ANTI-FOULING MATERIALS

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Introduction

Any unprotected surface which is introduced into the sea, such as a buoy, a ship's hull, an oil rig support or a fish cage, will become fouled by growths of marine organisms. Colonization of a newly immersed surface involves a typical ecological succession of different flora and fauna. Initially, the surface undergoes biochemical changes as macromolecules, such as glycoproteins, proteoglycans, and polysaccharides, become adsorbed on to it. Bacteria then colonize it within about an hour of submersion, followed by diatoms, yeasts, and protozoa. Subsequently, invertebrate larvae and algal spores settle on the surface and metamorphose and/or grow, often forming a dense covering over it. In the case of wooden structures, there are even some organisms, such as the shipworm (actually a mollusk, *Teredo*), which bore beneath the surface. The climax community can be highly diverse. Overall, there are >4000 known species of fouling organisms, including barnacles, hydroids, tube worms, bryozoans, seaweeds, and others.

This article will consider the problem of fouling on ships' hulls, and measures taken to prevent it. Antifouling coatings containing the biocide tributyltin, more commonly known as TBT, have been particularly effective during the past 25 or so years. However, TBT has leached from the coatings into the marine environment, harming nontarget species. The damage caused, and the extent to which this has been minimized by regulations limiting their use, will be discussed. There will also be consideration of the dangers of introducing a premature ban on TBT-based paints before suitable alternatives are available.

Historical Development

Fouling has caused problems to shipping throughout history. *Teredo* has been responsible for the destruction of many wooden sailing ships, even causing them to break up at sea. Modern steel hulls are not penetrated by these molluscs, nevertheless, their surfaces are highly vulnerable to fouling. Coverings by growths of organisms can be remarkable if they are left unchecked. The total weight of fouled organisms can be as high as $150\,kg/m^2$, representing 6000 tons of fouling attached to a large commercial vessel which has an underwater surface area of $40\,000\,m^2$. However, it is not solely the increased weight which causes the problem to shipping. Fouling leads to increased friction between the hull and seawater, causing so-called 'hull roughness'. As a result of these combined effects, badly fouled ships suffer from loss of speed and maneuverability. They are also expensive to operate, incurring fuel penalties of $\geq 50\%$.

Not surprisingly, there have been extensive efforts to reduce fouling, and its impacts, down the ages. The ancient Carthaginians and Phoenicians used pitch, and possibly copper sheathing, on the bottoms of ships to prevent fouling, and later coated hulls with sulfur and arsenical compounds. The Greeks and Romans both introduced lead sheathing. Copper cladding was then 're-invented' in the seventeenth and eighteenth centuries, but it became redundant after the introduction of steel vessels at the end of the eighteenth century, because of problems caused by galvanic corrosion. A new technology was needed to protect ships' hulls from fouling, but it took some 60 or so years until the mid-nineteenth century for the development of antifouling paints to provide it.

There have been substantial developments in paint technology since the first antifouling paints were introduced, and the search for more effective coatings still continues today. However, the large majority of antifouling paints incorporate biocides into the matrix and, in this respect, the technology has not changed. The biocides leach slowly from the paints, killing organisms which attempt to settle on the hull. Cuprous oxide was used in early formulations, but numerous other toxins – including organo-mercury, lead and arsenical compounds, and DDT – were added as boosters, in order to enhance the effectiveness and life expectancy of the paints. However, such compounds pose severe environmental and human health risks, and they were withdrawn voluntarily by the paint industry during the 1960s. They were replaced largely by tributyltin (TBT). Actually, TBT is not a chemical compound in its own right but a moiety which is part of a tributyltin compound. Different compounds exist which have different chemical properties. For example, bis-tributyltin oxide, which is generally known as TBTO, is a colorless liquid with a molecular weight of 596; tributyltin fluoride is a white crystalline solid with a molecular weight of 309; and (poly)tributyltinmethacrylate-methylmethacrylate is a solid resinous copolymer with a molecular weight in excess of 40 000. TBT was much less harmful environmentally (but see below) and was less dangerous to humans. It can cause dermatitis, irritation of the eyes, and respiratory problems, but risk assessments suggest that paint sprayers are not at serious risk, especially if they wear protective clothing. TBT in various guises became widely used and has dominated antifouling practices for the past three decades, replacing lead and mercury antifouling biocides.

Properties of the paint matrix determine qualities such as the rate of biocide release and therefore the long-term effectiveness of a paint as an antifoulant. Originally, active biocidal ingredients were dispersed in a soluble resinous matrix, which released the biocide as it dissolved slowly in sea water. A problem with these free association paints, as they became known, was that the release rates of biocides from them were uncontrolled. The initial rate was rapid so that the paint was highly effective when it was first applied (**Figure 1**). However, subsequent release of the biocide from the matrix declined steadily and antifouling performance diminished with time; it might be virtually exhausted within *c*. 12 months. Consequently, free association paints typically offered a maximum period of only 1–2 years service before dry-docking and repainting was necessary. There were limited improvements when matrices which were insoluble, using chlorinated rubber and vinyl resins, were developed in the 1940s. They had greater mechanical strength and allowed thicker coatings of paint to be applied, thereby providing effective antifouling performance over a full 2 year period.

However, a major breakthrough in antifouling paint technology occurred with the introduction of so-called self-polishing copolymer paints in the late 1960s. The term self-polishing was used because the biocide was released slowly as the paint surface was gradually worn away. The essential difference from free association paints was that the biocide was chemically bonded in a copolymer resin system, via an organotin–ester linkage. This ester group hydrolysed at the surface of the paint where it was in contact with sea water, and this resulted in the slow and controlled release of the biocide. The remaining surface of the paint was mechanically weakened by breakage of these bonds, and was eroded by moving sea water, resulting in the exposure of a fresh surface layer. The hydrolysis/erosion process was then repeated until there was no paint left. The technology has been particularly successful with TBT copolymer, (poly)tributyltinmethacrylate-methylmethacrylate, although cuprous oxide or other boosters have been included in the formulations. They were needed because, although TBT is active against most fouling organisms, some slime-forming diatoms are resistant to it.

TBT-based self-polishing copolymer antifouling systems (TBT SPC systems) brought enormous benefits to the shipping industry. They could provide effective antifouling cover for ≥ 5 years, more than doubling the performance of free association paints. Reduced fuel costs and less frequent need to dry-dock and repaint vessels were estimated to be worth

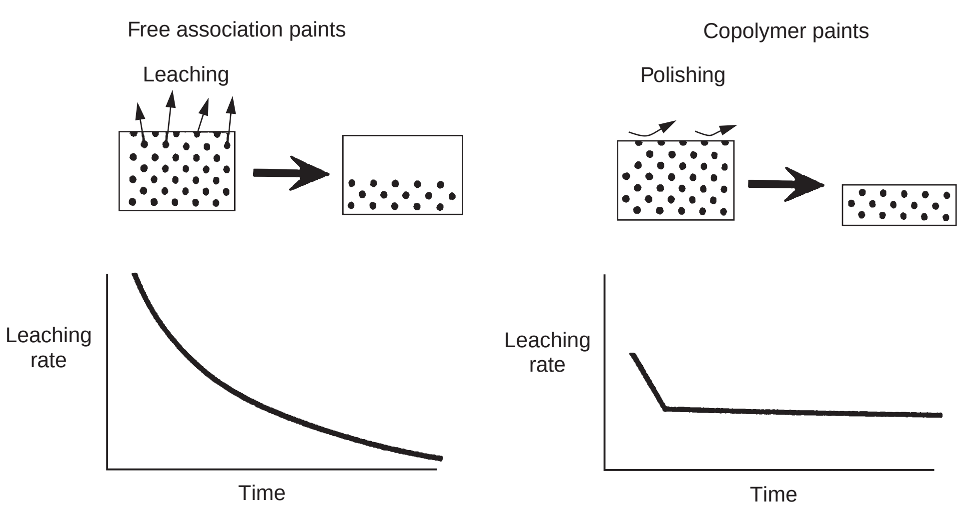

Figure 1 A diagrammatic comparison of the mode of action of free association paints and self-polishing copolymer paints, and the rates at which they release tributyltin into the water. (Reproduced with permission from Stebbing ARD (1985) Organatins and water quality: some lesson to be learned. *Marine Pollution Bulletin* 16: 383–390.)

some US$5.7 billion per annum to the industry during the mid-1990s. There were also huge environmental benefits because lower fuel consumption by the world's shipping fleet reduced the release of 'greenhouse' gases and emissions which were responsible for acid rain. Annual fuel savings, which could be attributed to the use of TBT-based antifoulants, were believed to be 7.2 million tonnes, reducing carbon dioxide emissions by 22 million tonnes, and sulfur dioxide by 0.6 million tonnes, per year. An additional benefit was that effective antifouling prevented the transport of invasive (nonnative) organisms across the world on ships' hulls. Such species can cause enormous economic and ecological damage once they become established. It was originally thought that these organisms hitch-hiked their way across the oceans in ballast water, but it is becoming increasingly clear that fouled hulls are an additional means of transport.

TBT SPC systems came into widespread use. They were, for example, first used by major shipping lines in Europe and the Far East in the mid-1970s, and were registered by the Environment Protection Agency in the USA in 1978. Subsequently, it was estimated that they were used on 70% of the world's commercial shipping fleet, and on high proportions of fishing vessels and pleasure craft.

The Downside of TBT-based Antifoulants: Persistence and Environmental Costs

Unfortunately, there are environmental costs of using TBT-based paints. The ideal antifouling biocide would be one which degraded into harmless residues immediately after release into the water column so that the toxic effects occurred at the ship's hull but nowhere else in the marine environment. In fact, TBT does degrade reasonably rapidly in seawater, where it has a residence time of only a few days. Nevertheless, this is sufficient time for it to become adsorbed on to particles, and to aggregate in sediments in which there are high levels of organic matter. Here degradation processes are considerably slower, and the half-life of TBT may then be a matter of months or years. Regrettably, TBT is so toxic that even low concentrations can harm marine life. For example, the lethal dose concentration (15 day LC_{50}) for larvae of the mussel *Mytilus edulis* is 10 ng/l, and that (96 h LC_{50}) for larvae of the sole *Solea solea* is 21 ng/l. Sublethal effects occur at even lower concentrations. A dose of > 0.4 ng/l can affect the growth and reproduction of phytoplankton and zooplankton, and one of > 2 ng/l can affect the process of shell formation in the oyster *Crassostrea gigas*. This latter concentration is also sufficient to cause the development of the condition known as imposex in the dogwhelk *Nucella lapillus*. In this case, TBT acts as a hormone disruptor affecting gender differentiation. Female dogwhelks develop male genital organs, including a pseudopenis and vas deferens, which become superimposed on their reproductive systems (**Figure 2**).

Not surprisingly, the widespread and uncontrolled use of TBT-based paints worldwide during the 1970s and 1980s (especially free association paints) resulted in unacceptably high levels of TBT in some coastal areas of intense boat use. The main problems were in enclosed bodies of water with poor flushing characteristics, such as harbors, dry-docks, marinas, estuaries, and bays. The first documented cases of serious biological impact on nontarget organisms came from Arcachon Bay in west France. The bay is a centre of both oyster culture and of high yachting activity, and TBT originating from paints used on yacht hulls was held responsible for abnormal growth and reproductive failure of cultured oysters. The oyster farming industry was in a state of near collapse. Production of oysters fell in the early 1980s to *c.* 33–50% of the normal harvest (**Table 1**). At about the same time, TBT pollution was also linked to serious declines in populations of dogwhelks (*N. lapillus*) in southwest England. They were suffering from imposex and it was so severe that populations of these organisms in areas of high boating activity, such as Plymouth Sound and the estuaries of the rivers Dart and Fal, had become partially or totally sterile. There was no juvenile recruitment at all at the worst affected sites and, evidently due to premature female mortality, populations were dominated by old males. The species became locally extinct at most of these places, although there were fecund populations in coastal areas between them. Subsequently, imposex has been described in more than 100 species of gastropods worldwide, and the condition in many of them has been used as a biological indicator of TBT contamination. It became evident from surveys using this indicator in, for example, North America, Australia, New Zealand, Hong Kong, Singapore, Japan, West Africa, and the Mediterranean Sea (accompanied in many cases by chemical measures of TBT and its derivatives), that TBT contamination had become a global problem.

There is also concern that these compounds can bio-accumulate in the tissues of marine organisms and thereby become incorporated into marine food chains. Their molecules have both lipophilic and ionic properties, encouraging them to accumulate

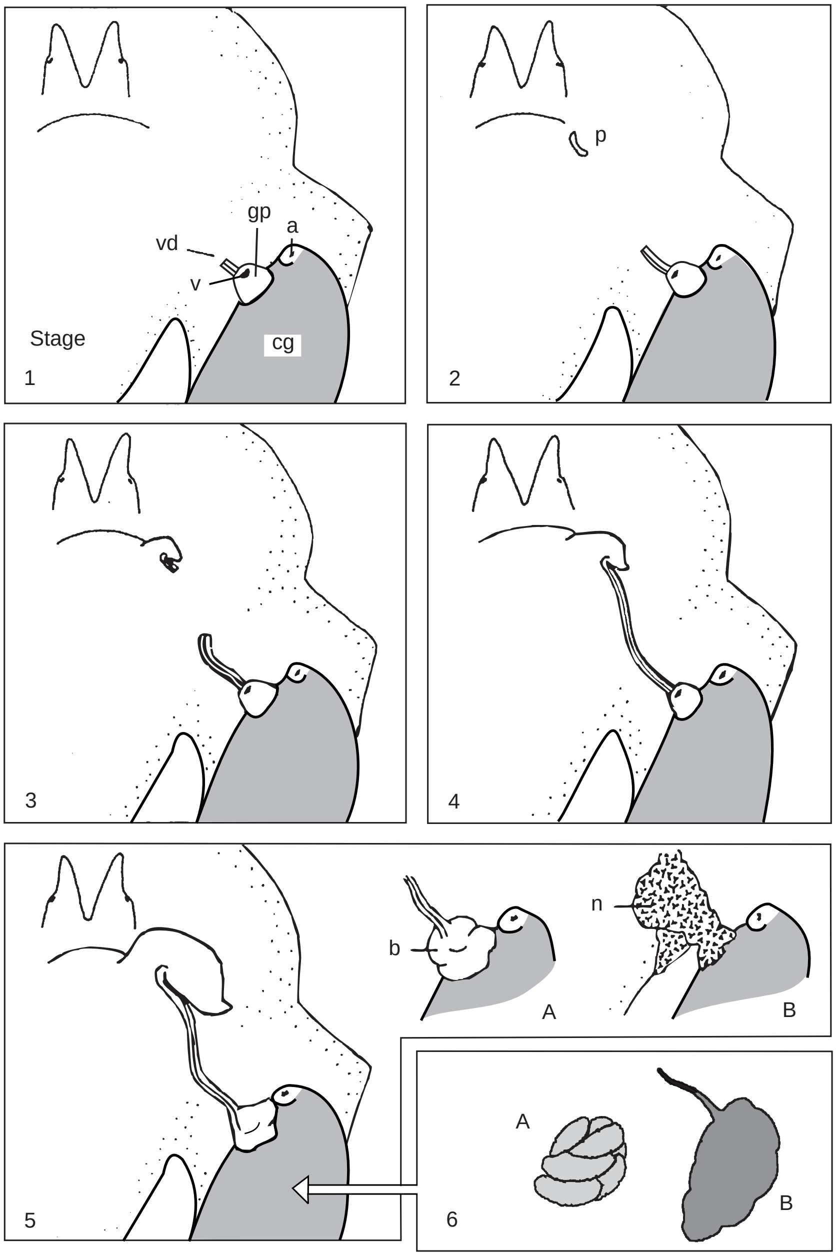

Figure 2 Six stages in the development of imposex in the dogwhelk *N. lapillus*. Abbreviations: a, anus; b, 'blister'; gp, genital papilla; n, 'nodule'; p, penis; v, vulva; vd, vas deferens. (Reproduced with permission from Gibbs PE, Bryan GW, Pascoe PL and Barl GR (1987). The use of the dogwhelk (*Nucella lapillus*) as an indicator of TBT contamination. *Journal of the Marine Biological Association of the United Kingdom* 67: 507–524).

in lipids and bind to macromolecules, such as glutathione. Molluscs are particularly prone to accumulate organotins, but they have also been reported in some fish, fish-eating birds, and marine mammals, including whales, dolphins, and porpoises. However, risk assessments of the oyster-catcher (as a representative bird), and the sea otter (as a representative mammal), both of which have diets which should put them at high risk, suggest that current levels of TBT do not pose a threat to top predators in the system.

Regulating the Use of TBT-based Antifoulants

It was clearly necessary to control the use of TBT-based paints. Pleasure craft, especially yachts, were believed to be the main source of pollution in

Table 1 Production of oysters in Arcachon Bay, France between 1978 and 1985

Period	*Production (tons)*
1978–9	10 000
1979–80	6 000
1980–1	3 000
1981–2	5 000
1982–3	8 000
1983–4	12 000
1984–5	12 000

(Reproduced with permission from Alzieu C (1998) In: de Mora SJ (ed.) *Tributyltin: Case Study of an Environmental Contaminant.* Cambridge: Cambridge University Press).

coastal waters and several countries banned the use of these antifoulants on vessels < 25 m in length. The French Government was the first to react, due to the oyster crisis, introducing controls in 1982. The UK followed in 1987, the USA in 1988, and subsequently Canada, New Zealand, Australia, South Africa, Hong Kong, and most European countries reacted in similar ways.

The regulations have been effective in reducing TBT contamination. Declining concentrations of TBT were reported during the 1990s in water samples, sediments (although less rapidly due to their persistence in them), and tissues of molluscs in monitoring programs worldwide. More dramatically, there have been enormous improvements in the health of marine biota which had been affected by TBT pollution in the previous decade. Oyster production in Arcachon Bay recovered spectacularly to former levels almost immediately after the introduction of regulations in France in 1982 (**Table 1**). There are many other examples of recovery, including those of scallops and the flame shell *Lima* in Ireland since the UK's 1987 regulations. Gastropods also benefited from improved water quality. There has been widespread recovery of populations of dogwhelks suffering from imposex in the Clyde Sea, North Sea, Irish coasts, and the Pacific coast of North America (**Figure 3**). This even applies to some shores where they had become locally extinct. *Nucella* species have difficulty in recolonizing such shores because they lack a dispersive, larval stage in their development. Nevertheless, they have 're-appeared' on some shores on which they could not be found during the period of the most severe TBT contamination.

While regulations have certainly been the primary cause of these reductions in ambient concentrations of TBT, there is also evidence that the development of slow-releasing TBT SPC systems have contributed to the decline. Large tankers, which visit the Oil

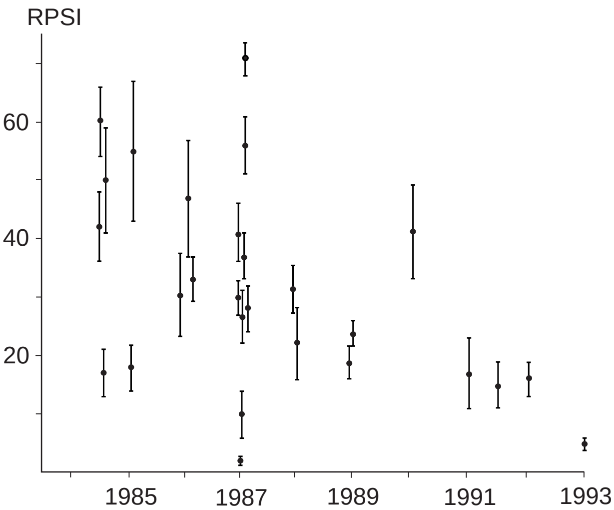

Figure 3 Reductions in measures of imposex (RPSI) in dogwhelks *N. lapillus* in British coastal areas, following the introduction of UK regulations in 1987 prohibiting the use of TBT-based antifoulants on small vessels. (Reproduced with permission from Evans SM, McKinnell PO and LeKsons T (1995) Tributyltin Pollution: a diminishing problem following legislation limiting the use of TBT-based anti-fouling paints. *Marine Pollution Bulletin* 30: 14–21).

Terminal Sullom Voe (Scotland), are virtually the only source of TBT there and, since the regulations do not apply to them, they have continued to use TBT-based paints. Nevertheless there has been significant recovery in symptoms of imposex in populations of dogwhelks in the Voe, since the adoption of TBT SPC systems.

Commercial harbors, especially those with dry-docking and repair facilities, are still hot spots of TBT contamination. However, the impact of these remaining hot spots is surprisingly localized. There were extremely high concentrations of TBT in measurements of sediments at shipyards in Hong Kong, but they decreased to background levels within < 100 m of the shipyards. There are multiple inputs of TBT in the coastal waters of Hong Kong, which is among the busiest ports in the world and, as might be expected, imposex in one of the local dogwhelks (*Thais clavigera*) was severe in marinas and commercial harbors. However, there were fecund populations, in which symptoms were mild, within 5–10 km of the island. Gradients of diminishing contamination and/or biological impact have also been described from centres of shipping activity in Iceland and Puget Sound, USA (**Table 2**).

Alternatives

A ban on the use of TBT as the active biocide in antifoulants is inevitable, and it is already on the

Table 2 Gradients of diminishing concentrations of organotins (total TBT and its metabolites DBT and MBT) in tissue samples, and of measures of imposex (VDSI and RPSI) in the dogwhelks *Nucella emarginata* and *N. lamellosa* from two 'hot spots' of TBT contamination in Puget Sound (USA): a shipyard at Anacortes and the complex of commercial harbors and shipyards at Seattle

Source	*Species*	*Distance of site from source (km)*	*Total organotins (ng/g)*	*% with imposex*	*VDSI*	*RPSI*
	N. lamellosa				–	–
Anacortes shipyard		0	668	[a]	–	–
		1.3	212	[a]	–	–
		2.4	61	100	4.0	1.2
		6.5	43	100	2.8	< 0.1
		8.0	24	100	3.3	< 0.1
	N. emarginata					
Seattle		0.9	–	–	–	–
		1.9	146	100	4.0	14.1
		2.3	65	100	3.9	9.1
		8.0	42	100	1.9	< 0.1
		9.0	72	94	1.9	< 0.1
	N. lamellosa					
Seattle		0.9	131	100	4.0	19.3
		1.9	141	100	4.0	4.3
		2.3	68	100	3.1	6.7
		8.0	66	100	3.5	0.5
		9.0	42	100	3.2	< 0.1

[a]Population consisted of males only.
(Reproduced with permission from Evans *et al.*)

agenda of the International Maritime Organisation. In an ideal world, it would be unacceptable to release any toxic compound into the environment, and the ultimate aim of research workers and the regulators must be to eliminate the use of biocides in paints altogether. Despite the success of regulations controlling the use of TBT-based antifoulants, there is still concern about them. Commercial shipping remains a source of TBT, and is continuing to add to sedimentary sinks of these compounds in remaining hot spots of pollution, such as major harbors and shipyards. Pollution of such artificial habitats would be regarded by most people as less serious than that of the open seas. Nevertheless, there are clear management implications with respect to the disposal of these contaminated sediments, because TBT may be remobilized from them either as a result of dredging or natural events, such as storms or tidal flow.

However, it is important that the ban on TBT is not premature. It should not be introduced until alternative formulations are available, which will perform at least as well as TBT paints on environmental and economic grounds. It is far from clear that this is currently the case. The race to find alternatives is now on among the paint manufacturers and a range of different biocides is being tested in TBT-free systems. They include zinc pyrithione and copper pyrithione, and various compounds which are marketed under trade names, such as Irgarol 1051™ (triazine), Sea-Nine 211™ (dichloro-isothiazolone) and Diuron™ (dichlorophenyl-dimethyl urea). However, additional 'booster' biocides are needed to ensure their effectiveness against the broad spectrum of antifouling organisms, and high concentrations of copper compounds, such as copper oxide, copper thiocyanate, and metallic copper, are incorporated into many of these paints. There is concern among some scientists that the environmental profiles of the new products are not yet well known, and there is insufficient published information on them to assess their effectiveness (**Table 3**). Some shipowners already claim to have had bad experiences with alternative formulations. There was optimism in the early 1990s that the performance of tin-free systems rivalled that of TBT SPC systems, but this turned out to be unfounded. There were serious performance failures with vessels using them, including premature fouling, high fuel consumption, and poor structural integrity of the paint resulting in cracking and flaking. Unexpected environmental harm has also been associated with the use of some alternatives. This is illustrated by experiences with the herbicide booster Irgarol 1051™, which has been used in some antifouling formulations since the introduction of

Table 3 Information on antifouling paints from data compiled by the Organotin Environmental Programme Association in September 1998 (gaps indicate that there are no available data)

Parameters	*TBT self-polishing*	*Copper acrylates*	*Silane methacrylates*	*Ion exchange copolymers*	*Copper ablatives*
Environmental monitoring data	Extensive, since 1980s				Limited published data
Aquatic toxicity data	Acute and chronic data available				Limited acute data available
Chronic risk assessment	Yes				
Worker exposure studies	Yes				
Booster biocides	Copper oxide	Copper oxide Copper pyrithione			Copper oxide and others, including triazine Zinc pyrithione
Proven dry-docking interval	Data for >60 months available	Data for 36 months are available			Data for 30–36 months are available
Cost comparison with TBT SPC	Not applicable	2–2.5-fold higher			2–4-fold higher
Antifouling performance	96% vessels report satisfactory performance after 5 years	90% vessels report satisfactory performance after 3 years			70–74% vessels report satisfactory performance after 30–36 months

regulations limiting the use of TBT-based paints on small vessels. It has been reported that it is now at levels in some coastal areas which are sufficient to damage microalgae and seagrass communities. Copper may also pose a problem if boat or ship owners either return to the old fashioned copper-based paints or use new formulations which incorporate high booster levels of copper. This has already happened in Arcachon Bay, where the copper content of oysters has increased following the ban on TBT-based paints on small vessels.

A different approach has been to develop 'non-stick surfaces', based on silicon elastomer technology. They may eventually offer the ideal solution, because toxins are not incorporated into them. They provide smooth, low energy surfaces to which fouling organisms cannot adhere. Unfortunately, there are reports that they have limited use at the present time. They perform effectively on fast moving vessels, such as catamarans, patrol boats, and fast ferries, but are said to be less efficient on slower moving craft, like most of the ocean-going vessels.

See also

Eutrophication. Metal Pollution. Pollution: Effects on Marine Communities. Pollution Control. Pollution, Solids. Ships. Shipping and Ports. Transition Metals and Heavy Metal Speciation.

Further Reading

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AQUACULTURE

See **MARICULTURE DISEASES AND HEALTH; MARICULTURE OF AQUARIUM FISHES; MARICULTURE OF MEDITERRANEAN SPECIES; MARICULTURE OVERVIEW; MARICULTURE, ENVIRONMENTAL, ECONOMIC AND SOCIAL IMPACTS OF**