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# In situ release rates of Cu and Zn from commercial antifouling paints at different salinities

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ABSTRACT

Antifouling paints are environmentally risk assessed based on their biocidal release rates to the water phase. In situ release rates of copper (Cu) and zinc (Zn) were derived for five commercial paints in two recreational marinas with different salinities (5 and 14 PSU) using an X-Ray Fluorescence spectrometer (XRF). Salinity was found to significantly affect the Cu release, with twice the amount of Cu released at the higher salinity, while its influence on the Zn release was paint-specific. Site-specific release rates for water bodies with salinity gradients, e.g. the Baltic Sea, are therefore necessary for more realistic risk assessments of antifouling paints. Furthermore, the in situ release rates were up to 8 times higher than those generated using standardized laboratory or calculation methods. The environmental risk assessment repeated with the field release rates concludes that it is questionable whether the studied products should be allowed on the Swedish market.

## 1. Introduction

To prevent fouling on submerged structures such as hulls, antifouling paints designed to kill or deter the settling organism through the slow release of toxins into the aquatic environment are commonly used (Almeida et al., 2007). Several different biocides have been used for this purpose throughout history, but today the main biocide is cuprous oxide ($Cu_2O$) (Yebra et al., 2004). The release of biocides from the paints directly into the aquatic environment leads to increased concentrations in water and/or sediments and may consequently negatively affect non-target organisms (Dafforn et al., 2011). Zinc oxide (ZnO) is also added to most paints as a means to control the erosion rate (Watermann et al., 2005). Although it is not classified as an active substance in the EU Biocidal Products Regulation (BPR, Regulation (EU) 528/2012), studies have shown that the release of Zn from antifouling paints can have toxic effects on organisms (Karlsson et al., 2010; Ytreberg et al., 2010). Within the EU, antifouling paints are regulated through the BPR which requires all biocidal products to obtain authorization before they can be made available on the market. In most member countries, the authorization process includes an environmental risk assessment, requiring manufacturers to submit the product's biocidal release rates. Regulatory bodies in the EU member states (as well as those in e.g. USA and New Zealand) accept leaching rate data generated from either of the only two standardized methods available (EU, 2006; Thomas, 2009; EPA New Zealand, 2011): (1) a rotating cylinder method (ASTM D6442-06/ISO 15181:2007) and (2) a mass balance method (ISO 10890:2010).

The rotating cylinder method (1) is a laboratory method where the paint is applied onto triplicate cylinders which are then stored in holding tanks containing artificial seawater under controlled conditions (pH: 7.9–8.1, salinity: 33–34‰, temperature: 25–26 °C) (ISO, 2007). On specified measurement days, each cylinder is moved into a cylindrical container with artificial seawater and rotated at a fixed speed for 1 h. Water samples are collected and analyzed to determine the release rate. The rates are determined in this way over a time period of 45 days and the average leaching rate between day 21 and 45 is reported. The mass balance method (2) is strictly a calculation method developed by the European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE) (ISO, 2010). Its equation was derived from a generic empirical model based on copper and organotin release rate data obtained using the rotation cylinder method. The model assumes an initial high release rate during the first 14 days, after which a constant "steady-state" leaching rate is achieved. The latter leaching rate is used for the risk assessment. The rotating cylinder method was never designed to reflect environmental release rates from antifouling paints and the rates derived from either of the two standardized methods have been shown to overestimate the real environmental release (IMO, 2009). Conservative default correction factors for each of the methods

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have been proposed in order to produce more realistic numbers: 5.4 for the rotating cylinder method and 2.9 for CEPE mass balance method (Finnie, 2006). These reduction factors were based on the comparison with in situ release rates for one ablative ship paint in one location (San Diego), obtained using a field method called the "dome method" (Finnie, 2006). This method was developed by the Space and Naval Surface Warfare Center in San Diego and allows the measurement of in situ leaching rates using a closed recirculating dome system which can be attached underwater to hulls or panels (Valkirs et al., 2003; Schiff et al., 2004). Although it has the benefit of yielding the in situ release rates, it has not been deemed economically or practically feasible to standardize (IMO, 2009). For risk assessment purposes, release rates reflecting in situ conditions are of great value. For one, the current standardized methods were designed for a strict set of exposure parameters when it comes to temperature and salinity. For brackish and colder water bodies, such as the Baltic Sea, these conditions are not representative. Secondly, the formation of natural biofilms on the paint surface have been found to affect the release rate of biocides from the coating (Valkirs et al., 2003; Yebra et al., 2006a), something the standardized methods cannot account for.

A novel method utilizing a handheld XRF, specifically calibrated to quantitatively measure the concentrations of Cu and Zn in antifouling paint films, has recently been developed (Ytreberg et al., 2017). It permits the measurement of the in situ release of metallic biocides and has the potential for standardization. Here, we present the first in situ Cu and Zn release rates for five different commercial antifouling paints for recreational vessels using the XRF method. Recreational boats in Sweden spend on average 90% of the boating season (May – September) moored in the harbor (The Swedish Transport Agency, 2010; The Swedish Transport Agency, 2015) and so, to simulate these conditions, antifouling paints coated on static panels were immersed for up to 84 days in two leisure boat marinas. The marinas were located in waters with different salinities: one on the Swedish East coast (5 PSU) and the other on the West Coast (14 PSU), allowing us to also investigate the effect of salinity on the release rate of Cu and Zn. The in situ release rates are compared to those derived using either of the two standardized methods and, finally, the environmental risk assessment of the products was repeated using the field release rates.

## 2. Materials & methods

### 2.1. Study sites and antifouling paints

Five commercial antifouling paints for leisure boats available on the Swedish market with $Cu_2O$ as the main biocide were used in this study (Table 1). All paints were rosin-based, ablative/erodible paints, except paint E that is marketed as a self-polishing coating. 10 × 10 cm polymethyl methacrylate (PMMA) Plexiglas® panels were lightly rugged with sandpaper and coated with primer, followed by the antifouling paint. An automatic film applicator (Elcometer 4340) was used for all paint application, with a wet film thickness setting of 100 μm (same as for the standards, see Supporting Information). The dry film thickness of the paints should be ≤ 40 μm to be within the linear response range of the XRF for Cu and Zn (Ytreberg et al., 2017). Three of the paints were therefore also applied with 100 μm wet film thickness onto polyester films (Melinex® O, 125 μm, DuPont Teijin Films) and a dry film thickness < 40 μm was confirmed using a coating thickness gauge (Elcometer 456).

The panels were attached in random order to polypropylene wires and immersed at 1 m depth in mid-July 2015 at two recreational marinas in Sweden: Bullandö Marina in the Stockholm area on the East coast (salinity of 5.1 PSU; 59.298°N, 18.653°E) and Fiskebäck Marina in the Gothenburg area on the West coast (salinity of 13.8 PSU; 57.647°N, 11.853°E). 4 replicate panels of each coating were retrieved at both locations after $t$ = 7, 14, 28, 56 and 84 days of immersion, with one exception: no panels coated with paint E were collected after 7 days at Bullandö. The panels were brought back to the lab and left to air dry before XRF analysis. The water temperature during the study, as monitored by the Swedish Meteorological and Hydrological Institute (Swedish Meteorological and Hydrological Institute, n.d.) at locations near the two marinas, were compared. No significant difference was found ($p$ = 0.2937) between the water temperature by the Stockholm marina (on average: 16.0 ± 1.7 °C; 58.933°N, 19.167°E) and by the Gothenburg marina (16.3 ± 1.7 °C; 57.685°N, 11.791°E). pH is expected to be similar at the two sites and between 8 and 8.3, based on measurements of coastal surface water in the Baltic Sea over recent years (Swedish Meteorological and Hydrological Institute, n.d.).

### 2.2. XRF method and calculation of release rates

A portable XRF (DELTA-50, InnovX) was used to measure the area concentration of Cu and Zn in the paint coatings (expressed as μg $cm^{-2}$), using the method described in Ytreberg et al. (Ytreberg et al., 2017). Minor modifications were carried out for the purpose of this study in order to improve the quantification (see detailed description in the Supporting Information). The same measurement time (30 s) and settings (50 kV beam) were kept, but a new calibration was established on the instrument. For this study, newly prepared painted film standards were mounted onto 10 × 10 cm PMMA panels, to exactly match the background of the paint panels utilized in the field study. Additionally, Compton normalization was applied to the signal as it improved the linearity of the calibration curves. The intensity of the

**Table 1**
Properties of the antifouling paints used in the study. Black color was used for all. Data was obtained from the Swedish Chemical Agency's pesticides register, from the paints' safety data sheet and technical data sheet.

| Antifouling paint | | Paint type | $Cu_2O$ (%) | ZnO (%)* | ZnO (%)** | Authorized usage |
|---|---|---|---|---|---|---|
| A | Hempel Mille Light Copper 71,430/19990 | Ablative | 6.9 | 10–25 | 11.0 ± 0.2 | Boats > 200 kg with main mooring on the East or West coast of Sweden. |
| B | Biltema antifouling Baltic Sea 30,630 | Ablative | 7.5 | 20–25 | 23.3 ± 1.4 | Boats > 200 kg with main mooring on the East coast of Sweden. |
| C | International cruiser one YBC011 | Ablative | 8.5 | 10–25 | 22.7 ± 0.7 | Boats > 200 kg with main mooring on the East or West coast of Sweden. |
| D | Biltema antifouling 30,600 | Ablative | 13 | 15–20 | 21.8 ± 1.5 | Boats > 200 kg with main mooring on the West coast of Sweden. |
| E | Hempel Mille Xtra 71,110/19990 | Self-polishing | 34.6 | 10–25 | 17.0 ± 0.3 | Boats > 200 kg with main mooring on the West coast of Sweden. |

* Range specified in the safety data sheet.
** Estimated from the reported $Cu_2O$ content and the average Cu:Zn ratio determined by XRF measurements on the panels before immersion, ± 1 standard deviation (n = 120).