ANTIFOULING PAINT BOOSTER BIOCIDES: THE CURRENT STATUS OF INPUTS AND IMPACTS IN THE UK COASTAL ENVIRONMENT

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Toxic antifouling paints are used to prevent marine life from colonising the bottoms of boats. A ban in the use of environmentally damaging tributyltin (TBT) formulations on small boats in the late 1980s has led to the development of copper-based alternatives containing organic biocides to boost their performance (Figure 1). The International Maritime Organisation (IMO) now intend to extend the TBT ban to all vessels by the year 2003 which will result in a further increase in booster biocide use. Here we present data relating to the rates at which some of these compounds are released into the environment, their concentrations in surface waters and sediments and present the findings of a preliminary risk assessment for the compounds most commonly used on small vessels in UK aquatic systems.

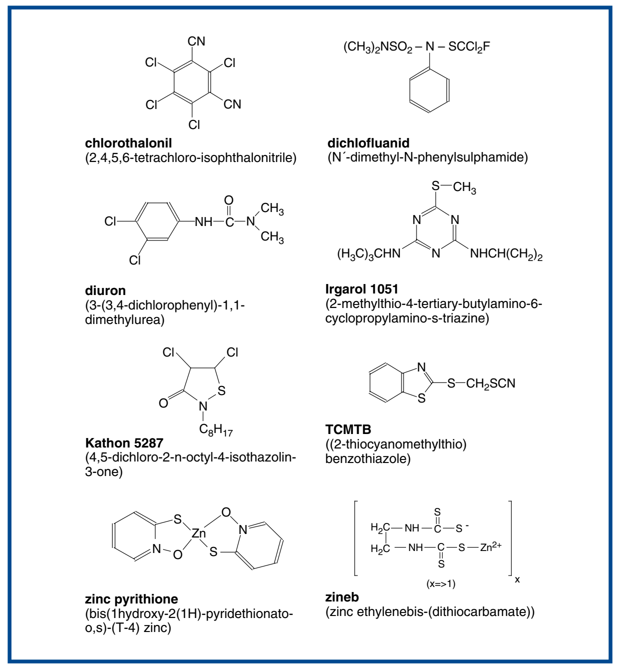

Figure 1. Activities approved for use in antifouling coatings by the UK HSE

Booster biocide release rate measurement

Understanding the effects of environmental variables on the rate of booster biocide release from antifouling formulations is necessary so that the measurements obtained by laboratory-based tests are correctly interpreted in environmental risk assessment. Data obtained from a standardised laboratory based release rate determination method (ISO/DIS 15181-1; Figure 2) were compared with data determined using a flume system designed to simulate environmental conditions (Figure 3&4).

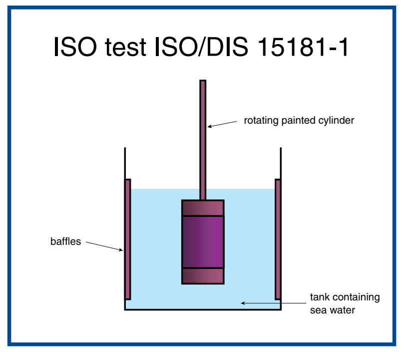

Figure 2. Schematic of ISO release rate mechanism

Figure 3. Flume release rate measurement system

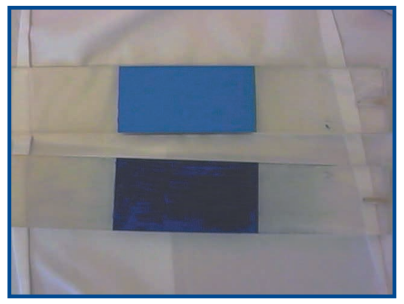

Figure 4. Painted test panels

Release rates determined using the flume system were consistently lower than those obtained using the ISO method for all biocides, excluding dichlofluanid and TCMS pyridine. It was observed that salinity, temperature, pH and suspended particulate matter had very little or no effect on the release rate of all biocides tested (Table 1).

Table 1. Comparison of biocide release rates from antifouling coatings

Biocide	Alternative trade name	Release Rate (μg cm^{-2} day^{-1}) ISO test system	Flume system
Cuprous oxide		25-40	18.6±6.5
TBT		1.5-4.0	1.6
Irgarol 1051		5.0	2.6
Diuron		3.3	0.8
Dichlofluanid		0.6	1.7
Zinc pyrithione	Zinc Omadine	3.3	-[a]
Kathon 5287	Sea-Nine 211	2.9	3.0
TCMTB	Busan	-[a]	0.9
TCMS pyridine	Densil S	0.6	3.8

[a] No data available.

Environmental Monitoring

Surface waters

In this study the concentrations of TBT and eight booster biocides were measured before and during the 1998 yachting season. The Crouch estuary, Sutton Harbour and Southampton Water were chosen as representative study sites for comparison with previous surveys of TBT concentrations (Figure 5-7). Diuron and Irgarol 1051 were the only organic booster biocides found at concentrations above the limits of detection. Diuron was measured at the highest concentrations, whilst detectable concentrations of both Irgarol 1051 and diuron were determined in areas of high yachting activity (e.g. mooring areas and marinas; Table 2). Maximum measured values were 1421 ng l^{-1} and 6740 ng l^{-1} respectively.
Lower concentrations of both compounds were found in open estuarine areas, although non-antifouling contributions of diuron may contribute to the overall inputs to estuarine systems.

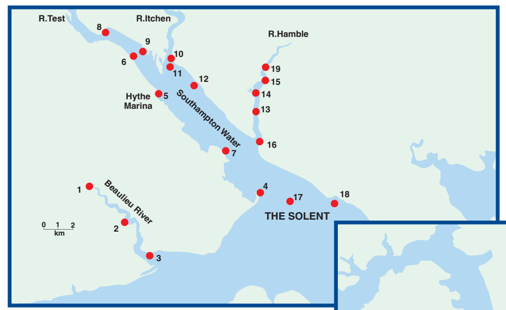

Figure 5. Sample locations on Southhampton Water, Hampshire, UK.

Figure 6. Sample locations at Sutton Harbour, Plymouth, Devon, UK.

Figure 7. Sample locations on the Crouch estuary, Essex, UK.

Table 2. Summary of 1998 yachting season monitoring data, April to October

Sample station	Location	Min.-Max. biocide[†] concentration (median) TBT (ng l^{-1})	Irgarol 1051 (ng l^{-1})	Diuron (ng l^{-1})
Southampton Water				
1	Beaulieu @ Penerley Fm	<1 (<1)	<1-3 (<1)	<1-5 (<1)
2	Beaulieu @ Bucklers Hard	<1-2 (2)	1-47 (22)	<1-141 (106)
3	Beaulieu @ Exbury River	<1-23 (4)	3-20 (9)	9-82 (32)
4	Calshot	<1-10 (5)	<1-7 (4)	4-58 (9)
5	Hythe Marina	<1-8 (<2)	118-403 (208)	112-6742 (632)
6	Cracknore Hard	<2-29 (4)	3-7 (4)	6-47 (25)
7	Fawley Refinery	<1-61 (<3)	<1-19 (4)	4-70 (24)
8	Docks (Upper)	<1-39 (19)	3-4 (3)	3-110 (21)
9	Docks (Lower)	<4-45 (17)	3-6 (5)	3-97 (21)
10	Ocean Village (Marina)	13-33 (27)	8-24 (13)	4-405 (82)
11	Itchen Mouth	<1-11 (6)	4-16 (8)	14-104 (32)
12	Netley Abbey Castle	<1-11 (10)	4-9 (6)	4-465 (30)
13	Hamble - Port Hamble Marina	<1-16 (3)	7-94 (27)	44-613 (150)
14	Hamble - Mercury Yacht Harbour	<1-17 (6)	22-141 (33)	113-214 (162)
15	Hamble - Swanwick Marina	<1-12 (4)	19-102 (39)	19-487 (117)
16	Hamble Mouth	<4-59 (5)	7-25 (13)	27-438 (52)
17	Outer Water	<1-2 (2)	2-33 (2)	1-23 (14)
18	Hill Head	<1-7 (2)	<1-8 (3)	1-27 (13)
19	Upper Hamble	<1-7 (4)	22-38 (31)	39-116 (101)
Sutton Harbour				
1	Melampus	<1-2 (<1)	<1-4 (1)	1-45 (8)
2	Mallard Beacon	<1-7 (<2)	<1-4 (1)	3-16 (8)
3	Sutton Harbour Berth B24/26	<1-40 (20)	4-69 (16)	40-331 (137)
4	Sutton Harbour Berth E2	<1-17 (<1)	9-65 (14)	12-189 (115)
5	Queen Ann's Battery	<1-39 (4)	<1-35 (3)	4-72 (26)
6	Sutton Harbour by Lock	<1-49 (30)	10-84 (16)	23-334 (93)
River Crouch				
1	Bridgemarsh Island	<1-3 (<1)	4-11 (7)	5-226 (32)
2	Fambridge Yacht Club	<1 (<1)	1-19 (11)	12-172 (44)
3	Crouch Outer	<1-4 (<2)	<1-4 (3)	6-46 (25)
4	Burnham Marina	<1-6 (<2)	12-49 (24)	36-305 (88)
5	Ringwood Bar	<1-1 (<1)	<1-18 (5)	6-60 (11)
6	Burnham Laboratory	<1-3 (<1)	2-19 (5)	8-64 (15)

[†] All other biocides below LOD

Sediments

Irgarol 1051 was detected (0.01-0.11 μg g^{-1}) in sediment collected from marinas where high concentrations of these compounds have been measured in surface waters (Figure 8). The Irgarol 1051 metabolite 2-methylthio-4-tert-butylamino-6-amino-s-triazine (M1/GS26575) was only detected at a few locations at concentrations <0.001 μg g^{-1}, although higher concentrations were determined in surface waters (13-99 ng l^{-1}). Diuron, thought to be present in the form of antifouling paint particles, was determined at a concentration of 1.4 μg g^{-1} in an enclosed marina. TBT was consistently determined at the highest concentrations and was detected in all sediments collected, along with the TBT degradation product dibutyltin (DBT) (Figure 9). All analytes were found to be below the limit of detection in sediments collected offshore.

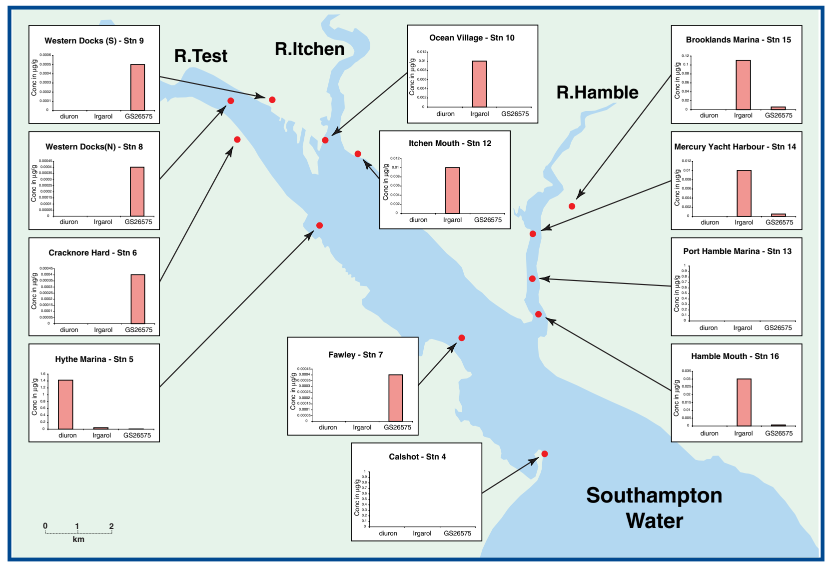

Figure 8. Irgarol 1051, diuron and GS26575 concentrations in Southampton Water sediments, 1998

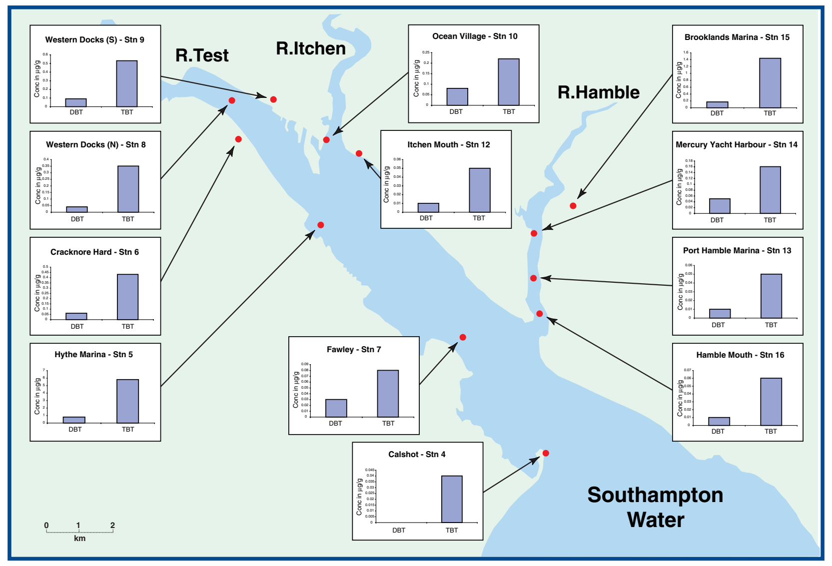

Figure 9. TBT concentrations in Southampton Water sediments, 1998

Risk assessment

Using the limited published environmental fate and toxicity data available for antifouling booster biocides, a comparative assessment to evaluate the risk posed by these compounds to the aquatic environment was performed. TBT still exceeds risk quotients by the greatest margins, but widespread effects due to Irgarol 1051 and less so diuron cannot be ruled out (particularly if use patterns change) and more information is required to provide a robust risk assessment (Table 3).

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Table 3. Risk quotients for Irgarol 1051, diuron and TBT

Sample station	Location	Risk quotient[a] (algae) Irgarol 1051	diuron	Risk quotient (fish and crustacea) Irgarol 1051	diuron	Risk quotient TBT (1998)	TBT[b] (1987)
Southampton Water							
1	Beaulieu @ Penerley Fm	-	<0.1	-	<0.1	-	-
2	Beaulieu @ Bucklers Hard	0.9	0.2	0.03	0.1	<1	15
3	Beaulieu @ Quay	0.4	0.1	0.01	<0.1	2	-
4	Calshot	0.2	0.0	0.01	<0.1	3	8
5	Hythe Marina	8.4	1.6	0.23	0.5	<1	980[c]
6	Cracknore Hard	0.2	0.1	0.01	<0.1	2	15
7	Fawley Refinery	0.2	0.1	0.01	<0.1	<2	9/38
8	Docks (Upper)	0.2	0.1	<0.01	<0.1	10	13
9	Docks (Lower)	0.2	0.1	0.01	<0.1	9	17
10	Ocean Village (Marina)	0.5	0.2	0.01	0.1	14	48[c]
11	Itchen Mouth	0.3	0.1	0.01	<0.1	3	32
12	Netley Abbey Castle	0.2	0.1	0.01	<0.1	5	19
13	Hamble - Port Hamble Marina	0.9	0.4	0.02	0.1	2	-
14	Hamble - Mercury Yacht Harbour	1.7	0.4	0.05	0.1	3	-
15	Hamble - Swanwick Marina	1.9	0.3	0.05	0.1	2	340
16	Hamble Mouth	0.5	0.1	0.01	<0.1	3	180
17	Outer Water	0.1	<0.1	<0.01	<0.1	1	23
18	Hill Head	0.1	<0.1	<0.01	<0.1	1	-
19	Upper Hamble	1.2	0.3	0.03	0.1	2	-
Sutton Harbour							
1	Melampus	<0.1	<0.1	<0.01	<0.1	<0.5	-
2	Mallard Beacon	<0.1	<0.1	<0.01	<0.1	<1	-
3	Sutton Harbour Berth B24/26	0.6	0.3	0.02	0.1	10	580
4	Sutton Harbour Berth E2	0.6	0.3	0.02	0.1	<0.5	-
5	Queen Ann's Battery	0.1	0.1	<0.01	<0.1	2	-
6	Sutton Harbour by Lock	0.6	0.2	0.02	0.1	15	-
River Crouch							
1	Bridgemarsh Island	0.3	0.1	0.01	<0.1	<0.5	9[d]
2	Fambridge Yacht Club	0.4	0.1	0.01	<0.1	<0.5	17
3	Crouch Outer	0.1	0.1	<0.1	<0.1	<1	3
4	Burnham Marina	1.0	0.2	0.03	0.1	<1	-[e]
5	Ringwood Bar	0.2	<0.1	0.01	<0.1	<0.5	13
6	Burnham Laboratory	0.2	<0.1	0.01	<0.1	<0.5	16

[a] measured environmental concentration (MEC)/no effect concentration (NEC), [b] all values for Southampton Water are based on single samples in June 1987 except where indicated; [c] 1989 values; [d] Crouch values are means of summer samples; [e] Burnham marina was built after 1987; - no equivalent sample data.

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References

Thomas, K.V. (1998) Determination of selected antifouling paint booster biocides by high performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. *Journal of Chromatography A* **825**, 29-35.

Thomas, K.V. (1999) Determination of the antifouling agent zinc pyrithione in water samples by copper chelate formation and high performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. *Journal of Chromatography A* **833**, 105-109.

Thomas, K.V., Chadwick, J., Raymond, K. and Waldock, M. (1999) The effects of short-term changes in environmental parameters on the release of biocides from antifouling coatings: Cuprous Oxide and tributyltin. *Applied Organometalic Chemistry* **13**, 1-8.

Thomas, K.V., Chadwick, J., Raymond, K. and Waldock, M. (1999) The effects of changes in environmental parameters on the release of organic booster biocides from antifouling coatings. *Proceedings of the 10th International Congress on Marine Corrosion and Fouling, Melbourne*, Australia.

Thomas, K.V., Blake, S. and Waldock, M. (In Press) Antifouling paint booster biocide contamination in UK marine sediments. *Marine Pollution Bulletin.*

Thomas, K.V., Fileman, T.W., Readman, J. and Waldock, M. (In press) Antifouling paint booster biocides in the UK coastal environment and potential risks of biological effects. *Environmental Science and Technology.*

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