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The Effects of Short-term Changes in Environmental Parameters on the Release of Biocides from Antifouling Coatings: Cuprous Oxide and Tributyltin

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Current and forthcoming UK and European legislation requires environmental risk assessment of antifouling paints. For assessments to be carried out successfully, the leaching rate of biocides from antifouling paints should be determined. Current methods for the measurement of biocide leach rate have been shown to be very susceptible to changes in parameters such as pH, salinity and temperature. Using apparatus designed to simulate environmental conditions the effect of short-term changes in salinity, pH, temperature, suspended particulate matter and simulated vessel speed on cuprous oxide and tributyltin (TBT) leaching from self-polishing antifouling paint was investigated. No effect on copper leaching was observed over a wide range of environmentally relevant conditions, whilst vessel speed was the only parameter found to influence TBT release rates significantly. It is suggested that the decrease observed may be due to the formation of a boundary layer which slows down the release of TBT from the paint surface. The environmental authenticity of this observation and its possible implications for the environmental risk assessment of TBT are discussed. Copyright © 1999 Crown Copyright.

Keywords: tributyltin; copper; antifouling paint; leach rate determination

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INTRODUCTION

Antifouling coatings are used to prevent marine life from colonizing the bottoms of boats. These coatings release biocides which obstruct any fouling organisms and are required since the effect of ‘fouling’ on a ship’s hull is the formation of a rough surface that can cause turbulent flow and drag. Such factors are important in the running costs of a ship as they result in increased fuel consumption and reduce speeds.

Cuprous oxide has been used as a biocide since the early 19th century and continues to be one of the most common components of modern antifouling products.[1] Organotins were first used as booster biocides in the early 1960s.[2] An awareness in the 1980s of the harmful effects of tributyltin (TBT) compounds originating from antifouling paints in the aquatic environment prompted a great deal of research on their fate and effects. Adverse toxic effects such as balling in Pacific oysters,[3] imposex in female dogwelks[4] and high environmental concentrations[5] resulted in 1987 in a UK ban on the use of TBT on small boats. Cuprous oxide is at present used in paint formulations suitable for all vessels, whereas in the UK the use of TBT is permitted only in formulations for vessels longer than 25 m.

Antifouling paints can be divided into three types: insoluble matrix, soluble matrix and self-polishing. Insoluble matrix paints contain biocides loose in the paint that are released by contact leaching and are characterized by a high initial leach rate followed by an exponential decrease in leaching over a relatively short period (approximately two years). Soluble matrix paints also contain biocides mixed in the paint matrix; however, the biocide is released as thin microlayers of paint peel off. Again these parts are characterized

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by a high initial leach rate followed by an exponential leaching. In self-polishing copolymer paints the biocide (TBT) is chemically bonded to a polymer backbone (e.g. TBT methacrylate copolymer) which has an unstable release layer that gradually erodes due to hydrolysis. Self-polishing paints are characterized by an initial short high leaching rate period followed by constant but prolonged release of biocide for up to five years.

Current and forthcoming legislation (The UK Control of Pesticides Regulations, 1986 and EC Biocidal Products Directive 98/8/EC) requires environmental risk assessment of antifouling paints. For assessments to be carried out, the leaching rate of biocides from antifouling paints should be determined. The United States Environmental Protection Agency (EPA) has adopted the American Society of Testing Materials (ASTM) method (D5108-80) for assessing leach rates under standard conditions. The test system consists of a polycarbonate cylinder painted with the candidate paint. The cylinder is rotated at 60 rpm in a baffled beaker containing synthetic seawater and concentrations of biocide are measured periodically to calculate the release in terms of micrograms of active ingredient released per square centimetre per day ($\mu g\ cm^{-2}\ day^{-1}$). The method is designed to allow close control of pH, temperature and salinity and provide a comparable laboratory measurement. A recent study[6] investigated the effect of deviations, within the ASTM limits, on pH, salinity and temperature. When tested using insoluble matrix, soluble matrix and self-polishing paints containing copper and/or tin, it was shown that slight changes in conditions have a significant effect on the leach rates observed; pH was found to have the greatest effect with a 2–3-fold change in leach rate per 0.5 pH unit change, whilst salinity and temperature changes also had measurable effects.

The International Standards Organisation (ISO) have also adopted an adaptation of this method and have been evaluating the robustness of a laboratory-based leach rate method for cuprous oxide. The method has been tested in a variety of laboratories throughout the world and is soon to be published as an ISO method (ISO/DIS 15181-1,2).

If laboratory-based leach rate measurements are to be used in environmental risk assessments then they need to be representative of actual environmental conditions. A number of researchers have contested that the above laboratory methods provide results that are significantly higher than those that occur in the environment.[7,8] The aim of this study was to derive environmentally representative TBT and cuprous oxide leach rates for a TBT-based, copper-containing, self-polishing paint and also to investigate the effects of short-term changes in environmental parameters on leaching rate.

METHODS

Two test systems were used for leach rate testing; a flume tank in which a painted panel was held under conditions of constant near-laminar flow, and a custom-designed rotary device by which the painted panel was moved through the water at constant velocity. Both tanks have temperature-controlled filtered seawater flowing through them.

Flume tank dimensions and design

The flume was 150 cm long, 47.5 cm wide and 64 cm deep and when full contained 450 litres of water (Fig. 1). The panel (30 cm × 5 cm; Perspex) was located 65 cm from one end of the tank and

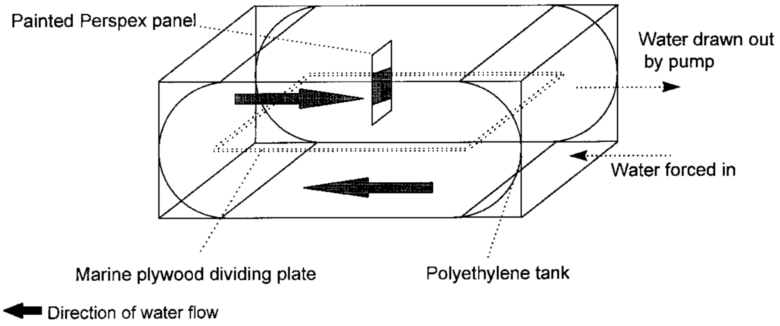

Figure 1 Schematic of flume test system.

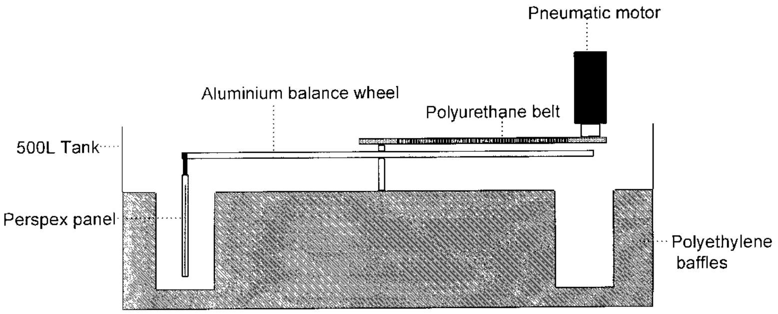

Figure 2 Schematic and rotary test system.

held in place by a stainless steel pin and an adjustable stainless steel panel-holding device. The position of the panel in the tank and the shear angle of the panel could be adjusted. The painted surface of the panel covered 50 cm^2. A pumping system allowed water to be drawn in at the front of the tank and forced out under a wooden dividing plate, creating a flow around the tank as shown in Fig. 1. The flow, and hence the velocity across the face of the panel, were controlled by a series of valves. Velocities of up to 5 knots (2.6 m s^{-1}) were achieved using this apparatus.

Rotary tank dimensions and design

The rotary system was housed in a 500-litre polyethylene tank and contained 400 litres of sea water (Fig. 2). Rotary movement of the panel was achieved using an aluminium/stainless steel balance wheel (68.5 cm in diameter). The panel (30 cm × 5 cm; Perspex) was attached on the outer rim of the wheel and held in place by a stainless steel rod. The shear angle of the panel was adjustable. The painted surface of the panel covered 50 cm^2. The wheel was attached by way of a polyurethane belt to a pneumatic motor. The motor speed was controlled by a needle valve. The speed of the panel was accurately determined using a digital tachometer. Speeds of between 1 and 10 knots (0.5–5.1 m s^{-1}) were obtained using this rotary design. A large baffle set diagonally in the tank prevented water movement and a general stirring effect in the tank.

The design specifications of both systems are summarized in Table 1.

Table 1. Summary of the design specifications of the flume and rotary systems

	Flume		Rotary	
Test conditions	Range	Stability	Range	Stability
Temperature (°C)	15–30	±0.1	2–35	±0.5
pH	6–8.5	±0.1	6–8.5	±0.1
Salinity (‰)	0–40	±0.1	0–40	±0.1
Flow rate (knots)	0–4.5	±0.1	0–10	±0.1
Suspended matter mg/l^{-1}	0–1000	—	Not possible	

Copper analysis

Copper concentration was measured in seawater by extraction with 1,1,2-trichlorofluroethane (Freon) and determined by ICP–MS.[9] The detection limit for copper using this method is 0.05 μg l^{-1}, with an extraction efficiency of 95%, RSD = 3% ($n = 8$).

TBT analysis

TBT concentration was determined as the hydride, following reduction by sodium borohydride, by gas chromatography flame photometric detection.[10] Samples (*ca* 25 ml) were collected in PTFE centrifuge tubes (100 ml) with an internal standard (tripropyltin chloride, together with dichloromethane (DCM; 5 ml) and sodium borohydride (250 mg) added. The tube was then shaken vigorously for 15 min and the DCM (*ca* 1 ml) was drawn off. GC analysis was carried out using an HP-5 (25 m × 0.32 mm i.d.; 0.52 μm film thickness; Hewlett Packard) and a flame photometric detector. The limit of detection using this modification was determined to be 0.1 μg l^{-1} with an extraction efficiency of 88%, RSD = 15% ($n = 8$).

Environmental parameter analysis

Salinity, pH and temperature were measured and logged hourly using Wissenchaftlich-Technische Werskstätten GmbH (WTW) Multiline P4 meters connected to a SenTix 41 pH electrode and Tetra Con 325 conductivity cell. Calibration was carried out following the manufacturers' recommendations. Data were downloaded to a PC using WTW Multi/ACHAT II software. The accuracy of the instrument was pH ± 0.01, salinity ± 1% of value, and temperature ± 0.01 °C (WTW, 1997).

Background copper and TBT concentrations

Natural seawater was obtained from the system installed at the CEFAS Burnham Laboratory and passed through a 1 µm filter (Gelman Polypure, UK); it had background copper concentrations of around 15 µg l^{-1}. The copper concentration entering the leach rate testing tanks was reduced to <2 µg l^{-1} by passing incoming seawater through a thermostatically controlled holding tank containing an ion-exchange-impregnated matting (Polyfilter®). Concentrations of TBT entering the system were below the limit of detection for the method described above.

Self-polishing copolymer antifouling paint

The leaching of a biocide from an antifouling paint is characteristic of the paint type. Self-polishing paints, of the type used in this study, display a leaching profile as shown in Fig. 3. The experiments described herein have been carried out at the time when the leach rates are most constant (Fig. 3). A 50 cm^2 section of a Perspex panel (30 cm × 5 cm) was painted with a copper- and tin-containing self-polishing paint and allowed to dry for seven days before any experiment.

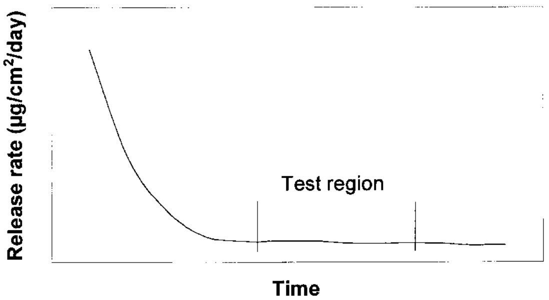

Figure 3 Leach rate profile of a self-polishing antifouling coating.

Table 2. Set points for environmental parameters

Parameter	Set points for test runs			
pH	8.2	6.5	7	8.5
Salinity (‰)	Linear decrease with time			
Temperature (°C)	25	1	15	30
Vessel speed (knots)	3	7	10	1
Suspended particulate matter (mg/l^{-1})	0	50	500	1000

Copper and TBT leach rate testing

The following method was used to determine the initial copper biocide leach rate in the flume tank before any changes were made to environmental variables.

Each tank was filled with 450 litres of filtered seawater. The concentration of copper was reduced to <2 µg l^{-1} and that of TBT to below the limit of detection using a Polyfilter®. Flume conditions were: temperature 25 °C; pH 8.2; salinity 35‰; flow rate 1 knot (0.5 m s^{-1}). The panel was placed in the flume/rotary system at a shear angle of 45° to the flow and the copper and TBT concentrations in the tank were allowed to rise to ~50 and ~5 µg l^{-1} respectively. Samples were then taken from the tank at various time intervals and the copper and TBT concentrations were determined for each sample. The concentrations of copper and TBT in each sample were then plotted against time and linear regression was used to obtain a fitted line.

The effect of separate parameters on copper and TBT leach rates was determined by allowing the concentration of copper and TBT to rise to ~50 and 5 µg l^{-1} through operation of the system and then maintaining these concentrations by controlling the flow through the system. Individual parameters of salinity, temperature, velocity, pH and suspended solids were then changed as summarized in Table 2, and the effect on copper and TBT leach rates was monitored.

RESULTS AND DISCUSSION

Initial leach rates

There was no significant difference between the leach rates obtained from the two systems. Using the flume tank method described above, copper and TBT leach rates were calculated as 18.6 ± 6.5 and 1.6 μg cm^{-2} day^{-1} respectively, whilst the rotary system produced leach rates of 21.6 and 1.7 μg cm^{-2} day^{-1} respectively. These values are lower than those obtained by the laboratory standard ASTM method for the same paint (25–40 μg cm^{-2} day^{-1} for copper and 1.5–4 μg cm^{-2} day^{-1} for TBT) and confirm previous findings that leach rates obtained by the ASTM method overestimate what may be observed in the field.

Effects of short-term changes in environmental parameters

Any change in leach rate would result in a significant change in copper and TBT concentrations within the test system. For example, if leach rates in the flume reflect changes demonstrated using the ASTM method, a decrease in pH of 0.5 unit will result in a 2–3-fold increase in copper leach rate. This would cause a ~5 μg l^{-1} increase in copper concentration in one day, i.e. a significant increase within the test system (Fig. 4).

No significant change in either copper or TBT concentration was observed with pH changes. Generally, the data showed a high degree of variability, with a general trend of copper concentration slowly decreasing. This is as would be expected if there was no pH-related effect. It appears that under environmentally simulated conditions a significant short-term change in pH does not result in a detectable change in copper and TBT biocide leach rate.

Short-term changes in temperature, once again, had very little effect on copper and TBT concentration. Little or no change was also observed in copper and TBT concentrations as salinity changed, whilst the effect of increased suspended particulate material on TBT concentration was insubstantial, although when suspended particulate material was initially introduced into the system there was a visible inexplicable decrease in total copper concentration. Total copper concentration for the whole experiment is very variable, yet it is similar whether suspended particulate matter is present or not, suggesting no relationship between the two. This is supported by previous studies which show that particulate material has little effect at speeds below 10 knots (5.1 m s^{-1}).[7] Copper concentrations also remain relatively constant as the vessel speed is changed (Fig. 5). The effect of short-term changes in speed on TBT concentration is distinct (Fig. 5). As the vessel speed is increased the TBT concentration decreases, with concentrations recovering only after a drop in speed from 10 to 1 knot (5.1 to 0.5 m s^{-1}). To confirm this observation the experiment was repeated and essentially the same result was obtained (Fig. 6). Comparison of the leach rates in terms of percentage change for both experiments shows a significant increase in TBT leach rate (~120%) as speed is reduced from 10 to 1 knot (Table 3). Previous research on the effect of speed on leaching rates has generally suggested that release rates are greater at higher speeds. This is based upon experiments which have shown greater erosion of the paint surface at higher speeds, often resulting from increased friction at the water–paint interface and turbulence in the boundary layer. Observations from the experiments carried out within this study suggest that, under the conditions described, TBT release is impaired at higher speeds. The weight of evidence suggests that this test system may not be precisely representative, yet the repeatability of the experiment suggests that the observed effect is real. The results provide evidence for a previously unreported effect on an

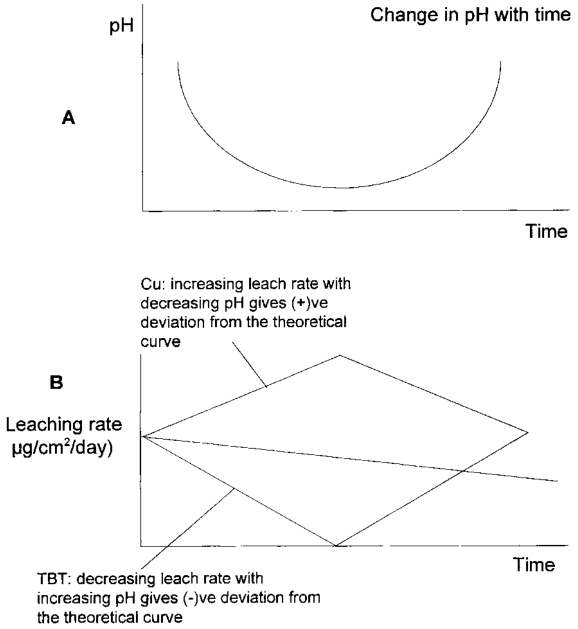

Figure 4 Theoretical change in TBT and copper leach rate with a change in pH. Graph A shows the change in pH with time whilst graph B shows the change in TBT and copper leach rates that would be expected following the pH change described in A. Based upon measurements obtained using the ASTM method (D5108–80).[6]

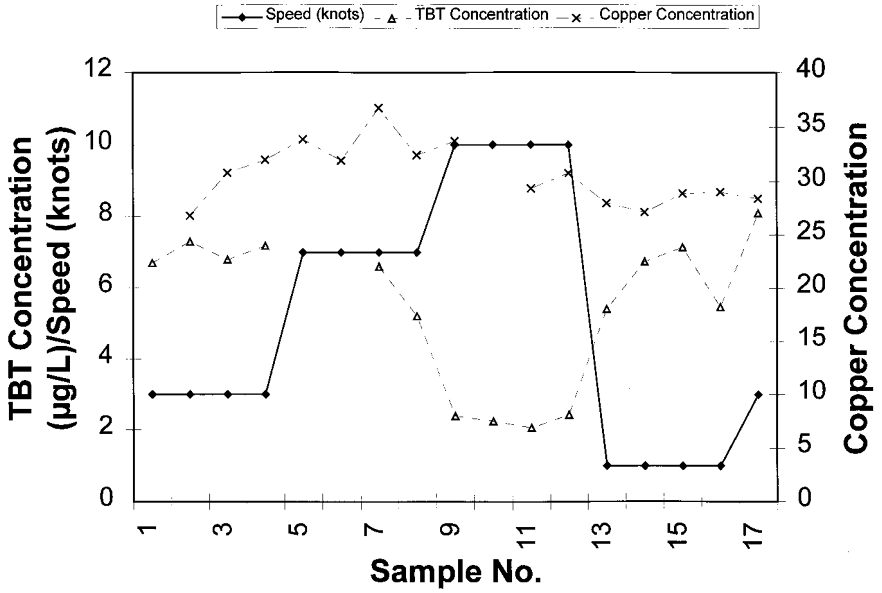

Figure 5 Effect of short-term changes in vessel speed on TBT and copper release at pH 8.2, 35‰ and 25 °C for a 17-day experiment.

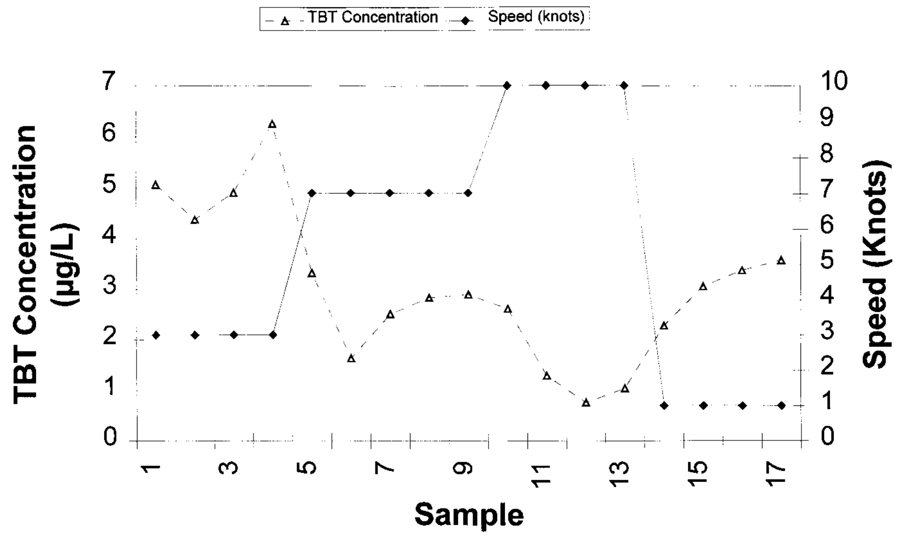

Figure 6 Confirmation the effect of short-term changes in vessel speed on TBT and copper release at pH 8.2, 35‰ and 25 °C (replicate of the experiment in Fig. 5, over 17 days).

antifouling-coated surface: a decrease in TBT release as water flow across the area of paint application increases.

The absence of any effect from short-term changes in pH, salinity, temperature and suspended particulate material may be due to the mode of copper release from the paint surface. Whilst TBT release in a self-polishing paint is dependent on reaction-controlled dissolution (i.e. hydrolysis of the TBT–copolymer bond), copper release is dependent on diffusion-controlled dissolution.[11] It appears that short-term changes in environmental

Table 3. The effects of changes in speed on TBT leach rate (decrease from 10 to 1 knot in bold)

	Experiment 1				Experiment 2			
Sample No.	TBT concn ($\mu g\ l^{-1}$)	Speed (knots)	Leach rate ($\mu g\ cm^{-2}\ day^{-1}$)	Leach rate (% change)	TBT concn ($\mu g\ l^{-1}$)	Speed (knots)	Leach rate ($\mu g\ cm^{-2}\ day^{-1}$)	Leach rate (% change)
1	6.7	3	1.7	—	5.1	3	1.7	—
2	7.3	3	1.9	9	4.4	3	1.5	−13.6
3	6.8	3	1.7	−6.8	4.9	3	1.6	12.1
4	7.2	3	1.8	5.6	6.3	3	2.1	27.5
5	7.2	7	1.8	0	3.3	7	1.1	−46.9
6	7.2	7	1.8	0	1.6	7	0.5	−50.8
7	6.6	7	1.7	−8.1	2.5	7	0.8	53.4
8	5.2	7	1.3	−21.2	2.8	7	1	13.1
9	2.4	10	0.6	−54	2.9	7	1	2.2
10	2.2	10	0.6	−6	2.6	10	0.9	−9.8
11	2.1	10	0.5	−8.1	1.3	10	0.4	−50.5
12	2.4	10	0.6	17.8	0.8	10	0.3	−41.2
13	5.4	1	1.4	**122.5**	1	10	0.3	37.1
14	6.8	1	1.7	24.8	2.3	1	0.8	**119.3**
15	7.2	1	1.8	6	3.1	1	1	34.2
16	5.5	1	1.4	−23.5	3.4	1	1.1	10.3
17	8.1	3	2.1	48.2	3.6	1	1.2	6

parameters have very little effect on the rate-determining factors governing diffusion-controlled dissolution. Due to the specific nature of the mechanism described, these assumptions can only be applied to self-polishing paints.

In general, it appears that antifouling coatings are stable to short-term changes in their surrounding environment. This does not rule out the effect of longer-term exposures (months rather than days) to varying environmental parameters on antifouling paint biocide leach rates. This will be the subject of further investigation.

CONCLUSIONS

Two experimental systems, designed to reproduce environmental conditions for biocide leach rate determination, have been applied to determine the copper and TBT leaching rate from a self-polishing antifouling paint. The results indicate that these leach rates are somewhat lower than those generated by the ASTM laboratory test protocol. The effects of short-term changes in five environmental parameters on cuprous oxide and TBT leaching was investigated. Vessel speed was found to have a significant effect on TBT release, whilst short-term environmental changes appear to have very little effect on copper-ion release. The TBT release rate was reduced with increasing water velocity, and vice versa. We speculate that this is due to a boundary layer effect. Regardless of the mechanism, it appears that vessel speed plays an important role in TBT leach rate from self-polishing antifouling paints and the consequences for environmental risk assessment are significant. These results give rise to the speculatation that a vessel slowing down to enter a harbour may deliver an increased dose of TBT.

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