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A novel XRF method to measure environmental release of copper and zinc from antifouling paints☆

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ABSTRACT

The release of copper (Cu) and zinc (Zn) from vessels and leisure crafts coated with antifouling paints can pose a threat to water quality in semi-enclosed areas such as harbors and marinas as well as to coastal archipelagos. However, no reliable, practical and low-cost method exists to measure the direct release of metals from antifouling paints. Therefore, the paint industry and regulatory authorities are obliged to use release rate measurements derived from either mathematical models or from laboratory studies. To bridge this gap, we have developed a novel method using a handheld X-Ray Fluorescence spectrometer (XRF) to determine the cumulative release of Cu and Zn from antifouling paints. The results showed a strong linear relationship between XRF K_α net intensities and metal concentrations, as determined by ICP-MS. The release of Cu and Zn were determined for coated panels exposed in harbors located in the Baltic Sea and in Kattegat. The field study showed salinity to have a strong impact on the release of Cu, i.e. the release increased with salinity. Contrary, the effect of salinity on Zn was not as evident. As exemplified in this work, the XRF method also makes it possible to identify the governing parameters to the release of Cu and Zn, e.g. salinity and type of paint formulation. Thus, the XRF method can be used to measure environmentally relevant releases of metallic compounds to design more efficient and optimized antifouling coatings.

1. Introduction

Fouling, i.e. the colonization of bacteria, plankton and animals on underwater structures, is a significant problem for shipping and leisure boating as attached organisms increase friction and drag, resulting in both higher fuel consumption and hull maintenance costs (Almeida et al., 2007). The most commonly used method to prevent fouling is to coat the hull with antifouling paints that contain and leach biocides. The efficacy of the paint depends on the prevailing fouling pressure in the areas where the boat or ship operates, what biocide(s) are used in the paint formulation and the biocidal release rate from the painted surface to the ambient water. Hence, knowing the release rate of biocides required to prevent fouling in the area where the ship operates is fundamental in order to develop efficient antifouling paints and to meet environmental standards.

The mechanisms controlling the release rate of biocides from antifouling paints are mainly chemical reactions and diffusion phenomena (Yebra et al., 2004) where sea water soluble pigment dissolution, binder reaction and paint polishing are key processes. Most of today's paints contain toxic soluble pigments where cuprous oxide (Cu_2O) and zinc oxide (ZnO) dominate the market (Ciriminna et al., 2015). The dissolution rate of these pigments will control the leaching of biocides from the paint surface (Yebra et al., 2006). The dissolution rate of the binder (matrix) system also governs the leaching rate as it directly affects the paints' polishing rate. Antifouling paints are based on either insoluble matrices (e.g. epoxy, acrylates, chlorinated rubber and vinyls), soluble matrixes (mainly rosins) or, in the case of self-polishing paints (SPC), on a matrix consisting of acrylic polymers such as copper acrylate (Almeida et al., 2007). The thickness of the so-called leached layer,

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which is a result of the relative dissolution rate of the pigments at the paint-water interface and the polishing rate of the binder, has a strong impact on the diffusion rate of e.g. dissolved copper species from the paint to the water (Kiil et al., 2003). The leaching rate of biocides is also governed by different abiotic factors. For example, salinity has shown to both increase the dissolution of Cu_2O particles (Yebra et al., 2004) and to increase the solubility of rosin (Rascio et al., 1988). Thus, the release rate of biocides can be assumed to be lower in brackish and fresh water compared to fully marine conditions, and the effect is presumably higher for rosin-based and self-polishing antifouling systems as compared to paints based on insoluble matrixes.

Today, several methods exist to determine the biocidal release rates from anti-fouling paints. These methods are based on laboratory studies, field measurements or model calculations. Rotating cylinder methods, developed under the American Society for Testing Materials (ASTM) and International Organization for Standardization (ISO), have frequently been used in the laboratory to determine release rates of both organic biocides (e.g. TBT) and inorganic biocides (e.g. Cu_2O) (ISO, 2000b, a). These methods involve application of the coating on test cylinders that are immersed in artificial standardized seawater for a 45 d period and are recognized to be time consuming, costly and to not reflect environmentally realistic conditions (Finnie, 2006). A few field methods have been developed to obtain more reliable and realistic release rate measurements. The most commonly used is the “Dome method” which was originally developed by the US Navy to measure organotin and Cu release rates *in situ* from a coated ship hull by using a closed re-circulating system (Valkirs et al., 2003; Schiff et al., 2004; Finnie, 2006). However, the use of this method has been restricted to the US Navy and also entails practical and economical challenges, including the use of divers. Hence, even though the method is recognized to be the most reliable indicator of environmental release rate, it has never been recommended to be adopted as a standardized method to be used in e.g. environmental risk assessment (Finnie, 2006). Other, strictly mathematically based methods are also used to calculate theoretical release rate of biocides, e.g. the mass-balance method developed by the “European Confederation of Paint, Printing Ink and Artists' Colours Manufacturers Associations” (CEPE). The advantage with the CEPE-method is its low cost, but since all the input data to the mass-balance formula, e.g. paint film thickness and service life time, comes from the paint manufacturer it is not possible to validate if the calculated release is environmentally realistic or not.

Thus, it is apparent that current methods for measuring release rates of biocides from antifouling paints have disadvantages of either being too costly (Dome method and rotating cylinder method), not represent field conditions (rotating cylinder method) or hold large uncertainties and to not be fully validated (CEPE-method). The aim of the current study was to bridge that gap by developing a cheap, fast and reliable release rate method based on X-ray spectrometry. The method was subsequently used to determine cumulative released Cu and Zn concentrations from five different coatings applied on static panels deployed in six different marinas located in the Baltic Sea and in Kattegat. An additional aim was to determine how salinity affects the release of Cu and Zn.

2. Materials and methods

2.1. Release measurements

Five different antifouling paints, holding a Cu_2O concentration between 6.9% and 34.6% (w/w), were used for the release study. Information about the tested paints and area of use in Swedish waters is presented in Table 1. The selected antifouling coatings were applied on one side of sandpaper rugged poly-methyl-meta acrylate (PMMA Plexi glass®) panels (20 × 20 cm) following the recommendations on to the product data sheet. Hence, one layer of primer was applied with a roller and left overnight to dry, and thereafter two layers of the antifouling paint were applied with sufficient drying time in between (>24 h). Three points were analyzed on each panel for total area concentrations of Cu and Zn (in $\mu g/cm^2$) with the XRF method, as described in section 2.2. The paint thickness on the Plexiglas panels was estimated by applying two rolled layers of the different antifouling coatings on plastic films (Melinex®, Putz Folien) holding a film thickness of 125 μm. For every paint, 10 replicates of plastic films were coated and 3 randomized points were measured on each film for paint thickness using a coating thickness gauge probe (Elcometer 456). Calibration foils were used to validate the measurements.

The coated panels (four replicates per paint) were attached, 30 cm apart and in random order, to a plastic rope. The panels were immersed along a pier in five different marinas in the Baltic Sea and Kattegat, i.e. Stockholm (59.298415°N 18.653049°E), Karlskrona (56.166362°N 15.825231°E), Simrishamn (55.560325°N 14.354432°E), Kiel (54.429409°N 10.172572°E) and Gothenburg (57.647232°N 11.853132°E) (Fig. 1). The exposure depth was approximately 1 m and the panels were submerged over the summer of 2014, from mid-May to mid-October, corresponding to 150 days exposure under static conditions.

After the exposure period, the panels were transported back to the laboratory and left to dry for > 48 h. The same measurement points analyzed before deployment were then measured again for total area concentrations of Cu and Zn with the XRF. The cumulative release of the two metals were determined for all measurement points by subtracting the end concentration from the start concentration. Moreover, the panels were checked for fouling under a stereo microscope and all paints tested completely deterred fouling of macroorganisms during the entire experiment. Only slime was detected on the panels.

2.2. XRF method

Handheld XRF analyzers are widely used for elemental measurements on e.g. soils and alloys and therefore most commercial instruments are equipped with calibrations for measurements of these matrices. However, since no commercial method for metal analysis in antifouling paints exists on the market, the first step was to develop an empirical method for metal analysis in antifouling paints.

2.2.1. Development of XRF release rate method

Two different commercial biocide-free antifouling paints were used to develop antifouling paint standards. Increasing amounts of Cu (as Cu_2O, Alfa Aeser, 99%) and Zn (as ZnO, Alfa Aeser, 98%) were added to the paints (both separately and in combination) to obtain wet weight (w/w) concentrations of 2, 4, 8, 16 and 32%. All paints were thoroughly mixed using wooden paint stirrers and subsequently applied on a 6.3 μm thick Mylar film with a Quadruplex film applicator (VF2170, TQC) to obtain a wet film thickness of 100 μm (corresponding to 25–35 μm in dry thickness). After a drying period of > 12 h, 25 mm Ø round discs were punched out and weighed, before measurement with the handheld XRF (DELTA-50, InnovX) attached to its benchtop test stand.

The standards were positioned directly on top of the XRF window and a circular area (28.3 mm^2) was analyzed using a 50 kV, 35.4 μA, 4 W setting beam for 30 s. The calibration was performed using the “empirical mode” in the PC software (Innov-X Delta advanced PC software). The empirical mode allows the user to utilize their own standards to create and store calibration models

Table 1
Summary of the characteristics of the antifouling paints used in the study.

Antifouling paint	Paint system	Copper(I)oxide content (%, w/w)	Zinc oxide content (%, w/w)
Mille Light Copper	Rosin-based	6.9	10–25
Biltema Baltic Sea	Rosin-based	7.5	20–25
Cruiser One	Rosin-based	8.5	10–25
Biltema West coast	Rosin-based	13	15–20
Mille Xtra	SPC	34.6	10–25

for custom applications directly on the analyzer. The program also allows the user to use different rate types. Here, the calibration was performed on the adjusted intensity of K_{alpha} signals, i.e. the intensity rates were (through the PC software) adjusted for air background and peak overlap, elemental interference from other elements in the sample that have peak energies close to the element of interest. Peak area integration was performed between 7.87 and 8.22 keV for Cu and between 8.45 and 8.81 keV for Zn. After the XRF analysis, the standards were chemically analyzed for their total concentration of Cu and Zn. Sample digestion and chemical analysis were performed by a commercial accredited laboratory (ALS Scandinavia). The standards were digested in aqua regia on a hotplate for 1 h. The sample solutions were analyzed by Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS) according to EPA method 200.8 rev 5.4 (1994) and SS EN ISO 17294-1 (2006).

The area concentration, C_{area} (μg/cm^2), of the standards were calculated with the following equation:

$$C_{area} = \frac{C_{paint} \times m}{A}$$

where C_{paint} is the (chemically analyzed) total concentration of Cu and Zn (μg/g), m is the weight (g) and A is the area of the standards (cm^2).

The calibration curves were established on the instrument, using the relationship between the measured adjusted Kα intensities of Cu and Zn, respectively, and the calculated area concentrations C_{area} of the standards. A regression analysis (for each element) was performed in JMP® 11.0.0 to evaluate the linearity of the calibration curves.

Fig. 1. Map showing the exposure sites.

2.2.2. Critical thickness of the coatings

To accurately determine the metal concentration in any matrix at least two processes should be taken into consideration: (1) the penetration of the primary X-ray beam into the sample and (2) the escape of fluorescent secondary X-rays which will be analyzed by the detector (Gauglitz and Vo-Dinh, 2006). The X-rays capacity to both penetrate into and escape the sample will depend on their energy – the higher the energy, the further the X-ray can travel through the sample. The penetration depth of the X-rays will therefore vary between elements since heavier elements (such as Cu and Zn) emit higher energy X-rays compared to lighter elements (such as Mg and Al) (Gauglitz and Vo-Dinh, 2006). Furthermore, the composition of the sample also plays a major role: the higher the concentration of heavy elements which can absorb the X-rays, the shallower the penetration depth will be (Potts and Webb, 1992). The critical penetration depth or saturation depth, d_{thick} is defined as the depth from which 99% of the signal will originate (Smith and Cresser, 2003). Beyond this depth, almost all photons are absorbed by the sample and will not be detected by the instrument. For bulk sample analysis, e.g. soil analysis, it is important to ensure that the sample is “infinitely thick” ($>d_{thick}$) so that the XRF signal is not dependent on the sample amount. On the other hand, for thin film analysis, it is important to instead define the thickness beneath which attenuation effects due to absorption can be neglected i.e. the depth beneath which the response range is linear (Fig. 2). This thickness is known as the critical thickness, d_{thin}, and is by convention defined as the thickness where 1% attenuation has occurred (Gauglitz and Vo-Dinh, 2006). As thin film analysis was utilized in this study, the thickness of the antifouling paint should

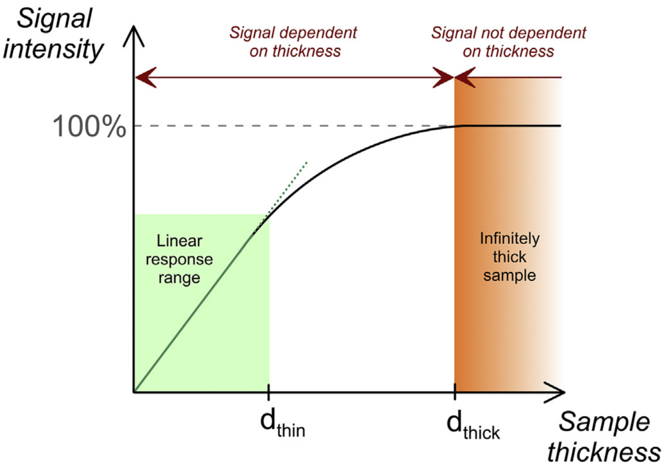

Fig. 2. Schematic showing the influence of sample thickness on the intensity of the XRF signal.

be below d_{thin} to avoid absorption effects and consequent underestimation.

Therefore, we designed an experiment to determine d_{thin} for Cu and Zn in two different antifouling paints. A paint with low Cu content (Biltema Baltic Sea, 7.5% Cu_2O) and one with high Cu content (Mille Xtra, 34.6% Cu_2O) were chosen to investigate potential differences in d_{thin} due to differences in heavy element content. Plastic films (Melinex®, Putz Folien) holding a film thickness of 125 µm was used as paint substrate. A motorized Film Applicator (Elcometer 4340) equipped with different applicators was used to produce wet paint thicknesses of 30, 50, 60, 90, 100, 120, 150, 200, 300 and 400 µm. The coated films were left to dry for one week. On each film, three measurement points were selected where XRF ($n = 1$) and dry film thickness ($n = 5$) measurements were performed.

2.3. Statistical analyses

Statistical analysis was performed in JMP® 11.0.0 to investigate the pairwise correlations ($\alpha = 0.05$) for all three parameters i.e. "Cu loss", "Zn loss" and "salinity". Multiple regression analysis was also performed to examine any potential combined contribution from "Zn loss" and "salinity" on "Cu loss". "Salinity" and "Zn loss" were set as explanatory variables for "Cu loss" according to the following statistical model: Cu loss = $\beta0 + \beta_1$ * Salinity + β_2 * Zn loss. The partial slopes β_1 and β_2 were then tested for significance at $\alpha = 0.05$.

3. Results

3.1. Release rate method

The regression analyses of Cu and Zn K_{alpha} net intensities and chemically analyzed metal concentrations are shown in Fig. 3. Both metals showed strong linear relationships between K_{alpha} net intensities and chemically analyzed concentrations; r^2 values were 0.998 (Cu) and 0.998 (Zn). The effect of dry paint thickness on K_{alpha} net intensities is presented in Fig. 4a and b. The paints show a linear increase in signal intensity up until ~50 µm, followed by an attenuation of the signal as the thickness increases further. The data points were fitted to a polynomial second degree curve ($r^2 \geq 0.995$ for all).

Linear regressions between 0 and 50 µm yielded with r^2 values

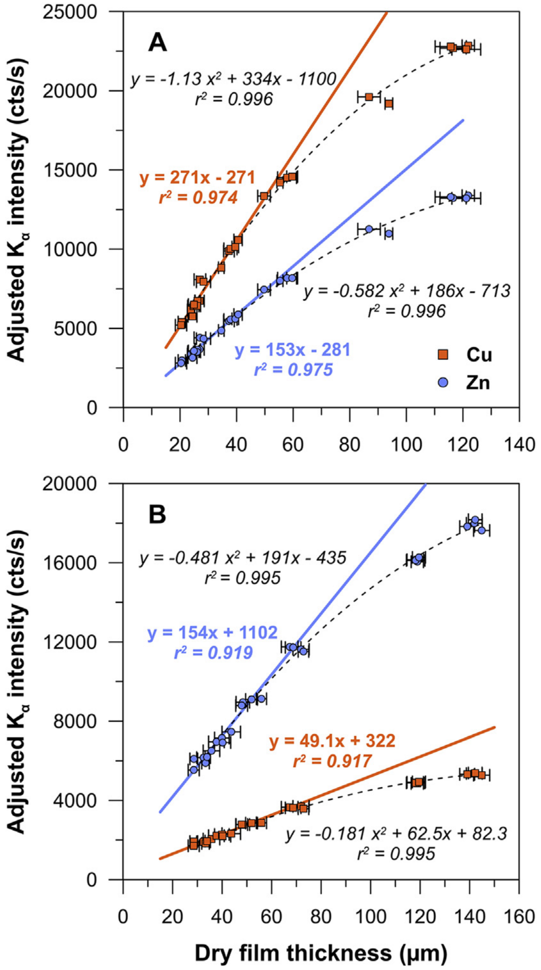

Fig. 4. Effect of dry paint film thickness on the XRF signal intensity for copper (orange squares) and zinc (blue circles) for two different antifouling paints: Mille Xtra (A) and Biltema Baltic Sea (B). The dashed lines show polynomial second degree curves fitted to all data points whereas the linear regression lines are based on data points with a dry thickness <50 µm. Horizontal error bars show the standard deviation of the dry film thickness measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

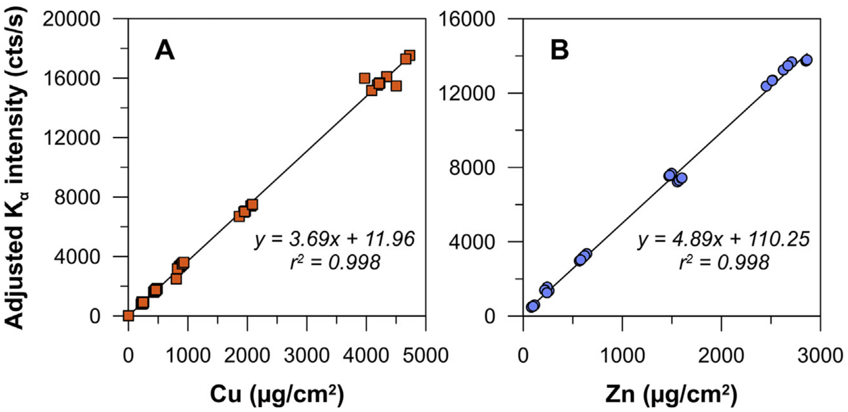

Fig. 3. XRF calibration curves for copper (A) and zinc (B). The standards used for the calibration were developed using biocide free paints where increasing amounts of copper and zinc were added. The wet thickness of the standards were 100 µm which corresponds to 30 ± 5 µm in dry thickness. The x-axis shows the chemically analyzed concentration while the y-axis shows the Kα adjusted intensities.

of 0.974 (Cu) and 0.975 (Zn) for Mille Xtra and of 0.919 (Cu) and 0.917 (Zn) for Biltema Baltic Sea (Fig. 4a and b). The critical thickness, d_{thin}, was then calculated as the thickness at which 1% attenuation is observed between the linear regression and the polynomial second degree curve. For Mille Xtra, d_{thin} was calculated to 40 μm (Cu) and 41 μm (Zn). For Biltema Baltic Sea, the determined d_{thin} was slightly higher at 52 μm (Cu) and 54 μm (Zn).

The coated (rolled) plastic films of Mille Xtra and Biltema Baltic Sea (see section 2.1) showed an average dry paint thickness of 64 ± 16 μm (SD) and 78 ± 15 μm, respectively. Provided that such thicknesses were also obtained on the Plexiglas® panels exposed in the field, an average underestimation of 8% (Mille Xtra) and 7% (Biltema Baltic Sea) are expected for Cu.

For Zn, the corresponding underestimation is calculated to be 7% (Mille Xtra) and 6% (Biltema Baltic Sea). For the remaining three paints, the underestimation at day 0 is likely of similar magnitude as their thicknesses were either lower or in the same range as Mille Xtra and Biltema Baltic Sea: thicknesses of 62 ± 10 μm, 61 ± 16 μm and 65 ± 16 μm, were measured respectively for Biltema West Coast, Mille Light Cu and Cruiser One. The thicknesses of the coatings after the field exposure (at day 150) were not determined. However, due to polishing, the coatings' thickness will be thinner after 150 d of exposure and presumably close to or within the d_{thin}.

3.2. Cumulative release of copper and zinc from antifouling paints

The total amount of Cu released during the exposure period (150 d) is presented in Fig. 5. For all the tested paints, the leached

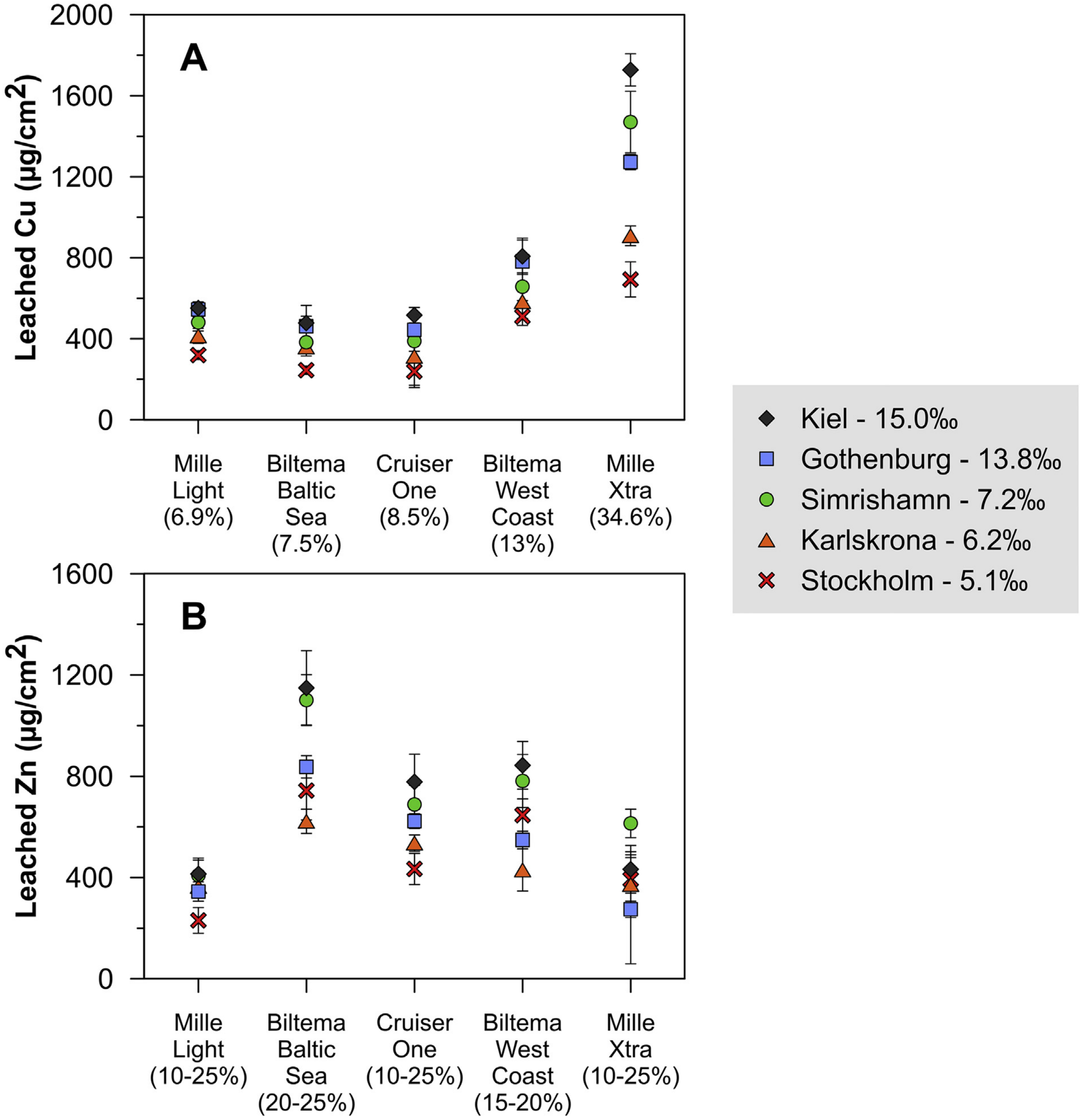

Fig. 5. Amounts of Cu (A) and Zn (B) leached from the panels during the whole exposure period (~155 days) for the five antifouling paints. Error bars show the standard deviation of the replicate measurement points. In parenthesis below the paint names are indicated the percentage of Cu_2O (A) and ZnO (B) as obtained from the Swedish Chemical Inspectorate's pesticides register and the safety data sheets of the paints. The salinity of the water is indicated in the legend, next to each location.

Table 2
R^2-values for the pairwise correlations and the multiple regression analysis. p-values are indicated within parenthesis and significant correlations ($\alpha = 0.05$) are highlighted in bold. For the multiple regressions, p-values for the partial slopes are shown and only the r^2-values of models where both the explanatory variables "Salinity" and "Zn loss" were found to contribute significantly are highlighted in bold.

	Variables/model	Mille Light	Biltema Baltic Sea	Cruiser One	Biltema West Coast	Mille Xtra
Pairwise correlations	Cu loss – Salinity	**0.759** *($p = 0.0439$)*	**0.827** *($p = 0.0365$)*	**0.855** *($p = 0.0247$)*	**0.902** *($p = 0.0078$)*	0.566 *($p = 0.1423$)*
	Zn loss – Salinity	0.228 *($p = 0.4017$)*	0.395 *($p = 0.3550$)*	0.549 *($p = 0.1520$)*	0.111 *($p = 0.5742$)*	0.103 *($p = 0.5980$)*
	Zn loss – Cu loss	0.606 *($p = 0.1142$)*	0.346 *($p = 0.3345$)*	**0.879** *($p = 0.0186$)*	0.166 *($p = 0.5219$)*	0.135 *($p = 0.5427$)*
Multiple regressions	Cu loss = $\beta0 + \beta1 * \text{Salinity} + \beta2 * \text{Zn loss}$	0.820 *($p_{\beta1} = 0.0652$ $p_{\beta2} = 0.1215$)*	0.935 *($p_{\beta1} = 0.1391$ $p_{\beta2} = 0.8043$)*	**0.996** *($p_{\beta1} = 0.0174$ $p_{\beta2} = 0.0145$)*	0.904 *($p_{\beta1} = 0.0389$ $p_{\beta2} = 0.7725$)*	**0.980** *($p_{\beta1} = 0.0231$ $p_{\beta2} = 0.0115$)*

amount of Cu was lowest in the locality with the lowest salinity, i.e. Stockholm. The pairwise correlations between leached amount of Cu and salinity were significant for all paints except Mille Xtra (Table 2), i.e. the leaching increased with higher salinity.

For Zn, no statistical salinity effect was observed. With the exception of Cruiser One, no statistically significant correlation between the leached amount of copper and the leached amount of Zn was observed. The statistical analysis of the multiple regressions showed that the leached amount of Cu can be explained by both the loss of Zn and the salinity for two of the paints: Cruiser One and Mille Xtra. Hence, for Mille Xtra, even though neither the loss of Zn nor the salinity alone showed any correlation with the loss of Cu, these two parameters can together explain the leaching of Cu.

4. Discussion

4.1. Release rate method

As emphasized previously, several release rate methods exist on the market that have the drawback of either being too expensive, not reflect field conditions or hold large uncertainties. In the present study, we have developed a new method based on XRF that has the advantage that it can be used to analyze discharges of Cu and Zn from antifouling paints exposed in the field. The calibration curves for Cu and Zn, i.e. the relationship between Cu and Zn K_{alpha} net intensities and Cu and Zn concentrations, showed that the XRF release rate model can be used for quantitative measurements ($r^2 = 0.998$ for both elements) (Fig. 3). The critical thickness (d_{thin}) of Cu and Zn for Biltema Baltic Sea was determined to be 52 and 54 μm, respectively. The corresponding d_{thin} of Mille Xtra were 40 and 41 μm. Hence, for both coatings, d_{thin} was similar for Cu and Zn, likely due to the fact that the secondary X-rays for these two elements have similar energy levels at 8.04 keV and 8.64 keV, respectively. The observed difference between the coatings is presumably a result of differing sample composition. Mille Xtra, the paint with the highest combined metal concentration (Cu and Zn), showed the lowest d_{thin}, presumably due to a higher degree of absorption of X-Rays by the heavy elements in the paint.

As the coatings' thicknesses were likely thicker than d_{thin}, the start concentrations of Cu and Zn were calculated to be underestimated by 6–8%. As a consequence, the total released amounts of Cu and Zn presented here would also be slightly underestimated. In future studies it is thus recommended to use coatings with dry film thicknesses < 40 μm.

4.2. Cumulative release of copper and zinc from antifouling paints

The cumulative release of Cu and Zn during the 150 d exposure time is presented in Fig. 5. The variation in leaching between the replicates for the respective paints was in general low within each harbor, shown by the low standard deviation. The data show the leaching of Cu to be governed by salinity, at least for the rosin-based paints for which a significant correlation between leached amount of Cu and salinity was observed. Salinity has shown to increase both the rate of Cu_2O dissolution (Kiil et al., 2001; Singh and Turner, 2009) and the polishing rate, where the latter is expected to be very low or to stop completely in areas with brackish or fresh water, at least for SPC paints (Kiil et al., 2002). However, salinity did not show any significant effect on the leached amount of Zn. The observed pattern may partly be described by the difference in dissolution rates, where ZnO dissolution rates have been reported to be markedly lower than Cu_2O particles (Yebra et al., 2006). The effect of salinity on the dissolution rate of ZnO is not known (Yebra et al., 2006), but recent studies on spent antifouling paint particles have shown the leaching of Zn to decrease with increasing salinity up until ~15‰ after which any further increase in salinity does not appear to have any effect on the leaching (Singh and Turner, 2009). However, in the study by Singh and Turner (2009), the form of Zn in the paint matrix was unknown and it cannot be ruled out that forms other than ZnO (e.g. Zn acrylates, Zn pyrithione) were also present in the paint matrixes. Thus, the observed difference in leaching behavior of Cu and Zn may be explained by the different dissolution rates of the two pigments, with salinity having a larger impact on the dissolution rate of Cu_2O particles then on ZnO particles.

The current data also suggest the release of both Cu and Zn to be paint specific and that neither Zn nor salinity alone can explain the release of Cu for all the investigated paints. In light of this, it seems quite problematic to set up a general model such as the CEPE model to generate paint specific release rates of biocides. Therefore, it is recommended that the developed XRF method is used to derive site- or area-specific release rates of metallic biocides. Such knowledge is highly valuable for both environmental regulators to set limit values for Cu for water quality as well as for the paint industry to design area-specific paints that meet environmental standards.

5. Conclusion

A direct method for environmentally realistic release rate measurement with the potential for standardization has long been requested by regulatory bodies, industry and academia. This new XRF method allows for the first time the direct measurement of the release of metallic biocides in the field, in a cost and time efficient manner. As exemplified in this work, this method makes it possible to identify parameters key to the release of Cu and Zn. It is therefore not only useful for the measurement of environmentally relevant release rate, but also as a tool for designing more efficient and optimized antifouling coatings. Using this new technique, more realistic release models based on field data could be developed. Furthermore, it could allow the identification of the minimum release of Cu necessary to avoid fouling at different sites, enabling the design of antifouling paints that are efficient while at the same time minimizing the negative effects on the environment.

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