decreasing pH values for all study sites. Stockholm had the highest pH values during the study period.



**Figure 10:** pH values obtained for each study site, ranging through the complete study period.

To enable visualization of seasonal changes in pH and temperature, Figure 11 presents different periods for each study site. Periods were divided for each study site of 63 days per period. Period one corresponds to spring season, period two to summer and period three represents autumn values. Values in Stockholm clearly indicate a seasonal change. Generally, the periods with lower temperature (eg. period one and period three) resulted in higher pH values at the Stockholm, Gothenburg and Stavern study sites, while the Vigo study site did not show as much of a seasonal change regarding pH and temperature, the seasonal values overlapped. Girona had higher pH values during period one, and during period two and three the pH values overlapped.



**Figure 11:** Illustration of temperature versus pH for each study site. Values are divided into three periods of approximately 63 days each, representing spring, summer and autumn values.

#### 4.6 Cu RR model for the Baltic Sea

Results for the calculation for the leisure boat water surface area in the Baltic Sea and the average RR of Cu from the AF paints (used in this study) exposed in Stockholm are presented as the release of Cu in tonnes per year and also for a study period of 180 days, in Table 3. Boats with 26 m<sup>2</sup> water surface area showed the highest release of Cu, corresponding to 30 tonnes per 180 days and

60.8 tonnes per year when P3 AF was chosen.

**Table 3:** Average release rates of copper from antifouling paints P3, P7, P8 and P9 in Stockholm, calculated in tonnes per boat water surface area sizes; 7, 11, 16, and 26 m<sup>2</sup>. Results are shown for time periods of 180 days (upper part of table) and 365 days (lower part of table). A total of Cu release during the different time periods for each paint are shown to the right in the table.

180 days					
AF paint	7 m <sup>2</sup>	11 m <sup>2</sup>	16 m <sup>2</sup>	26 m <sup>2</sup>	Total
P3	3.8 t	25.5 t	17.8 t	30.0 t	77.0 t
P7	1.9 t	12.7t	8.9 t	15.0 t	38.5 t
P8	1.9 t	12.7t	8.9 t	15.0 t	38.5 t
P9	0.5 t	3.2 t	2.2 t	3.7 t	9.6 t
365 days					
AF paint	7 m <sup>2</sup>	11 m <sup>2</sup>	16 m <sup>2</sup>	26 m <sup>2</sup>	Total
P3	7.7 t	51.6 t	36.1 t	60.8 t	156.2 t
P7	3.9 t	25.8 t	18.0 t	30.4 t	78.1 t
P8	3.9 t	25.8 t	18.0 t	30.4 t	78.1 t
P9	1.0 t	6.5 t	4.5 t	7.6 t	19.5 t



## 5 Discussion

The RR of  $\text{Cu}_2\text{O}$  to the environment from AF paints have been shown to be dependent on multiple physico-chemical factors, including pH, temperature, salinity, water flow and biofilms (Thomas et al., 1999; Yebra et al., 2004). An increase in pH decreases the dissolution rate of  $\text{Cu}_2\text{O}$ , while an increase in sea water temperature increases the dissolution rate (Rascio et al., 1988). Increase in salinity has been shown to increase the RR, and  $\text{CuSCN}$  has been shown to be nearly 20 times more soluble than  $\text{Cu}_2\text{O}$  in seawater at pH 8.2 and  $[\text{Cl}^-] = 0.6 \text{ M}$  (Chasse et al., 2020).

### 5.1 Impact of salinity and temperature

Vigo and Girona were the study sites with the highest mean temperature and salinity, the two study sites also had the highest RRs of Cu, for all paints. The lowest RRs of Cu were found in Stockholm and even though the mean salinity for Stockholm was the lowest, the temperature values were similar to Gothenburg and Stavern. Furthermore, Stockholm had the highest pH values during the study period and it was the only study site that did not have overlapping pH values with the other study sites' pH values.

The Vigo site had the most stable temperature curve while Girona had the

most stable salinity curve. One of the parameters that might have influenced the lower RR of Cu, could have been fresh water supplied from nearby rivers. For example, the panel immersed in Gothenburg was affected by the fresh water supplied from the Göta river, resulting in fluctuating salinity values (see Table 1 and Figure 8). The panel immersed in Vigo, Spain, was also affected by fresh water to some extent, this too resulting in fluctuating salinity values. The panel in Stavern was the only panel located inside a sheltered marina, and although the mean salinity value was high, the overall RR for all the paints were lower than expected. This could thus be explained due to the panel being protected from water shear force. P3 and P7 were ablative paints and when comparing the RRs for the Gothenburg site, which had similar results to Stavern in the mean temperature, it shows that P3 had a lower RR in Stavern than in Gothenburg. It was not statistically different between the two sites for P7 and P9, although P8 had a lower RR in Stavern as well. This finding would suggest that the water shear force has an impact on the RR since it was expected that the RR would be higher in Stavern than in Gothenburg for all paints due to the higher salinity values. This also indicates a difference between ablative and hard AF coatings in static conditions

with low impact of water shear force, i.e., in protected marinas.

Earlier studies have shown that the initial RR of Cu in rotating cylinders initially have a peak which then steadily increase the first period of immersion. [Howell and Behrends \(2006\)](#) presented a steady increase in RR until day 28 of an experiment, at which it stabilised. The high initial leaching rate has been concluded to exponentially decrease within a short period of time ( $\sim 2$  years), according to [Hellio and Yebra \(2009\)](#), regardless of which matrix is used; hard or ablative coating. Research performed in natural seawater in San Diego Bay by [Valkirs et al. \(2003\)](#), showed that Cu RRs had a high initial rate ranging between 25-65  $\mu\text{g}/\text{cm}^2/\text{day}$ , between different paint types. These RRs then declined to significantly lower rates of 8-22  $\mu\text{g}/\text{cm}^2/\text{day}$  within two months, with a continued decreasing RR for another approximate of six months, where most coatings reached a constant RR. It has also been shown that the release of Cu in lower salinity generally increase and then stabilize after 14 days ([Lagerström et al., 2020](#)).

Furthermore, it is important to note that similar studies on RRs of Cu from AF paints conducted earlier ([Lagerström et al., 2018](#)), have only been performed during a time period of 84 days and therefore the results

are not fully comparable to this study. [Lagerström et al. \(2018\)](#) presented results for five commercial AF paints coated on static panels and immersed in Gothenburg area (14 ‰) and Stockholm area (5 ‰). The panels were collected after seven, 14, 28, 56 and 84 days of immersion and then XRF analysis was performed. It was concluded that the Cu release was twice the amount at the higher salinity at 84 days.

## 5.2 Paint biofouling efficacy

Since P3 showed the highest starting concentration of Cu, it could be expected that this paint also had the highest RR of Cu as compared to the other paints. This was true for all study sites except for in Vigo, where P7 had the highest RR. P3 was also the only paint analysed that contained  $\text{Cu}_2\text{O}$  instead of CuSCN. Regarding the growth on the panels it was obvious that P3 was the most effective coating to prevent biofouling, at all study sites. This could be explained due to the fact that the paint contained the highest Cu concentration of the analysed paints. It has been discovered that  $\text{Cu}_2\text{O}$  is more effective than CuSCN in regards of keeping the hull clean from biofouling ([Chasse et al., 2020](#)). Even though CuSCN in many respects have similar properties to those of  $\text{Cu}_2\text{O}$ , it has been shown that CuSCN is nearly five times

less oxidizable than  $\text{Cu}_2\text{O}$  in seawater (Vetere et al., 1997). Although this could be disregarded for the analysed paints in this study since the results shown in Figure 7 showed that there was no Cu RR increase of five times comparing the  $\text{Cu}_2\text{O}$  paint (P3) to the CuSCN paints (P7, P8 and P9).

It is of interest to discuss the average RR suggested from earlier studies; a critical RR of Cu of  $10 \mu\text{g}/\text{cm}^2/\text{day}$  has been assumed to be sufficient enough to prevent most animal forms fouling, although it should be noted that some algae species can withstand and attach at even higher values (Chasse et al., 2020; Hellig and Yebra, 2009). De Wolf and Van Londen (1966) determined under laboratory conditions that the above mentioned only should be indicative since subsequent studies has shown that even lower leaching rates can be efficient against the settlement of e.g. barnacles. Lindgren et al. (2018) concluded an average RR of Cu of  $4.68 \mu\text{g}/\text{cm}^2/\text{day}$  in their study, stating it was sufficient to deter settlement of barnacles in the Kattegat area, during a time period of 84 days. It has also been suggested that a RR of  $4.2 \mu\text{g}/\text{cm}^2/\text{day}$  is sufficient to prevent macrofouling in the Gothenburg area (Lagerström et al., 2020) during the same time period.

According to the pictures of the immersed panels (see Figure 5) it is possible to make

visual conclusions regarding the fouling. In Gothenburg and Stavern the RRs for all the AF paints analysed were more or less sufficient in deterring fouling during the time period of 182 and 184 days respectively. P9 in Gothenburg had some growth of barnacles at the bottom of the stripe. Although P9 had the lowest RR of Cu. This could indicate that a RR less than  $4.68 \mu\text{g}/\text{cm}^2/\text{day}$ , and even  $4.2 \mu\text{g}/\text{cm}^2/\text{day}$ , still would be able to deter fouling, since P7 and P8 had RRs of  $3.8 (\pm 0.2)$  and  $3.8 (\pm 0.1) \mu\text{g}/\text{cm}^2/\text{day}$  respectively in Gothenburg and  $3.6 (\pm 0.2)$  and  $3.4 (\pm 0.1) \mu\text{g}/\text{cm}^2/\text{day}$  in Stavern, without any hard fouling present.

In Lagerström et al. (2020) a compilation of results for RR of  $2.2 \mu\text{g}/\text{cm}^2/\text{day}$  was proposed to be sufficient to deter all macrofouling on a painted panel immersed in the Baltic region for five months in static conditions. The result is consistent to what was found in this study for the Stockholm panel, where there was no macrofouling for either of the lower Cu RR AF paints, P7, P8 and P9, with values of  $2.8 (\pm 0.4)$ ,  $2.8 (\pm 0.1)$  and  $0.7 (\pm 0.0) \mu\text{g}/\text{cm}^2/\text{day}$  respectively. Furthermore it was concluded in Lagerström et al. (2020) that there was a potential to reduce Cu RRs by approximately 80% from the highest leaching AF products used on recreational vessels in the Baltic Sea and Kattegat area, without losing any efficiency.

### 5.3 Environmental implications

A strategy to reduce the Cu load into the marine environment, while still maintaining an effective AF could be achieved by implementing site specific regulations amongst others. By using a paint with a lower Cu concentration there could be a significant decrease in the environmental loading of anthropogenic Cu. In this study the paint P9, which had the lowest RR, would have been effective enough in Stockholm for example, instead of using a paint with a higher Cu concentration and RR, in this case P3. In Gothenburg the AF paints P7 and P8 would also have been effective enough to prevent biofouling. The fouling pressure was low in Stavern and the results showed that P7 would have been effective enough to deter fouling, furthermore P8 and P9 would possibly have been efficient enough as well since there was only a small amount of algae growth on the AF paint stripes. The AF paints in Girona showed that P7 and P8 deterred fouling best of the paints at this study site. The only study site where the highest Cu RR and concentration was needed, was the Vigo site.

A recent study performed by [Ytreberg et al. \(2021a\)](#) concluded that the use of AF paints on leisure boats and ships is the single largest anthropogenic source of Cu to the Baltic Sea, accounting for a third of the total

load. Calculations made according to presented data in [Johansson et al. \(2020\)](#), showed an average result of input of leached Cu to the marine environment in the Baltic Sea, consisting of 77 tonnes from P3 during a time period of 180 days, 38.5 tonnes from P7 and P8, and 9.6 tonnes from P9. P3 release of Cu was 8× as much as the release of Cu from P9 during this time period. The amount of Cu input also depends on the boat size and the largest contribution comes from boats with 26 m<sup>2</sup> water surface area (large motor sailing boats), with approximately 30 tonnes from P3. Regarding the choice of AF paint, these boats could minimize their contribution by choosing P7 or P8 in areas where the biofouling pressure is not as high. In this case where the Baltic Sea was modelled, this would have resulted in half the load of Cu input with approximately 15 tonnes Cu instead.

Less toxic AF paints on the market include biocide-free silicone foul-release coatings (FRC), acting to prevent the attachment of fouling organisms through physical rather than chemical action ([Hu et al., 2020](#); [Lagerström et al., 2021](#)). A recent study conducted by [Oliveira and Granhag \(2020\)](#) in a Gothenburg harbour (Kattegat), found a biocide-free silicone FRC to be more effective than Cu-based coatings in deterring biofouling when coated panels

were exposed statically for 12 months. The silicone FRCs prevent attachment by their non-stick properties, acting as a slippery surface to reduce the adhesion strength of the fouling organisms (Selim et al., 2017). The coating is able to "self-clean" as the water shear force during cleaning or navigation will readily remove any present fouling (Hu et al., 2020). Furthermore silicone FRCs have a lower surface roughness and compared to traditional biocidal coatings they are hydrodynamically smoother which results in a reduced drag when unfouled (Anderson et al., 2009). Currently every major coating company, with marine paint products available, market at least one silicone based product (Kim, 2021). Drawbacks of the FRCs are poor mechanical strength and poor AF pressure under static conditions, allowing for diatoms and bacteria to settle, resulting in a slime layer (Hu et al., 2020). Although they are biocide-free, these coatings may not be completely environmentally benign. There has been coatings that have displayed toxicity to marine organisms during the first months of their immersion and the responsible substance(s) are currently unknown (Lagerström et al., 2021).

#### *5.4 Uncertainties and potential for improvement*

Since this method is relatively new, it is evident that further method development is required to avoid significant uncertainties. The method developed in this study, requires that the sample is homogeneous when measuring and preferably with a DFT <40  $\mu\text{m}$  to avoid biased results. However, this is difficult to achieve with modern paint formulations containing Cu particles of different sizes, as can be seen in the light-microscopy pictures provided by Jotun (see appendix). Therefore, it was of significant importance to have a triplicate measurement of each stripe, to ensure higher certainty of actual Cu concentrations.

Furthermore, the information regarding the  $\text{Cu}_2\text{O}$  particle size was not disclosed by Jotun and would have been an interesting parameter to analyse, since it has been concluded in earlier studies that when the average  $\text{Cu}_2\text{O}$  particle diameter increases the dissolution rate decreases (Rascio et al., 1988).

A source of error that occurred was the uncertainty of the AF, containing Cu, that was painted on the backside of the panel. Even though the results of the backside paint showed a weak Cu signal, it could still be detected with the XRF and therefore it affected the results obtained from the XRF

measurements.

It should also be noted that the temperature, salinity and pH-values were obtained from stations nearby the study site and not from the exact same spot, which may have led to deviations in the data. The temperature and salinity values were obtained from an approximate distance of between 300 meters to 4.5 kilometers from the study sites. While the pH values were obtained with ranging distances of between one to 15 kilometers from the study site.

Lindgren et al. (2018) suggested a time period of performing XRF measurements after 0, 14 and 56 days. It would have been of interest to add measurements during this study, to evaluate the seasonal changes and also to analyse the speed at which the initial release of Cu from the AF paints occurs at the different study sites.

In future studies, a method to geographically determine the lowest RR of Cu needed to deter fouling would be preferred. Certain regions with large differences in fouling pressures could benefit from a specific needed cut-off RR. This would theoretically assist manufacturers, both to reduce the costs and also to prevent excess input of biocides (eg. Cu and Zn) to the marine environment. Lagerström and Ytreberg (2021a) mentioned that the panel testing, as performed in this study, is not

only useful for efficacy testing of AF paints but can also act as a tool to monitor local biofouling pressure and therefor provide indications if a marina has high or low fouling problems, this would further act as a guiding tool for boat owners and might influence them to change their preferred AF practices.

Marine fouling is diverse and depending on location, it varies greatly. Future research need to take these stages into account as well as establishing appropriate biocide concentrations for AF paints used on leisure boats in marinas in specific areas.

## 6 Conclusion

In this project it was concluded that there was an increase in RR of Cu for all AF paints exposed in the more saline study sites, Vigo and Girona. The highest RR was found for P3 in Girona (mean salinity 37.7‰ and mean temperature 20.2°C), with a RR of 10.1 ( $\pm 0.4$ )  $\mu\text{g}/\text{cm}^2/\text{day}$ , although P7 and P8 were found to be sufficient enough to deter fouling at this site (RRs of 6.7 ( $\pm 0.1$ ) and 6.3 ( $\pm 0.3$ )  $\mu\text{g}/\text{cm}^2/\text{day}$  respectively). It was also shown that the fouling pressure in Vigo was the highest and at this site, the highest leaching AF paints (P3 and P7, 8.4 ( $\pm 0.2$ ) and 8.6 ( $\pm 0.0$ )  $\mu\text{g}/\text{cm}^2/\text{day}$  respectively) did not prevent fouling

efficiently enough since the panel was covered in slime and algae. The panel immersed in Stockholm had the lowest Cu RR for three of the paints (P7, P8 and P9), possibly correlated to the low salinity and temperature, and also the higher pH at the study site. All AF paints on the Stockholm panel were able to deter fouling, regardless of the fact that they contained and leaked different amounts of Cu. Thus, indicating that a mayor reduction of Cu input to the Baltic Sea region could be achieved by using an AF paint with lower Cu RR. Calculations of the average Cu RR for the four AF paints during a boating season (180 days) showed that if all leisure boats in the Baltic Sea were coated with P3, the average Cu input would have been 77 tonnes. Although, if all leisure boats were coated with P9, with the lowest RR of Cu and evaluated equally efficient in deterring fouling, the average input of Cu would be reduced to 9.6 tonnes. The results thus show that it is possible to reduce the anthropogenic input of Cu to the Baltic Sea from AF paints without having to compromise the paints efficiency in deterring fouling.

## Acknowledgements

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## References

- E. Almeida, T. C. Diamantino, and O. de Sousa. Marine paints: the particular case of antifouling paints. *Progress in Organic Coatings*, 59(1):2–20, 2007.
- C. Anderson et al. Fouling control coatings using low surface energy, foul release technology. In *Advances in marine antifouling coatings and technologies*, pages 693–708. Elsevier, 2009.
- A. Anisimov, M. Mikhailova, and E. Uvarova. Modern approaches to the development of marine antifouling coatings. *Inorganic Materials: Applied Research*, 10(6):1384–1389, 2019.
- P. A. Azis, I. Al-Tisan, M. Al-Daili, T. N. Green, K. Ba-Mardouf, S. A. Al-Qahtani, and K. Al-Sabai. Marine macrofouling: a review of control technology in the context of an on-line experiment in the turbine condenser water box of al-jubail phase-1 power/msf plants. *Desalination*, 154(3):277–290, 2003.
- S. Brooks and M. Waldo. The use of copper as a biocide in marine antifouling paints. In *Advances in marine antifouling coatings and technologies*, pages 492–521. Elsevier, 2009.
- P. Brouwer. Theory of XRF. *Almelo, Netherlands: PANalytical BV*, 2006.
- K. Chasse, A. Scardino, and G. Swain. Corrosion and fouling study of copper-based antifouling coatings on 5083 aluminum alloy. *Progress in Organic Coatings*, 141:105555, 2020.
- Copernicus. Copernicus Marine Viewer Service MyOcean. <https://myocean.marine.copernicus.eu/data>, April 2022.
- P. De Wolf and A. Van Londen. Anti-fouling compositions. *Nature*, 209(5020):272–274, 1966.
- EU. Harmonisation of leaching rate determination for antifouling products under the biocidal products directive., 2006. Workshop Report Endorsed at the 26th Meeting of Representatives of Members States Competent Authorities for the Implementation of Directive 98/8/EC Concerning the Placing of Biocidal Products on the Market (11-14 September 2007). Workshop Report Ispra, Italy, 12 December 2006.
- F. Fay, I. Linossier, V. Langlois, D. Haras, and K. Vallee-Rehel. SEM and EDX analysis: two powerful techniques for the study of antifouling paints. *Progress in Organic Coatings*, 54(3):216–223, 2005.
- J. Ferry. The physical chemistry of compounds of copper and mercury and their interactions with sea water. *Woods Hole Oceanographic Institution, Marine Fouling and its Prevention. United States Naval Institute, Annapolis, MD*, pages 264–276, 1952.
- J. D. Ferry and D. E. Carritt. Action of antifouling paints. *Industrial & Engineering Chemistry*, 38(6):612–617, 1946.
- A. A. Finnie. Improved estimates of environmental copper release rates from antifouling products. *Biofouling*, 22(5):279–291, 2006.
- C. Hellio and D. Yebra. *Advances in marine antifouling coatings and technologies*. Elsevier, 2009.
- P. Higuera, R. Oyarzun, J. Iraizoz, S. Lorenzo, J. Esbrí, and A. Martínez-Coronado. Low-cost geochemical surveys for environmental studies in developing countries: Testing a field portable

- xrf instrument under quasi-realistic conditions. *Journal of Geochemical Exploration*, 113:3–12, 2012.
- D. Howell and B. Behrends. A methodology for evaluating biocide release rate, surface roughness and leach layer formation in a TBT-free, self-polishing antifouling coating. *Biofouling*, 22(5):303–315, 2006.
- P. Hu, Q. Xie, C. Ma, and G. Zhang. Silicone-based fouling-release coatings for marine antifouling. *Langmuir*, 36(9):2170–2183, 2020.
- IMO. *The generation of biocide leaching rate estimates for anti-fouling coatings and their use in the development of proposals to amend annex 1 of the AFS Convention*. MEPC 60/13, 2009.
- L. Johansson, E. Ytreberg, J.-P. Jalkanen, E. Fridell, K. M. Eriksson, M. Lagerström, I. Maljutenko, U. Raudsepp, V. Fischer, and E. Roth. Model for leisure boat activities and emissions—implementation for the Baltic Sea. *Ocean Science*, 16(5):1143–1163, 2020.
- E. Johnston, E. Marzinelli, C. Wood, D. Speranza, and J. Bishop. Bearing the burden of boat harbours: heavy contaminant and fouling loads in a native habitat-forming alga. *Marine Pollution Bulletin*, 62(10):2137–2144, 2011.
- Jotun. About Jotun – What we do, Retrieved 03/05, 2022. URL <https://www.jotun.com/ww-en/about-jotun/who-we-are/what-we-do/>.
- S. Kiil, K. Dam-Johansen, C. E. Weinell, M. S. Pedersen, and S. A. Codolar. Estimation of polishing and leaching behaviour of antifouling paints using mathematical modelling: a literature review. *Biofouling*, 19(S1):37–43, 2003.
- H.-J. Kim. Strategic actions for sustainable vessel hull coatings in line with the un sdgs. , 45(4):231–242, 2021.
- S. Knuuttila, L. Svendsen, H. Staaf, P. Kotilainen, S. Boutrup, M. Pyhala, and M. Durkin. Fifth baltic sea pollution load compilation (plc-5). 2011.
- M. Lagerström and E. Ytreberg. Assessment of efficacy and excess toxicity of antifouling paints for leisure boats. 2021a.
- M. Lagerström and E. Ytreberg. Quantification of Cu and Zn in antifouling paint films by XRF. *Talanta*, 223:121820, 2021b.
- M. Lagerström, J. F. Lindgren, A. Holmqvist, M. Dahlström, and E. Ytreberg. In situ release rates of Cu and Zn from commercial antifouling paints at different salinities. *Marine Pollution Bulletin*, 127:289–296, 2018.
- M. Lagerström, E. Ytreberg, A.-K. E. Wiklund, and L. Granhag. Antifouling paints leach copper in excess—study of metal release rates and efficacy along a salinity gradient. *Water Research*, 186:116383, 2020.
- M. Lagerström, A. Wrangé, L. Granhag, A. Larsson, and E. Ytreberg. Are silicone foul-release coatings a viable and sustainable alternative to biocidal antifouling coatings in the baltic sea region?, 2021.
- J. F. Lindgren, E. Ytreberg, A. Holmqvist, M. Dahlström, P. Dahl, M. Berglin, A.-L. Wrangé, and M. Dahlström. Copper release rate needed to inhibit fouling on the west coast of Sweden and control of copper release using zinc oxide. *Biofouling*, 34(4):453–463, 2018.
- S. Marceaux, C. Martin, A. Margailan, and C. Bressy. Effects of accelerated ageing conditions

- on the mechanism of chemically-active antifouling coatings. *Progress in Organic Coatings*, 125:257–265, 2018.
- L. Moens, A. von Bohlen, and P. Vandenaabeele. X-ray fluorescence. In *Modern analytical methods in art and archaeology*, volume 155, pages 55–79. John Wiley & Sons, 2000.
- V. Ochoa-Herrera, G. León, Q. Banihani, J. A. Field, and R. Sierra-Alvarez. Toxicity of copper (II) ions to microorganisms in biological wastewater treatment systems. *Science of the total environment*, 412:380–385, 2011.
- D. R. Oliveira and L. Granhag. Ship hull in-water cleaning and its effects on fouling-control coatings. *Biofouling*, 36(3):332–350, 2020.
- L. A. Perrett, E. L. Johnston, and A. G. Poore. Impact by association: direct and indirect effects of copper exposure on mobile invertebrate fauna. *Marine Ecology Progress Series*, 326:195–205, 2006.
- V. J. Rascio, C. A. Giúdice, and B. del Amo. Research and development of soluble matrix antifouling paints for ships, offshore platforms and power stations. A review. *Corrosion Reviews*, 8(1-2):87–154, 1988.
- M. S. Selim, M. Shenashen, S. A. El-Safty, S. Higazy, M. M. Selim, H. Isago, and A. Elmarakbi. Recent progress in marine foul-release polymeric nanocomposite coatings. *Progress in Materials Science*, 87:1–32, 2017.
- M. S. Shackley. An introduction to X-ray fluorescence (XRF) analysis in archaeology. In *X-ray fluorescence spectrometry (XRF) in geoarchaeology*, pages 7–44. Springer, 2011.
- K. Takahashi. Release rate of biocides from antifouling paints. In *Ecotoxicology of antifouling biocides*, pages 3–22. Springer, 2009.
- K. Thomas, K. Raymond, J. Chadwick, and M. Waldock. The effects of short-term changes in environmental parameters on the release of biocides from antifouling coatings: cuprous oxide and tributyltin. *Applied organometallic chemistry*, 13(6):453–460, 1999.
- A. Turner. Marine pollution from antifouling paint particles. *Marine Pollution Bulletin*, 60(2):159–171, 2010.
- A. Turner, S. Comber, A. B. Rees, D. Gkiokas, and K. Solman. Metals in boat paint fragments from slipways, repair facilities and abandoned vessels: an evaluation using field portable XRF. *Talanta*, 131:372–378, 2015.
- A. O. Valkirs, P. F. Seligman, E. Haslbeck, and J. S. Caso. Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: implications for loading estimation to marine water bodies. *Marine Pollution Bulletin*, 46(6):763–779, 2003.
- V. Vetere, M. Perez, R. Romagnoli, M. Stupak, and B. Del Amo. Solubility and toxic effect of the cuprous thiocyanate antifouling pigment on barnacle larvae. *Journal of Coatings Technology*, 69(866):39–45, 1997.
- T. Vo-Dinh et al. *Handbook of spectroscopy*. John Wiley & Sons, 2006.
- B. Watermann and B. Eklund. Can the input of biocides and polymeric substances from antifouling paints into the sea be reduced by the use of non-toxic hard coatings? *Marine pollution bulletin*, 144:146–151, 2019.

- B. Watermann, B. Daehne, S. Sievers, R. Dannenberg, J. Overbeke, J. Klijnstra, and O. Heemken. Bioassays and selected chemical analysis of biocide-free antifouling coatings. *Chemosphere*, 60(11):1530–1541, 2005.
- D. M. Yebra, S. Kiil, and K. Dam-Johansen. Antifouling technology—past, present and future steps towards efficient and environmentally friendly antifouling coatings. *Progress in organic coatings*, 50(2):75–104, 2004.
- E. Ytreberg, M. A. Bighiu, L. Lundgren, and B. Eklund. XRF measurements of tin, copper and zinc in antifouling paints coated on leisure boats. *Environmental Pollution*, 213:594–599, 2016.
- E. Ytreberg, M. Lagerström, A. Holmqvist, B. Eklund, H. Elwing, M. Dahlström, P. Dahl, and M. Dahlström. A novel XRF method to measure environmental release of copper and zinc from antifouling paints. *Environmental pollution*, 225:490–496, 2017.
- E. Ytreberg, K. Hansson, A. Lunde Hermansson, R. Parsmo, M. Lagerström, J.-P. Jalkanen, and I.-M. Hassellöv. Metal and PAH loads from ships and boats, relative other sources, in the baltic sea. 10 2021a. doi: 10.13140/RG.2.2.34937.19046.
- E. Ytreberg, M. Lagerström, S. Nöu, and A.-K. E. Wiklund. Environmental risk assessment of using antifouling paints on pleasure crafts in European Union waters. *Journal of Environmental Management*, 281:111846, 2021b.

# Appendix

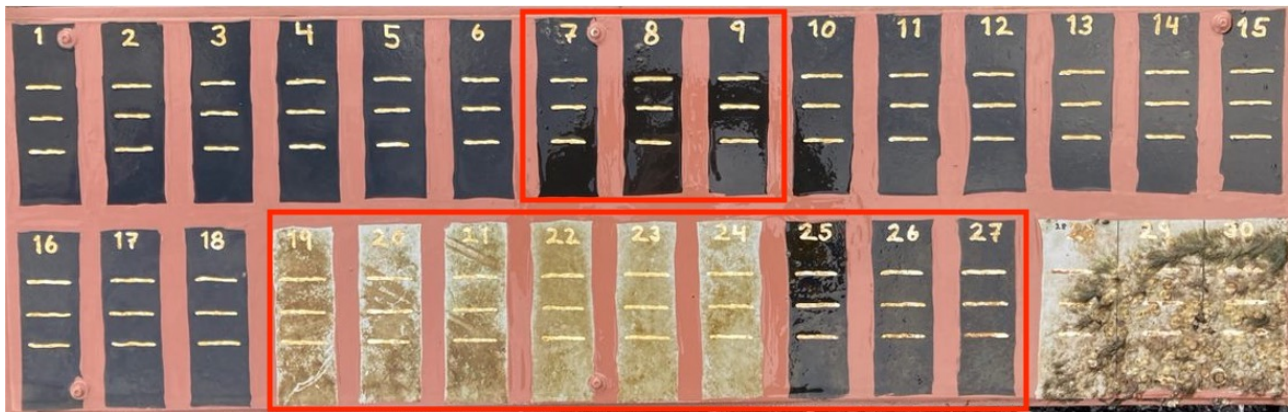


Figure 12: Full picture of panel retrieved from Stockholm site. Red boxes indicate the analysed paints in this study.



Figure 13: Full picture of panel retrieved from Gothenburg site. Red boxes indicate the analysed paints in this study.

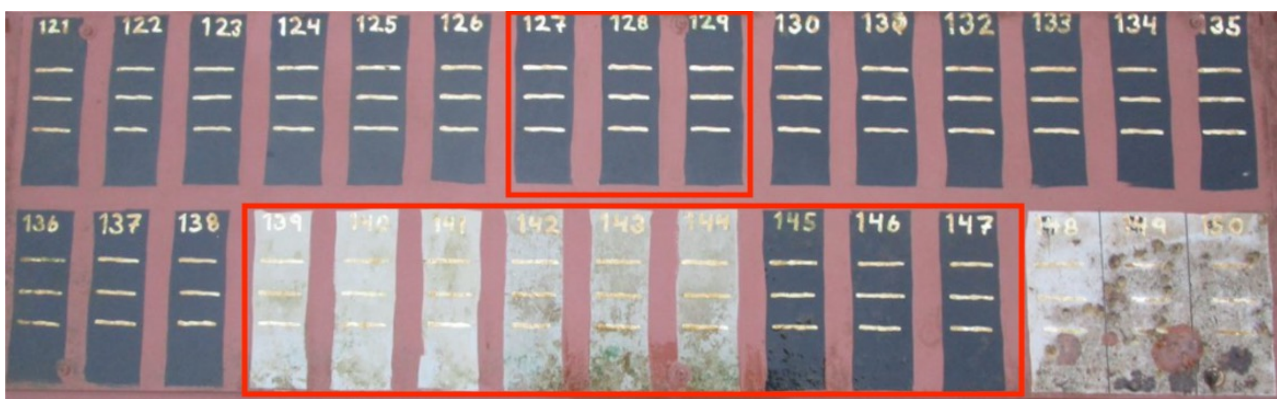


Figure 14: Full picture of panel retrieved from Stavern site. Red boxes indicate the analysed paints in this study.



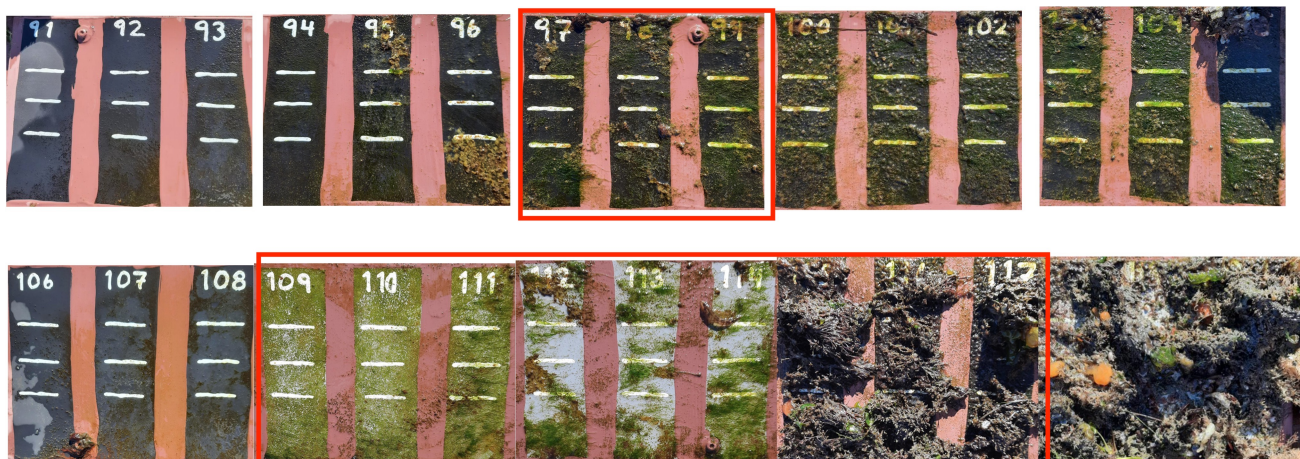


Figure 15: Full picture of panel retrieved from Vigo site. Red boxes indicate the analysed paints in this study.



Figure 16: Full picture of panel retrieved from Girona site. Red boxes indicate the analysed paints in this study.

### P3

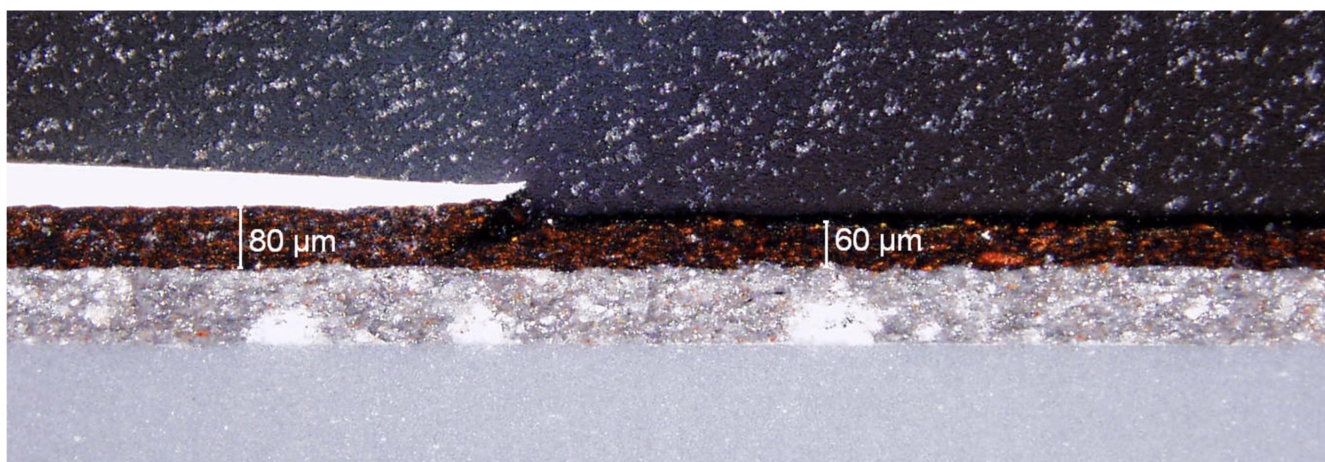


Figure 17: Cross section of panel with paint 9, light microscopy picture. The white in the middle to left in the picture represents the non-polishing paint reference, used to derive a start value for the DFT (80  $\mu\text{m}$ ) underneath. To the right in the picture, 60  $\mu\text{m}$  is concluded as the end value for DFT, and the thin black line above this is the leached layer. Red particles in the paint film are Cu particles, noticeably different size distributions (see the big flake to the right of the 60  $\mu\text{m}$  text).