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Efficacy testing of novel antifouling systems for marine sensors

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ABSTRACT

Marine sensors are widely employed tools for remotely providing a representation of their environment. The primary factor limiting measurement accuracy and deployment longevity is biofouling. For prevention, copper is the most widely applied biocide, often in form of adhesive copper tapes. However, for complex shapes these tapes are challenging to apply. Furthermore, sensor operating life frequently exceeds the antifouling protective period of the tape and the exchange of antifouling systems can be prohibitively time consuming and expensive. Alternative antifouling systems are needed to improve the cost-effectiveness of marine monitoring.

This study tested a novel adhesive antifouling film based on copper cold spray technology in two concentrations (586 g m^{-2} and 306 g m^{-2}) against a commercial copper tape (367 g m^{-2}) and an uncoated control. After ten months of immersion, the lower concentration adhesive film performed equal to the commercial copper tape while achieving higher durability and better leaching control. In contrast, the antifouling performance of the high-concentration film was at times lower than that of the commercial copper tape, likely due to high embedment depth of copper particles. Customizable, cold spray metallised adhesive films may offer an advantage compared to 'traditional' tapes, including the potential to reduce copper emissions.

1. Introduction

Underwater sensors are widely employed tools for monitoring environmental conditions at sea and their data is essential for numerous scientific applications as well as a broad range of industrial operations (Bean et al., 2017; Mills and Fones, 2012). Marine aquaculture is one of the industries where the use of sensor technology has gained in significance over the last decade (Parra et al., 2018). Here, sensors are facilitating the shift towards 'precision fish farming' where monitoring data are applied to enable more sustainable fish farming through improved control and decision-support (Føre et al., 2018).

Sensors are relied upon to deliver accurate data that provide a true representation of their environment. Biofouling, the growth of micro- and macro-organisms on submerged surfaces, is the primary factor limiting measurement accuracy and deployment longevity (Manov et al., 2004; Parra et al., 2018). Once exposed to seawater, biofouling can develop in days, altering the sensor environment (e.g., obstructing currents or views, generating or depleting oxygen) and its functionality (e.g., blocking the actual sensor surface as well as hinges or pipes), thus impacting the measurements and causing sensor drift or failure (Delauney et al., 2010; Donnelly et al., 2019; Manov et al., 2004; Venkatesan et al., 2017; Whelan and Regan, 2006). Consequently, biofouling protection is a vital part of sensor technology, and it is important that biofouling is prevented not only on the sensor head, but also on the sensor housing. Current antifouling technologies protect sensor surfaces via active or passive mechanisms. 'Active technologies' prevent settlement through mechanical tools such as wipers or scrapers (Delauney et al., 2010), bubble blasting (Yali and Zhang, 2015), or UV irradiation (MacKenzie et al., 2019). 'Passive technologies' in their most basic form include wrapping sensors in clear adhesive tape (e.g. standard packing tape), and removing biofouling when exchanging the tape during service intervals (Venkatesan et al., 2017). However, most passive antifouling systems rely on the use of biocides, in particular copper (Delauney et al., 2010; Manov et al., 2004; Whelan and Regan, 2006). It can be used to manufacture entire sensor parts or it can be applied to the surface of the sensor (Delauney et al., 2010; Manov et al., 2004). The latter can be achieved via coatings, but as these do not adhere well to all surfaces (Pistone et al., 2021) and often fail to provide long-term protection (Bloecher and Floerl, 2020a), adhesive copper tapes are a widely used alternative. These tapes consist of a copper shim (foil) with

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adhesive applied to one side and are supplied by the roll. However, as sensor operating life often exceeds the lifetime of the tape's antifouling capacity, the tape needs to be replaced – a time-consuming and relatively expensive task, particularly if the sensors are installed in a remote location (Venkatesan et al., 2017).

The application of antifouling tape to the complex 3D shape of a sensor body can be challenging. To improve this situation, the Commonwealth Scientific and Industrial Research Organisation (CSIRO; Australia) has developed robust antifouling film of self-adhesive polyurethane (PU) impregnated with copper particles. The film is produced using a high velocity particle spray (known as cold spray) to embed copper metal particles into the polymer film matrix (process described in detail in King et al., 2013; Poole et al., 2012; Vucko et al., 2012). The film is suitable for cutting into complex designs to cover 3D shapes, and is removed cleanly so it can be applied and re-applied in the field. Cold spray copper embedment imparts surface antifouling abilities similar to copper coatings without changing the inherent material properties of the underlying polymer matrix (Vucko et al., 2013). The copper particles remain in contact with the environment via the impact tunnels, and the concentration and depth of embedment can be used to control the antifouling function of the material (King et al., 2013; Vucko et al., 2014). The potential of cold spray copper embedment as an antifouling mechanism has been shown in the prevention of settlement of hard fouling organisms on PU seismic streamer cables for 210 days (Vucko et al., 2013) and on metallised nylon for 250 days (Vucko et al., 2012).

Sensors used in aquaculture typically include cameras to monitor feeding, as well as oxygen and current sensors. Some farms also deploy sensors to monitor salinity, turbidity, and fish behaviour. The lifetime of these sensors, and their ability to deliver real-time data without frequent maintenance are severely limited by biofouling (Delauney et al., 2010; Manov et al., 2004; Whelan and Regan, 2006), adding cost and being at odds with efforts towards automating farming operations (Føre et al., 2018; Parra et al., 2018). Novel antifouling systems would enable significant advances toward cost-efficient precision aquaculture and the associated benefits for health, welfare, biomass and quality of farmed species (Bloecher and Floerl, 2020b; Føre et al., 2018). This study evaluated the performance of PU films embedded with two different copper concentrations at a Norwegian salmon farm where biofouling is ubiquitous and compared it to a commercially available copper shim tape currently used to protect sensors.

2. Material and methods

2.1. Sample preparation and placement

Two variants of a self-adhering antifouling PU film embedded with a concentration of either 586 g m^{-2} ('High-Cu') or 306 g m^{-2} ('Low-Cu') of copper particles (copper coloured, matte) using cold spray technology were compared to two controls: untreated adhesive film ('Blank', transparent) and a commercially available copper shim tape ('Tape'), with a copper concentration of 367 g m^{-2} (McMaster-Carr Supply Co, USA; copper coloured, metallic). The experimental antifouling films were manufactured by CSIRO (Australia, according to methods described in Vucko et al., 2012) and, along with the blank and the copper tape, attached to grey PVC panels (20 × 20 cm, n = 12 per treatment) before shipping to Trondheim, Norway. Panels were mounted to four metal frames in random order using cable ties. Individually numbered tags (micro ear tags, OS ID) were attached to the metal frame above each sample. Each individually marked frame held 12 samples, three replicates of each surface protection, with samples placed one panel size apart. The frames were distributed to four locations in close proximity (5–15 m) to the sea pens at the SINTEF ACE research salmon farm site Rataren (63.782383° N, 8.52635° E) in Mid-Norway. The samples were suspended to 5 m depth from a buoy anchored to a rope between two net pens on March 31, 2017 and recovered on January 18, 2018 at the end of the biofouling season and following ten months of immersion.

2.2. Sampling and analysis

Biofouling growth on the samples was monitored monthly via high-resolution photographs. Before photographing, the metal frames were cleared of biofouling and the samples were gently rinsed with a fine spray of sea water at a maximum rate of 5 L min^{-1} per panel to remove silt and entangled debris. The samples were then photographed vertically under artificial light to optimise contrast. To limit air exposure and prevent desiccation, samples were processed in small batches of twelve. Due to adverse weather conditions it was not possible to sample in June and December 2017.

Biofouling accumulation on the samples visible in monthly photographs was described (to broad taxon level) using the Fouling Resistance (FR) scale, based on the ASTM standard for antifouling coatings (D 3623–78a; American Society for Testing and Materials ASTM, 1998). The FR scale ranges from 100 (complete fouling resistance – clean surface) to 0 (nil fouling resistance – entirely fouled surface). On each sample panel, 66 randomly spaced sample points (projected onto the target surface) were assessed and translated into FR scores. The outer 1 cm of each sample panel was not included in the analysis to avoid edge effects (e.g. biofouling growing on the outer, unprotected panel edge or backside, obscuring the sample, or unique hydrodynamic conditions affecting settlement relative to other panel areas). Slimes and algal spores <3 mm were not counted towards fouling reduction (FR score = 100 even in their presence), while the presence of larger fouling organisms resulted in a default reduction of the FR score to 95, or lower depending on fouling abundance (American Society for Testing and Materials ASTM, 1998).

Biofouling prevalence, taxonomic richness and community composition were assessed. Biofouling prevalence was calculated as the percentage of fouled replicates within one treatment (12 replicates) per sampling event. Taxonomic richness was calculated for each treatment based on the sum of taxa found on all replicates per sampling event. Community composition was calculated as percentage contribution of individual taxonomic groups to the biofouling community of each treatment and the total duration of the trial.

Over the course of the experiment, areas of the copper shim tape, starting from the outer edge inwards, lost their copper colour to the point of becoming see-through. To visually quantify the affected area, a dedicated software developed in LabVIEW (National Instruments) was employed. The original image was segmented by first setting a region of interest (ROI) to the PVC panel, and secondly by selecting the colour model (e.g., red/green/blue (RGB) or hue/saturation/value (HSV)), adjusting thresholding on the particular channels (e.g., RGB or HSV) until the resulting binary image best resembled the remaining copper on the depicted panel. The number of pixels representing the remaining copper was compared to the number of pixels representing the entire ROI, allowing the calculation of the remaining percentage of copper cover.

Statistical analysis of biofouling patterns was limited to the months where biofouling was encountered on the antifouling protected panels. Differences in Fouling Resistance between treatments were tested for using permutational analysis of variance (PERMANOVA, PRIMER v.7.0; Anderson, 2017) based on Euclidean distance with 9999 unrestricted permutations of residuals under a reduced model and a significance level of 5%. The FR of the treatments was compared using a repeated measures model taking into account the surface treatment ("Coating": Blank, Tape, High- or Low-Cu; fixed factor), the immersion time of the samples ("Time": seven, eight or ten months; fixed factor), and the placement of the frames ("Location": four locations; random factor). Of the 48 sample panels deployed, one 'Blank' control panel, one copper tape panel and two High-Cu film panels were lost due to adverse weather conditions. All values presented in the text are averages of a treatment if not indicated otherwise.

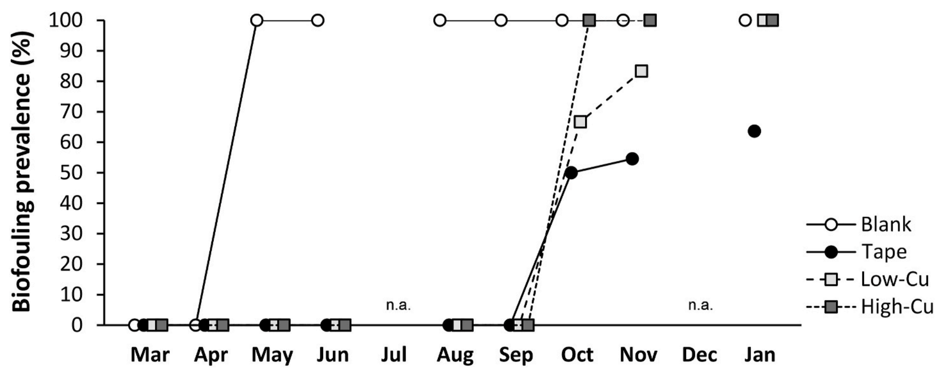

Fig. 1. Biofouling development. Prevalence of macrofouling organisms on four surface treatments during the ten-month trial.

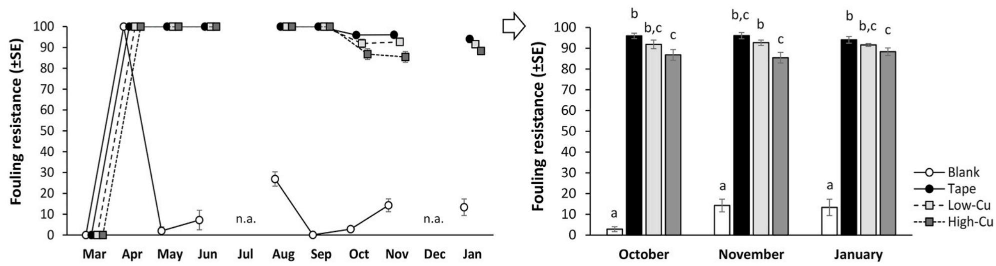

Fig. 2. Antifouling performance. Average fouling resistance (±SE) of four tested surface treatments during the ten months trial, with a detailed depiction of the last three sampling events. Lower-case letters above bars indicate results of pairwise comparison for levels of the factor 'Coating' within 'Coating x Time'. No statistical differences ($p > 0.05$) exist between bars associated with the same lower-case letters.

3. Results & discussion

3.1. Biofouling composition and prevalence

Over the course of the 10 months at sea, 19 taxonomic groups were identified on all samples (Table S1 in the supplemental material). Algal taxa were the most abundant biofouling group, accounting for 34% of organisms present. Hydroids (*Ectopleura larynx*) were the second-most abundant taxon (27%), followed by solitary and colonial ascidians (19%). Most taxa were exclusively found on the 'Blank' control panels, with a maximum of 11 taxa on both September and October samples. On the antifouling protected panels (Tape, High-Cu, Low-Cu) hydroids were the dominating taxon, followed by a low number of algae and tube-building amphipods (*Jassa* sp.). With the exception of several species of mussel present on the blank control samples, no encrusting hard fouling organisms such as barnacles or serpulid worms were recorded on any of the experimental surfaces.

The occurrence of a small suite of taxa on the antifouling protected surfaces was not surprising (Swain and Shinjo, 2014) given the known tolerance to copper for certain biofouling species including algae (Callow, 1986; Floerl et al., 2004; Hall, 1980; Tait et al., 2018) and especially also the hydroid *E. larynx* (Barnes, 1948). The latter is often one of the first organisms to settle on aquaculture surfaces with copper-based antifouling coatings (Bloecher and Floerl, 2020a; Edwards et al., 2014).

All 'Blank' panels were heavily fouled following two months' immersion, while it took much longer for the copper-protected samples to accumulate biofouling. In October, after seven months of immersion, the first fouling organisms were detected on the copper films and tape. At that time, some biofouling was present on all of the high-concentration film samples but was less prevalent on the low-concentration film samples (67%) and the tape samples (50%; Fig. 1). At the end of the trial in January, all of the copper film samples (High- and Low-Cu) and 64% of the copper tape samples were fouled to some extent (Fig. 1).

3.2. Fouling resistance

Fouling Resistance (FR) of the 'Blank' control samples was 0 (fully fouled) after 1 month at sea and stayed below 30 after that – consistently lower than the FR of any antifouling treatments (Fig. 2). This variation of FR over time even after initial FR values of 0 was likely because some fouling organisms developed to a size where they were easily removed by stronger currents in severe weather (Coutts et al., 2010).

The three antifouling treatments retained complete Fouling Resistance (= 100) for the first six months of the trial. In October, seven months after immersion, FR started to decrease. The high-concentration film samples reached their lowest average FR in November (85 ± 3 SE), while FR on the low-concentration samples and the tape was lowest in January (92 ± 1 and 94 ± 2, respectively; Fig. 2), at the end of the trial. Fouling resistance over the period of October 2017 to January 2018 varied between coatings with time (Coating x Time: $F_{6;86} = 2.81$; $p = 0.038$) and sampling locations (Coating x Location: $F_{9;86} = 6.48$; $p < 0.001$). The FR of the low-concentration copper film never differed from the copper tape control, while the high-concentration copper film had a significantly lower FR in two out of the final three sampling months ($p > 0.05$, pairwise comparisons; Fig. 2). The high-concentration copper film had a lower FR than the copper tape in October and January, and a lower FR than the low-concentration films in November ($p > 0.05$, pairwise comparisons; Fig. 2).

During antifouling tests on pen net samples conducted simultaneously at the study site the commercial copper 'control' coating had a FR < 10 after 6 months at sea (Bloecher and Floerl, 2020a). In comparison, the tape and film-based antifouling systems evaluated in this study provided a more efficient protection against biofouling. By keeping the test surfaces free of fouling for at least 185 days, the performance of the antifouling films was (i) similar to that reported from a similar trial with cold spray metallised surfaces, where soft fouling was not recorded for the first 181 days of exposure (Vucko et al., 2012), and (ii) superior in performance to metallised seismic streamer skins where soft fouling occurred after 42 days (Vucko et al., 2013). However, these tests

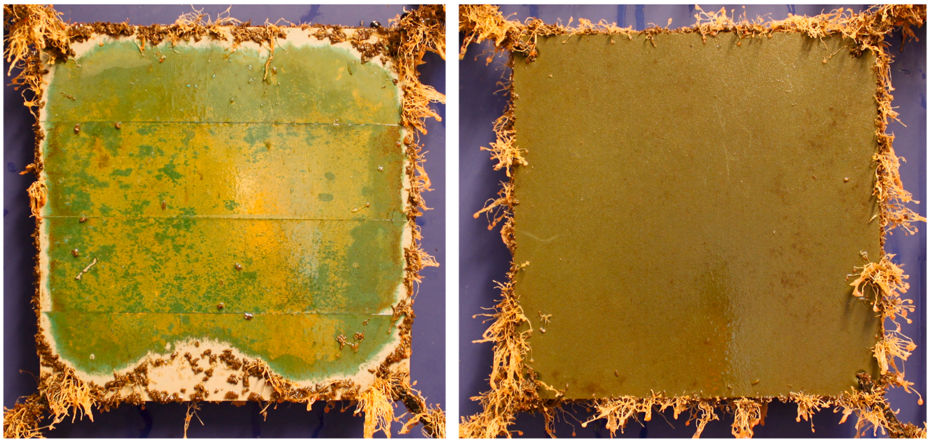

Fig. 3. Examples of experimental panels. Left: PVC panel where copper shim tape (oxidised green/yellow) was applied. Where the copper has leached out, the grey PVC base plate is visible through the residual transparent adhesive and biofouling organisms start to grow. Right: In comparison, no patchy leaching is visible from the low-concentration copper-embedded antifouling film after 10 months at sea. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

occurred in tropical water and involved lower copper loadings (between 101 and 125 g m^{-2}; Vucko et al., 2012; Vucko et al., 2013).

In summary, the results show that the low-concentration copper film performed equally well as the conventional copper shim tape. While prevalence of biofouling was lower on the tape, average fouling resistance did not differ. Both materials offered good antifouling control over a 10-month period under considerable fouling pressure.

The lack of superior antifouling performance in the presence of higher concentrations of copper particles (High-Cu films) compared to the Low-Cu treatment (586 g m^{-2} vs. 306 g m^{-2}) was in contrast to expectations. According to the manufacturer, a possible explanation is that the depth at which the particles are embedded during production of the films plays a crucial role in the availability of the copper and thus the antifouling activity of the film (CSIRO, pers. comm.). Higher loadings sometimes result in deeper embedment, decreasing the contact between copper particles and seawater, thus reducing erosion and leaching rates, which may affect antifouling performance (Vucko et al., 2012, 2014). We suspect that this phenomenon explains the counter-intuitive, reduced performance of the High-Cu relative to the Low-Cu treatment.

The slight differences in colour and surface texture between the treatments are unlikely to have influenced the test results. While some organisms show colour or texture preferences during settlement, others are unaffected (Hodson et al., 2000; Lin and Shao, 2002; Ralston and Swain, 2011; Scardino and de Nys, 2011; Swain et al., 2006). Previous studies have shown that the hydroid *E. larynx*, one of the most dominant colonisers in this trial, settles independent of the colour or texture of a surface (Bloecher et al., 2013; Guenther et al., 2009).

3.3. Copper leaching

While the antifouling performance of the low-Cu adhesive was similar to that of the copper shim tape, indications for differences in functionality became evident during this 10-month assessment. On the copper tape, the leaching of copper was visible through the loss of colour of the tape, showing the PVC panel beneath the transparent layer of adhesive (Fig. 3). On average, 16% of the visible copper surface was lost from the tape panels by the end of the 10-month trial. In contrast, no copper loss was visible from the films embedded with copper particles (Fig. 3), consistent with the intended antifouling mechanism associated with cold spray technology (King et al., 2013; Vucko et al., 2012).

When biofouling organisms began to settle on the antifouling surfaces following 7 months of immersion, this happened with relatively equal distribution of organisms on the copper-loaded films, indicating a uniform loss of antifouling protection of the surface. In contrast, the copper shim tape leached ions following a distinct pattern from the outside towards the inside. Biofouling organisms settled heavily following this gradient from the outside (sooner) towards the inside (later), with few organisms settling on intact copper tape. A potential explanation for this phenomenon is the electric conductivity of the copper shim tape that can cause galvanic effects at the edges and thus locally increased erosion of copper. In contrast, electric connectivity is unable to form between the individual copper particles embedded in cold sprayed surfaces, such as the adhesive films examined in this study, preventing galvanic effects (King et al., 2013). With regard to long-term use, this trend indicates a patchier protection of the surface where areas of heavy fouling are adjacent to areas relatively free of fouling. In a worst-case scenario, this could result in an impact on sensor performance from small patches of the copper tape, necessitating premature maintenance despite the average fouling load on the surface being low. In comparison, biofouling on the antifouling films accumulates uniformly, making colonisation more predictable and enabling optimised maintenance regimes. When maintenance is required, any adhered growth will be attached to the PU base film and so will be removed cleanly when the film is peeled off for replacement.

3.4. Conclusion

This study shows that adhesive antifouling films with embedded copper particles are an alternative and equally-well performing antifouling system to currently used copper shim tape. They may, in fact, offer an advantage of convenience with regard to durability and ease of replacement of the protective film. Furthermore, the adhesive films can be fabricated in varying and custom-made shapes, allowing attachment to complex surfaces, and avoiding overlap or gaps likely to occur when using tape strips to cover larger areas. The latter is an important factor considering the environmental concerns regarding the release of copper into the marine environment. While copper is currently one of the most widely used antifouling biocides (Blossom et al., 2018), it can negatively impact non-target organisms and accumulate in the environment (Burridge et al., 2010; Thomas and Brooks, 2010). Good leaching control, as demonstrated via the consistent and non-patchy protection against fouling organisms, may be an advantage of films over traditional copper tapes.

Further studies are recommended to confirm and optimise the performance of cold spray antifouling films for protecting sensor surfaces in a range of environments. First, they should investigate the leaching and depletion rate of cold spray antifouling films in relation to embedment depth in order to identify ideal design parameters and to allow customisation depending on application duration and expected fouling pressure in the deployment region. This could further reduce copper release into the marine environment while ensuring sensor functionality and cost-efficiency. Second, cold spray antifouling films should be evaluated on a representative range of geometrically complex test surfaces to confirm their performance across a range of applications.

CRediT authorship contribution statement

Nina Bloecher: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Funding acquisition. **Torfinn Solvang:** Methodology, Formal analysis, Writing – review & editing. **Oliver Floerl:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.oceaneng.2021.109983.

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