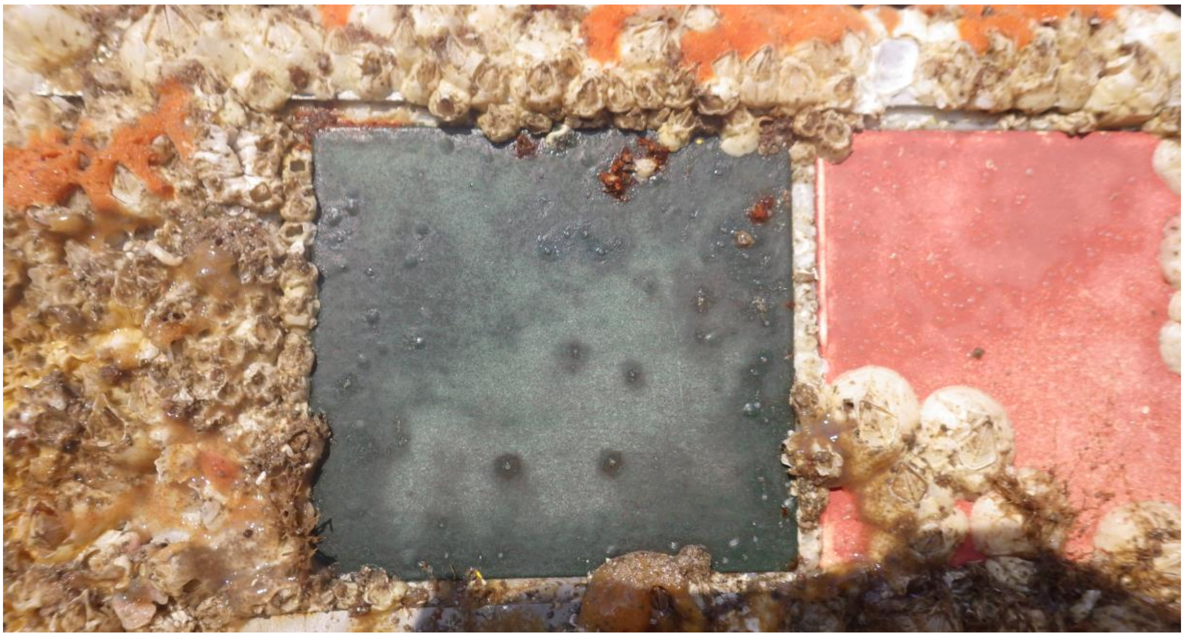
PML | Applications Ltd

Marine Matters

Copper Loss from a Coppercoat Antifouling System over Time

Report V7



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Solutions for
Sustainable Seas

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PML Applications is your gateway to accessing the latest in marine research that will benefit your business, especially in ballast water management, biofouling, survey work and satellite remote sensing.

Through our parent company Plymouth Marine Laboratory (a world renowned marine research organisation with over 500 global partners) PML Applications has access to cutting edge marine technology and knowledge, enabling our experts to provide you with independent and impartial advice, assessments, surveys and testing.

Operating in a complex, and often extreme, environment presents numerous challenges, the implications of which can be costly to operators and to the environment itself. We provide services, expertise and guidance to a diverse range of commercial customers and through greater understanding of the marine environment both time and money can be saved.

Specialties

Biofouling, Ballast Water, Ballast Water Treatment Systems, Marine Surveys, Marine Environment Assessment, Remote Sensing, Earth Observation, Harmful Algal Blooms.

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1 Executive Summary

Coppercoat has requested PML Applications Ltd to re-analyse some thickness data describing their antifouling paint from panels deployed in a high energy marine environment for 5 years.

The aim of this work is to calculate the loss of copper to the marine environment over time and make a comparison of this loss rate to another more conventional antifouling coating system.

The Coppercoat paint resulted one of the best performing antifouling systems tested with a mean total loss of thickness of 12.894μm for the whole duration of the experiment.

We bring here for comparison an anonymous Self-polishing AFC which had an estimated loss rate of 0.099μm/day (181.07μm in total) against a rate of 0.0071μm/day for Coppercoat.

From these results we estimate that during the 5 years exposure in the marine environment copper loss totalled to 2600μg/cm² which translates into a copper loss rate of **1.42μg/cm²/day**.

In terms of mean volume loss over the five year period, Coppercoat showed a loss of around 4.3% in terms of coating thickness. In contrast the standard SPC coating lost between 90 – 100% of the copper containing topcoat.

From water velocity measurements taken at the deployment site during the test we have assessed that the *average peak tidal* velocity near the pods was approximately 3.5 knots or **1.8 m/s.** In comparison, commercial ships generally steam at around 17 – 23 knots or 8.74 - 11.83 m/s.

2 Background

Between 2012 and 2017, as part of the Energy Technology Institute's ReDAPT project, PML Applications Ltd was commissioned to conduct *in-situ* testing of protective and antifouling coatings in a tidal stream. The aim of the work was to inform the tidal industry of the optimum coating options to protect tidal infrastructure from fouling and corrosion in harsh tidal environments.

The tidal industry requested the test as most antifouling coatings are designed for commercial or recreational vessel hulls, which in general do not experience the same degree of physical abrasion as tidal infrastructure. In addition, tidal infrastructure was being designed with a 25 year life expectancy, which is well beyond the operational life of most antifouling coating schemes.

PML deployed 2 benthic pods in the Fall of Warness in Orkney, Scotland, carrying a total of 100 panels coated in a selection of antifouling technologies. After 24 months one pod was recovered and analysed while the second pod remained deployed for a total of 5 years for continuous *in-situ* testing.

Coppercoat has requested further work for PML Applications Ltd to use the panel thickness data collected during this project to calculate loss of volume across time per unit area. This can then be used to estimate copper loss to the environment over a 5 year period.

Additionally PML Applications Ltd can offer comparative data from anonymous standard self-polishing coating system to be used as a reference to the Coppercoat's performance.

Figure 1: pods and panel units pre-deployment in Orkney.

<u>Please note:</u>
This report seeks to re-analyse and interpret data that were originally collected for a different purpose. Therefore, it is not possible in all cases to provide the level of experimental rigour that would normally be required in a study solely designed to investigate the loss of copper over time from a coating system.

3 Experimental Design

3.1 Setup

Two experimental pods were fabricated for the ETI's ReDAPT project. A full description of their design can be found in the ReDAPT ME8.2 report. In summary, the pods were designed to be hard wearing, resistant to tipping in the tide, and able to support a number of coated panels in the tidal stream.

3.2 Pod Deployment History

In 2014, after 24 months exposure, the pods were recovered from the water. The South pod was disassembled and the panels returned to Plymouth Marine Laboratory for full analysis for the ReDAPT project. The East Pod was lifted, photographed and redeployed in the same location +/-2m.

Table 1: Summary of deployment history of the pods.

Task	Date	Total duration of test
Pods assembled and deployed	May 2012	0
Pods surveyed by ROV	May 2013	1 year
One pod recovered for ReDAPT project	May 2014	2 years
Remaining pod surveyed by ROV	May 2015	3 years
Remaining pod surveyed by ROV	May 2016	4 years
Remaining pod recovered	May 2017	5 years

3.2.1 2015 visit

- The pod was not visible on the echo sounder, even though the vessel passed over the co-ordinates several times. However the ROV located the pod almost immediately after reaching the seabed using the same co-ordinates.

- The ROV footage explained why the pod was not visible on the depth sounder. The pod itself was then lower in the seabed than seen on previous site visits. It appeared that storms and currents have resulted in rocks and debris building up around the pod effectively 'sinking' it into the seabed.

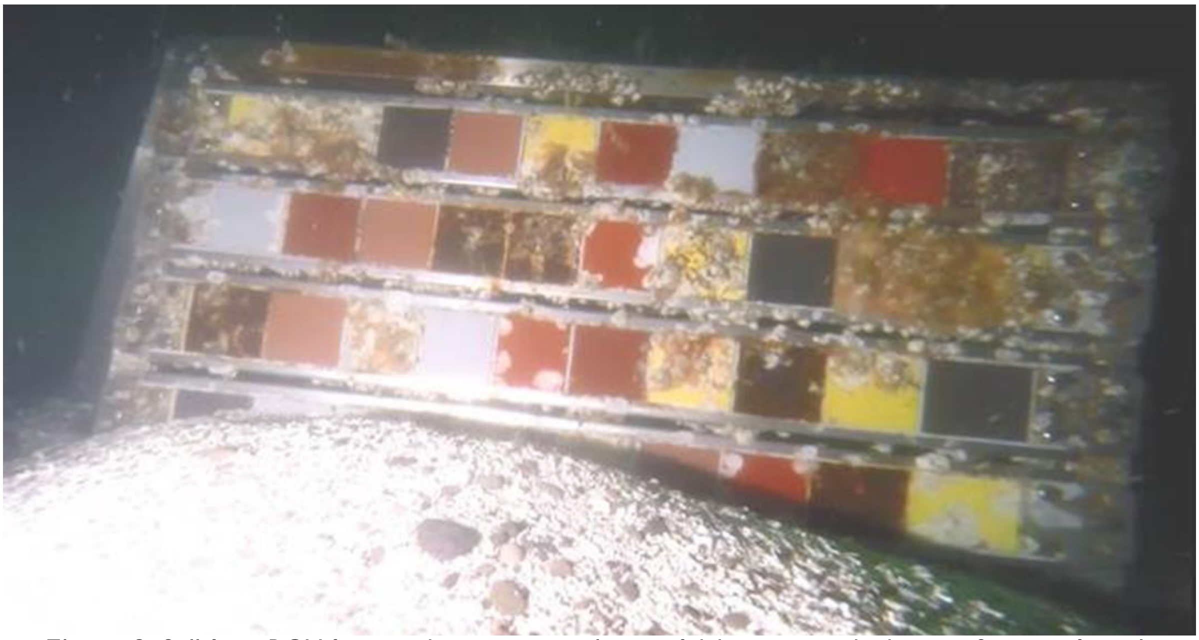

Figure 2: Still from ROV footage showing accumulation of debris against the bottom 2 rows of panels.

- On the east facing side the debris has built up to the extent that the concrete base and most of the bottom 2 rows of panels were obscured. Stones were also seen wedged between the rows of panels, suggesting that previously currents have been strong enough to lift and carry large debris which would have made contact with the panels even on the top row

3.2.2 2016 visit

The pod was visible on the depth sounder on arrival at the site in this year.

- Debris was clearly building up around the lander on the 2015 survey, but was much less evident on the 2016 visit. The lander did not appear to be in a depression, and no banking of debris was seen against the sides therefore it was decided that the lander should remain in that current position and not be lifted and moved.

- Five rows of panels were visible on the east side, as opposed to three the previous year. However the bottom row on the west side was then mostly obscured by debris.

- It seems likely that debris possibly increases and decreases periodically around the lander. The panels were clearly still being subjected to scouring by debris picked up and carried in strong currents, and to a larger extent than seen in 2015. While fouling levels in 2016 were generally at lower levels than seen in 2015, possibly due to scouring, damage to panels was still of great interest.

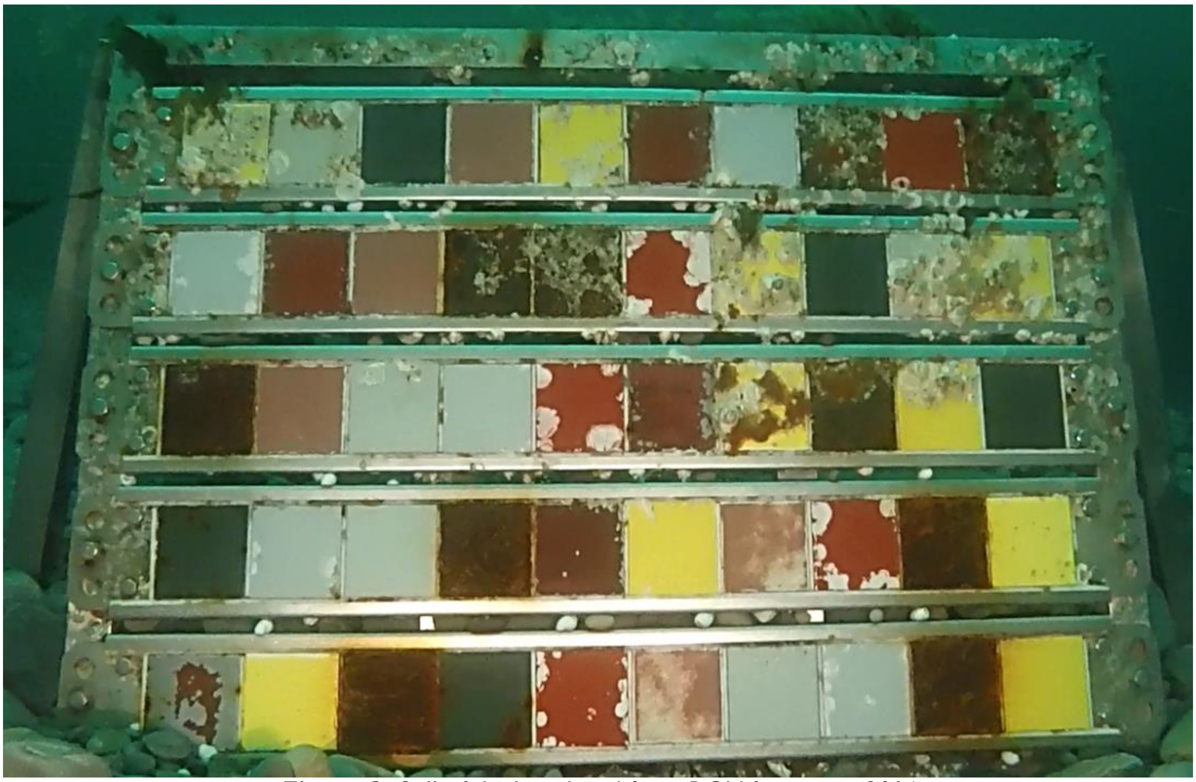

Figure 3: Still of deployed pod from ROV footage in 2016.

4 Environmental Parameters

Environmental parameters such as temperature, pH, salinity and water velocity can alter the performance of antifouling coatings considerably. This effect can be particularly marked on the performance of biocidal coatings where these parameters can alter the rate at which the biocidal component is released from the paint matrix. Consequently, by altering the release rate of biocides from coatings, environmental parameters can influence the efficacy and longevity of coating technologies.

It is a requirement therefore to characterise environmental parameters when investigating the efficacy of antifouling coatings to enable results to be extrapolated beyond the specific test site. For these reasons, the ReDAPT project initially aimed to characterise environmental parameters (temperature, pH, dissolved oxygen and salinity) of the seawater at the test site.

However, due to a series of technical and funding issues, this attempt was not successful and consequently the whole range of environmental data that it was hoped would be available to contextualise the coating performance we encountered was not available.

4.1 Salinity

The mean salinity at the test site was recorded as 34.75 PSU in 2011 based on data supplied by NASA (Aquarious). This is well within the range of normal oceanic salinity conditions and within the design specifications for all of the marine coatings tested for this project.

4.2 Temperature

The temperature of the water at the test site was recorded as a minimum of 6.1°C in March 2014 and a maximum temperature of 14.8°C in August 2014.

4.3 Water Velocity

Water velocity is a crucial descriptor of the test site as the water speed will not only influence the rate of leaching and polishing of the coatings, the water velocity will also influence the settlement and growth of fouling organisms. The figure below describes the relationship between depth and mean water velocity during flood tides.

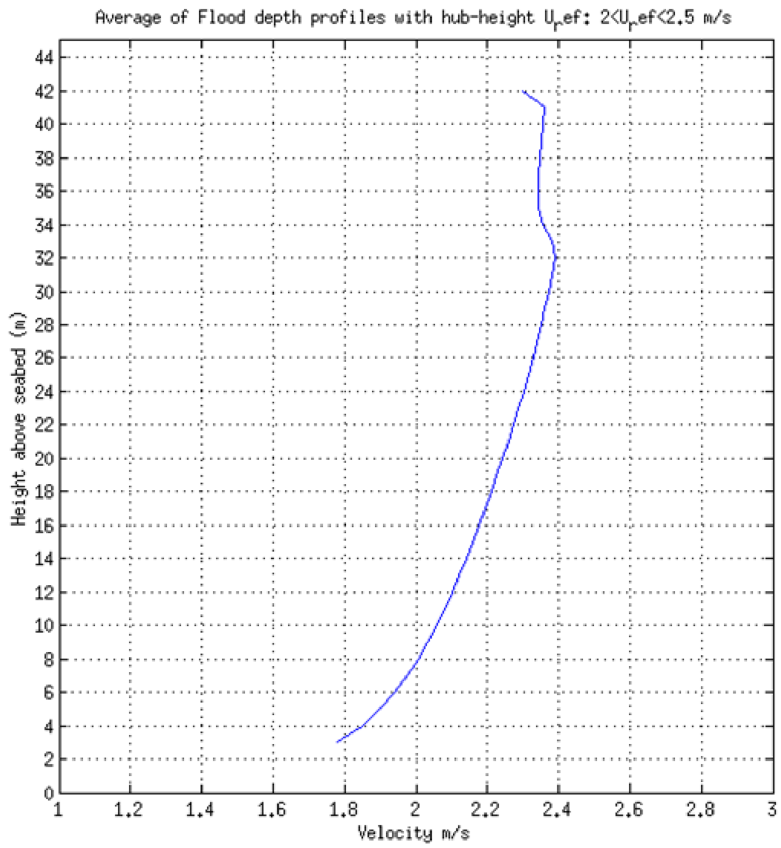

Figure 4: Plot showing the average velocity of water movement with height above the seabed at the tidal site.

Commercial ships generally steam at around 17 – 23 knots or 8.74 - 11.83 m/s. The water near the pods was approximately 3.5 knots or 1.8 m/s. Unfortunately, we do not have access to the tidal velocity throughout the whole tidal cycle. However, based on *average peak velocity* (which is an acknowledged overestimate) we can estimate that the coatings have been subject to an equivalent trip of 283,824km at a speed of 3.5 knots over the five year period.

distance (m) = speed (m/s) x time (s)

where:
speed = 1.8 m/s average peak water velocity (155,520 m/day)
time = 5 years of experiment running (1825 days)
distance = 283,824,000 m (283,824 km)

It is beyond the scope of this report to improve the accuracy of this figure, but with more resource it might be possible to collect data to more accurately define the tidal velocity throughout the whole tidal cycle and get closer to an "equivalent distance" travelled by the coatings.

When comparing coating longevity predictions between the shipping industry and high energy environments, it is important to consider that although the water velocity is generally slower at tidal sites, the wash out rate of any biocides and wear down rate of the coatings is also likely to be influenced by mechanical scouring of water borne debris.

5 Panels Treatment

5.1 Coating specifications

The test panels were made of carbon steel to simulate the material used in most marine energy devices.

The panels were fixed into bespoke panel holders before bolting to the pods. The panels were held firmly in nylon plastic channels, with plastic spacers in between the panels and the ends of the panel holder. In this way, each panel was electrically isolated from all other panels and the panel holder.

Table 2: Description and specification of the Coppercoat system as provided by manufacturer.

Name	Coppercoat
Technology Type	Biocidal copper filled epoxy resin
Anticorrosive	GP120 (DFT 250-300µm)
Top Coat	Coppercoat (DFT 250-300µm)
Commercial availability	Available – March 2019
Notes	Manufacturer applied

5.1.1 Application Procedures

The coating application process and conditions can have a significant impact on the performance of a coating system. Consequently, it was decided that with the exception of the low cost self-polishing coating and the anticorrosive control, all coatings would be applied by the manufacturers. PML Applications Ltd delivered the carbon steel panels to the manufacturer, and the manufacturer returned the coated panels back to PML Applications Ltd for testing.

Coppercoat confirms that they apply the product at a rate of 1 unit per 4 m^2 which gives a dry film thickness of ~250 µm.

6 Coating Thickness

6.1 Measurement

Coating thickness data were compared within and between coating types at two time points (0 and 60 months) pre-and post-deployment, to help assess the likely operational life of the coatings systems in the harsh test environment.

6.1.1 Time$_0$ measurements

In 2012 Faculty of Engineering and the Environment National Centre for Advanced Tribology at Southampton (nCATS) were subcontracted to undertake thickness measurements of all coated panels prior to deployment in the marine environment.

The analysis was carried out with an Elcometer® magnetic digital coating thickness gauge. Sixteen measurements were performed per panel in a square 4 x 4 pattern, with no measurements less than 1 cm away from the edge. The mean, highest value, lowest value, and standard deviation for each coated panel were recorded. The gauge was recalibrated before every panel analysis, using the 52.5, 105, 524 or 980 µm calibration standards, based on the thickness of each coating.

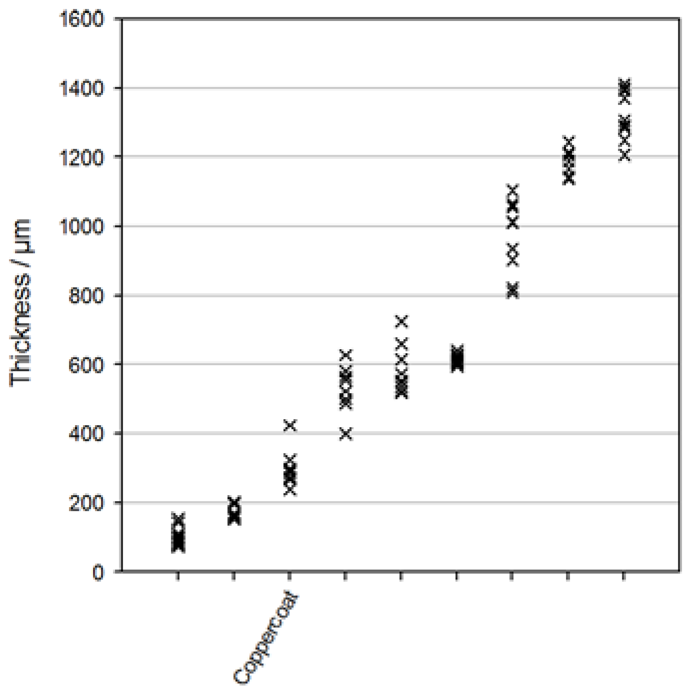

Figure 5: Mean coating thickness for each panel, Separated by coating type. Each point is a mean of 16 measurements taken for each panel.

6.1.2 Time$_f$ measurement

For this sampling event, coating thickness from the panel mounted on the second pod was assessed in house using an Elcometer® magnetic digital thickness gauge which was calibrated at 1300 microns and 126 microns to cover the expected dry film thickness range. Thickness measurements were taken at 10 points evenly distributed across each panel surface where possible, ensuring no point was closer than 1cm to the edge. These measures were then used to generate an average surface thickness per panel.

6.2 Sample Number

Due to the requirements of the previous ReDAPT project, it was not always possible to take measurements on the exact same panels at each time point. Therefore inter-coating variability in coating thickness is unavoidably included in the data.

The table below clarifies the total number of sampled points for each panel across time.

Table 3: total number of measurements.

<table>
<tr><th>Time</th><th>Type</th><th>Number</th><th>Total</th></tr>
<tr><td rowspan="2">Zero</td><td>Panels</td><td>9</td><td rowspan="2">144</td></tr>
<tr><td>Measurements within panel</td><td>16</td></tr>
<tr><td rowspan="2">Final</td><td>Panels</td><td>7</td><td rowspan="2">70</td></tr>
<tr><td>Measurements within panel</td><td>10</td></tr>
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6.3 Overall Results

Coppercoat showed little significant change in thickness over time, excluding inter-panel variability.

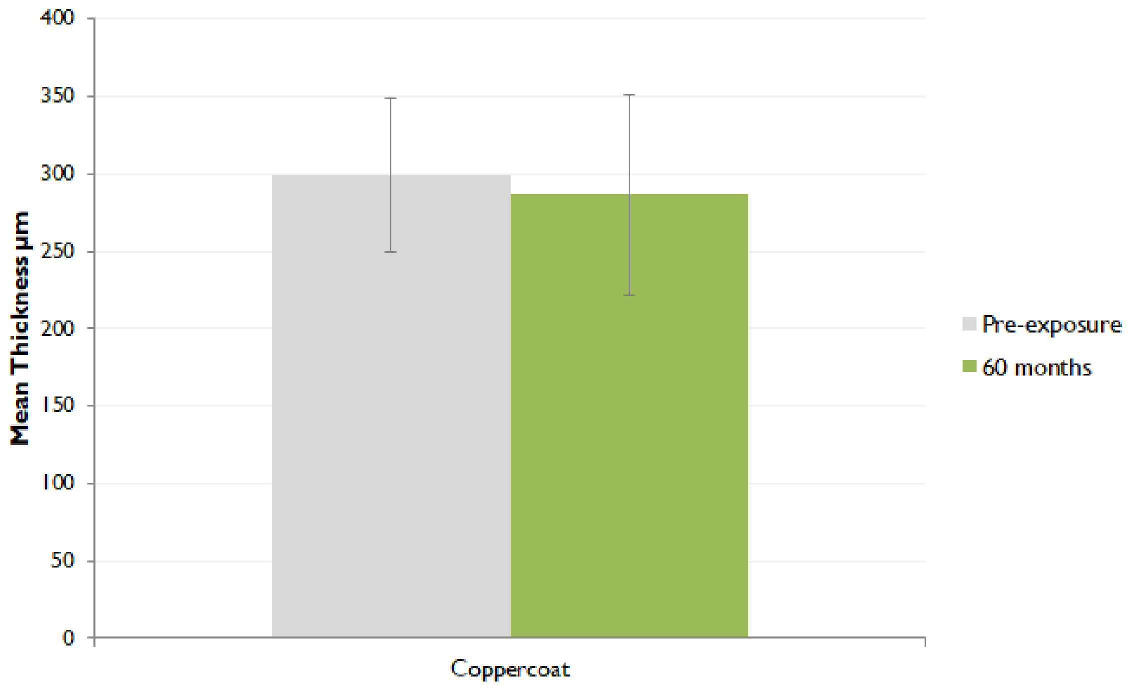

Figure 6: Mean coating thickness pre-exposure and at 60 months. Error bars show standard deviation, and n=144 & 70 respectively.

6.4 Conclusions on ReDAPT Thickness Results

It was hoped that by measuring the coating thickness pre and post exposure, it would be possible to provide a predictive assessment of coating longevity. Although this was attempted, there are several aspects which severely limit the accuracy of these predictions.

Firstly, when the thickness measurements were taken post exposure, only areas of the coating that were obviously not delaminated were selected. This step was taken because the damage encountered by the coatings was highly variable and uncontrolled. Therefore, the longevity of the coating cannot be assessed on thickness alone as in some cases the areas of coating damage not characterised by the thickness measurements may have resulted in coating failure.

Secondly, in the predicted longevity values, we have assumed a linear decrease in thickness over time, which is unlikely to be the case for all technology types. As a result of these considerations, the predicted longevity of the different coating types over time assuming a linear reduction in thickness is highly variable and requires further investigation to provide sufficient confidence in the results.

6.5 Experimental Quality Control

Quality Control details from the first thickness measurements are not available as the services were subcontracted to a third party; however the results obtained were in line with thickness expected according to manufacturer specification.

The final measurements were taken in-house using an Elcometer® magnetic digital thickness gauge which was calibrated at 1300 microns and 126 microns and with a measurement capability to ±1% accuracy.

6.6 PML Applications Ltd Quality Standards

Quality Assurance is provided at all steps in PML Applications Ltd environmental services approach. We apply robust QA/QC measures to ensure efficient execution of tasks and continuity of best practices. The PML Group (Plymouth Marine Laboratory & PML Applications Ltd) has been certified to the ISO9001:2015 Quality Management Standard.

7 Results

7.1 Thickness Data

In this section data are presented describing thickness prior to deployment and after five years.

Table 4: Pre-deployment thickness data

Panel Type	Mean µm (n=16)	SD	min	max	SD within batch
Coppercoat	239	17.9	195	260	34.8
	287	39.3	242	356	
	323	38.3	267	407	
	266	24.7	208	305	
	298	26.6	242	337	
	424	60.1	321	565	
	286	24.9	239	325	
	296	25.5	261	349	
	274	40.0	215	348	
Overall mean (n=144)	**299.22**				

Table 5: Thickness data after 5 years exposure in a tidal stream

Panel Type	Mean µm (n=10)	SD	min	max	SD within batch
Coppercoat	313.1	36.9	264	371	64.3
	287.8	35.5	225	360	
	298.5	128.5	194	615	
	254.8	23.1	218	281	
	269.7	18.0	244	297	
	323.7	73.0	237	441	
	256.7	38.1	219	323	
Overall mean (n=70)	**286.32**				

7.2 Thickness Loss over Time

From 2012 till 2017 we have measured a mean reduction of coating thickness of 12.894 µm, this translates to a rate of 0.0071 µm per day (12.894/1825=0.0071). This result is compared to a different self polising coating system also tested during the trials which showed a mean reduction of coating thickness of of 0.0992 µm/day or 181.04 µm in total.

In other words, the thickness reduction of Coppercoat represented circa **4.3%** (End thickness · 100/ Start thickness = 95.69 this is % of remaining thickness. Then 100 – 95.69= 4.3 thickness loss) of the orginal DFT of the whole scheme. The competitor brand showed a reduction of ~29.35% of the DFT of the whole scheme.

As stated by the manufacture, the top coat of the competitor brand was assumed to have an average thickness of 125 μm. From our results, therefore, we can assume that by the end of the testing period of 5 years between 90 and 100% of the top coat, and up to 106 μm (17% - tie coat loss · 100 / start thickness) of tie coat had been lost from this self-polishing system.

Please note:

- *all calculations are based on mean dry film thickness at T_0 and mean coating thickness at T_f.*
- *Variability existed with coating thickness between samples at both time points.*
- *We only have access to mean values, however mode averages might provide a more accurate representation of coating thickness change.*
- *We have assumed all change in coating thickness is attributed to coating wear down, and have not accounted for coating swelling etc due to immersion.*
- *Coatings were dry when measured at T_f. However, we have no control data to differentiate between the effect of coating thickness change due to immersion in seawater following curing, and effects of coating wear down in the field.*

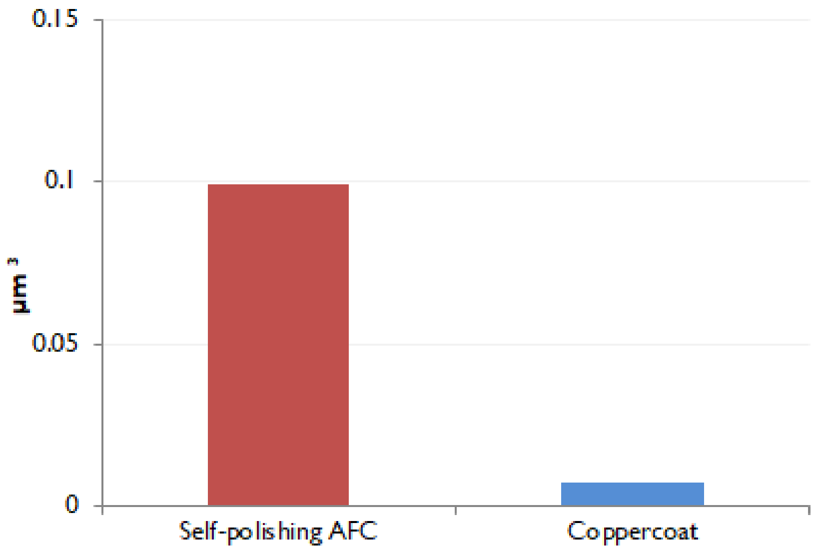

Figure 7: Loss of volume per day.

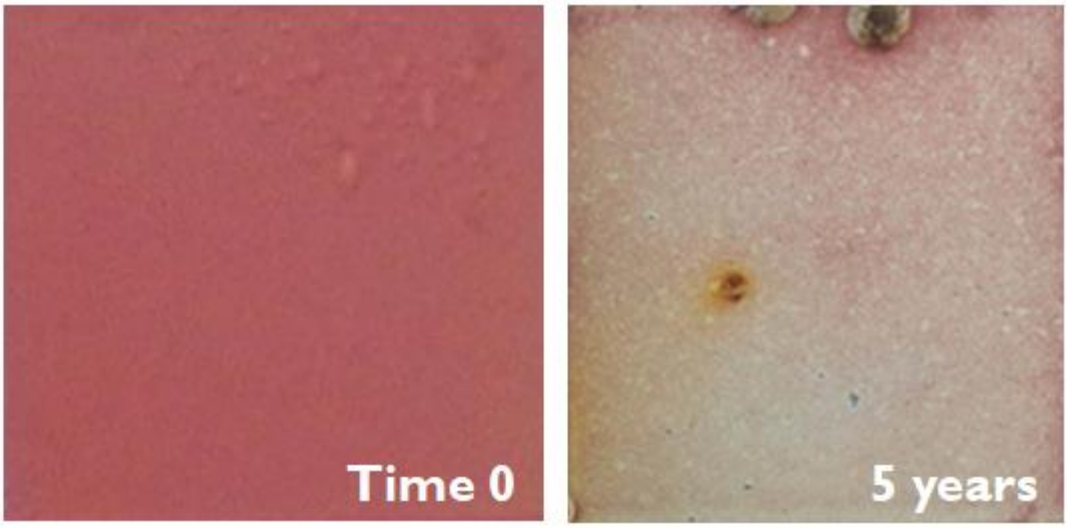

Figure 8: Top coat loss over 5 years – Self polishing anonymous coating system.

7.3 Copper Loss over Time

As disclosed by Coppercoat in 1 litre of paint there is 2000g of copper powder which will be applied for a unit area of $4m^2$. From this information we can estimate that the total copper content lost during the length of the experiment was **2600 µg/cm²** which translates to a daily rate of **1.42 µg/cm²/day**.

For the calculation it was assumed that for $1m^2$ there are 500g of copper powder. This equals 0.05 g/cm².

From the data we calculate that at a mean dry film thickness of 299.222 µm at T_0, we would find a copper content of 14.96 g/cm²/µm (299.222 · 0.05, where 0.05 is copper content g/cm² as per manufacturer) while at T_f with a mean dry film thickness of 286.328 µm, copper concentration would have been 14.32 g/cm²/µm (286.328 · 0.05).

$$Cu\ Loss\ per\ day = \frac{\left(0.05\frac{g}{cm^2} \Big/ 250\ \mu m\right) \cdot 13\mu m}{365 \cdot 5} = 1.42\ \mu g/cm^2/day$$

Figure 9: Calculations details where 0.05 g/cm² is the Cu content, 250 µm is the standard coating thickness and 13 µm is the measured lost thickness at the end of the 5 years exposure.

7.4 Possible Coating Longevity

Field observations suggest that approximately 13.0 µm of coating thickness was lost from the coppercoat system over five years (2.6 µm per year). If this rate of loss continues, the coating could thoretically last for 86 years before 90% of the thickness was removed. However, this is subject to the integrity of the coating remaining and the estimated wear down and leach rates persisting.

Please note that we have no further knowledge of the leach rate profile before or after this time point and cannot therefore assume the wear out rate of the coating will continue at this observed rate beyond the observational period. Please see section 6.4 for details of limitations on the prediction of coating longevity.

8 Discussion

8.1 Conclusion

Based on the data collected during our original study, which have been re-purposed to address a different question, it is clear that the loss of coating matrix from the Coppercoat system is much reduced compared to a conventional self-polishing antifouling system during a 5 year *in-situ* test in a tidal stream.

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