12 Booster biocide antifoulants: is history repeating itself?

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Tributyltin (TBT) was widely used as an effective antifouling agent in paints for ships and boats until the European Community restricted its use in 1989 because of its proven harm to the environment and shellfisheries. Thereafter, booster biocides were introduced to enhance the performance of antifouling paints. They were believed to be less damaging to aquatic life than TBT. Subsequently, however, it has been established that booster biocides can also create significant environmental risks.

This chapter outlines the background to booster biocide use, the early warnings about their potential physiological and ecological impacts on non-target species, and the actions taken in response. The science that set some alarm bells ringing is described, along with lessons that could influence the future of an industry still searching for less environmentally invasive solutions.

Booster biocide antifouling agents threaten a variety of habitats — from coral reefs and seagrass beds to open moorings — within the EU and globally. Their primarily herbicidal properties mean that coral zooxanthellae, phytoplankton and periphyton are particularly vulnerable. Compared to TBT, an antifouling agent with a quite specific action, booster biocides have more broad-spectrum impacts. The wider ecological effect of shifting to booster biocides remain poorly understood but of considerable concern because they may affect the base of marine food chains.

From a toxicological viewpoint, booster biocides do not threaten to have endocrine disrupting properties similar to TBTs. At current environmental concentrations, however, some can damage primary producers and some are persistent. While legislation has been introduced to control their use, the rigour of regulations varies between countries. These geographical disparities need to be addressed, and future biocidal products and novel approaches to antifouling should be better appraised.

For policymakers, the challenge is to protect non-target biological communities from selective change resulting from booster biocide use. Persistence, bioaccumulative and toxic (PBT) criteria can be used to evaluate the relative potential impact from the available biocides, and consequently target appropriate legislation. Nevertheless, lateral thinking, aiming to identify novel materials and strategies to address antifouling, could pay dividends in the future.

12.1 Introduction

12.1.1 The need for antifoulants

Preventing plants and animals from growing on and fouling the hulls of boats is essential for the shipping industry and boating communities. The application of coatings to vessel hulls to prevent fouling organisms from settling dates back to Ancient Greece (Yebra et al., 2004) and possibly even earlier.

Protecting the hull was initially the principal concern and the earliest antifoulants often acted more as physical barriers than chemical toxicants. They prevented the isopod crustacean 'gribble' (*Limnoria*) and the infamous *Teredo* worm (actually a mollusc) from reducing hardwood planking to pulp within a matter of months. However, hull damage was not the only concern. Fouling organisms made sailing ships sluggish and severely limited their capacity to sail to windward. For naval and fighting ships, severely reduced speed and impaired manoeuvrability could mean losing sea battles ([1]).

Fouling organisms create 'hull roughness', increasing friction between the hull and the water (Evans et al., 2000). Combined with the weight of fouling organisms attached to the hull, this can lead to considerable increases in fuel consumption. A layer of algal slime only 1 mm thick will increase hull friction by 80 % and cause a 15 % loss in ship speed, while a 5 % increase in fouling for a tanker weighing 250 000 deadweight tonnes will increase fuel usage by 17 % (MER, 1996; Evans et al., 2000).

Antifouling agents, applied as paint, are the most economically efficient solution found so far. Yet they come at an environmental cost, as graphically illustrated by the organotin compound tributyltin (TBT).

12.1.2 The rise and fall of TBT

Shortly after World War II, TBT became a common additive in antifouling paints, especially in 'self-polishing' formulations which, by design, release toxic persistent substances into the environment. The use of powerful antifoulants enabled the periods between dry-docking for repainting to be extended and TBT was particularly valued because it does not cause galvanic corrosion to aluminium hulls. By the 1980s, however, TBT had been recognised as a global pollutant and its environmental effects on non-target organisms are now infamous (Santillo et al., 2002).

TBT's effects include shell malformations in oysters, which can render the produce worthless. In Arcachon Bay (France) alone TBT caused an estimated loss of USD 147 million through reduced production of the oyster *Crassostrea gigas* (Alzieu, 1991). A more serious and pervasive impact was 'imposex' — the development of male sexual organs in female marine gastropods. Worldwide, imposex has been documented for around 150 species (Vos et al., 2000). This endocrine disruption was first discovered in the early 1970s (reviewed in Santillo et al., 2001). Because of limited analytical capabilities, however, the physiological and ecological consequences were only attributed to TBT in the 1980s when many gastropod populations had declined. Importantly, mollusc species can be affected at very low concentrations — less than 10 billionths of a gram per litre (10 ng/L). By the late 1980s, the TBT problem was global.

Steps were taken to ban TBT because of its unacceptable toxic effects on commercial shellfish (especially oysters) and other non-target organisms. Regulatory controls included the EC Directive 89/677/EEC (1989) banning TBT use on small boats (< 25 m, primarily pleasure craft). Important legislation to phase out TBT use on larger vessels includes the International Maritime Organization (IMO) International Convention on the Control of Harmful Anti-fouling Systems (IMO, 2008). Santillo et al. (2001) provide further insights into the complexities surrounding TBT, its ban and the delay in controls

Barnacles on a boat. Application of coatings is used to prevent plants and animals from fouling on the hulls of boats.

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([1]) Yebra et al. (2004) provide additional information on the historical development of antifouling systems.

coming into force. The extent of hazard was initially underestimated for both technical and socioeconomic reasons. Specifically:

- it was incorrectly assumed that an environmental quality target (EQT) of 20 ng/l would be sufficiently protective;
- persistence, accumulation and wider dissemination in the environment were underestimated;
- organotin bioaccumulation was underestimated (Labare et al., 1997);
- the geographical scale of the problem was not fully appreciated (inadequate data collection);
- imposex observed in 1970 in predatory gastropods in Arcachon Bay was considered acceptable — it had no immediately obvious economic cost — whereas the failure of the oyster stocks soon after was not acceptable;
- the transboundary nature of the problem was not fully appreciated until continuing TBT problems in Japan (despite a national ban in the late 1990s) highlighted the issue.

Many of these findings from TBT are useful reminders for managing booster biocides. They highlight the value of recognising potential environmental hazards early, and introducing protocols for monitoring and appropriate regulatory measures.

12.1.3 Effects of the TBT ban

EU and national legislative prohibitions on using TBT for small craft reduced pollution substantially. In Arcachon Bay, for example, concentrations fell from 900 ng/L in 1983 to below 10 ng/L in the late 1980s. The oyster beds recovered and commercial harvesting resumed during the same period. The (limited) controls imposed were hailed by some as a 'solution' to the TBT problem. Evans et al. (2000) reported a general recovery of dogwhelk populations in the United Kingdom, partially confirming this claim. However, in other European areas recovery appears to have been mixed, or slower than expected, despite the imposition of regulations for small craft (see Santillo et al., 2001).

Experience in New Zealand is one of several examples illustrating the complex interactions between TBT inputs, concentrations, accumulation and biological effects and, most importantly, the beneficial effects of legislation (Table 12.1).

On the other hand, the ban on TBT does not seem to have been very effective everywhere. Levels are still going up in Asia, implying either that it is still being used or that there are issues surrounding persistence and transportation that are not yet fully understood.

12.2 Early warnings, actions and inactions

Booster biocides were developed, at least initially, for the 'small boat' market, following the European Community ban on TBT for vessels of less than 25 m in 1989. A wide range of booster biocide compounds have been used or promoted (Box 12.1). Whilst the list is substantial, not all products have been marketed and some newly introduced compounds such as phenylborane pyridine, Econea, capsaicin and medetomidine (Thomas and Brooks, 2010) are not included.

For example, in the United Kingdom during the 1990s, antifouling agent use was massively dominated by copper(I) oxide, followed by (in order of use) diuron, Irgarol 1051, zinc pyrithione and dichlofluanid. Some of these are now banned (see Section 12.4.1). The organic biocides included agrochemicals (e.g. diuron), other compounds that were previously registered as biocides (e.g. Irgarol 1051) and personal care products such as the anti-dandruff agent zinc pyrithione.

Contamination of coastal waters by booster biocides was first reported in the early 1990s. Irgarol 1051 concentrations of up to 1700 ng/L were reported around the Cote d'Azur on the French Riviera (Readman et al., 1993). These high levels were actually discovered during a survey of agricultural triazine herbicides, which are measured using the same analytical protocol. That study triggered subsequent research, which confirmed broad contamination of boating areas in Europe, Bermuda, the United States of America, Japan, Singapore and Australia (Konstantinou and Albanis, 2004; Readman, 2006; Scarlett et al., 1999). Interestingly, Irgarol 1051 was detected in Australia, despite not being used in Australia's boating industry.

Readman et al. (1993) was followed by the pioneering studies of Dahl and Blanck (1996) on Irgarol 1051's toxicity to periphyton communities. These algae and microbes live in a surface film attached to submerged surfaces including plants,

Table 12.1 Complexities associated with TBT accumulation and legislative controls for leisure boats and ships in New Zealand from studies in 1988/1989 and 1994/1995

Issue	Environmental and governance implications
Imposex measured at different resolution (% imposex, or penis length in females relative to males)	Judging the effect of TBT on gastropods depends partly on the sensitivity of the measure used
Re-release of TBT residues in sediments and long half-life of TBT (2.5–3 years) in sediments	Can obscure actual TBT levels and the effectiveness of legislation
1989 legislation (TBT ban on < 25 m leisure craft)	No fall in % imposex at Evans Bay marina in Wellington harbour, despite TBT ban for small craft, due to close proximity of commercial Burnham Warf and leaching of TBT. Continual monitoring needed to determine the effectiveness of legislation for larger ships
1993 legislation (TBT banned completely for New Zealand vessels but not for foreign ships)	
Sampling strategy (e.g. presence of commercial ships near leisure craft)	

Source: Smith, 1996.

rocks and the hulls of boats. Periphyton is also an important indicator of water quality. The authors demonstrated the potential for ecological effects to occur at the concentrations of Irgarol 1051 present in coastal waters. Together, these studies raised concerns and inspired other scientists to conduct more in-depth research.

Besides antifouling paints, however, booster biocides in aquatic environments derive from a variety of other sources, including:

- agricultural and domestic uses of chlorothalonil, dichlofluanid and diuron as agents to deal with weeds, fungi and other unwanted plant growth;
- some anti-dandruff shampoos, in which zinc pyrithione (ZPT) is the active agent against the scalp fungus, *Malasseziaglobosa*.

A comprehensive picture of booster biocide distributions and concentrations in European waters emerged from the Assessment of Antifouling Agents in Coastal Environments (ACE) project, which ran from 1999 to 2002. In the course of the project, water samples (and sediments from some areas) were collected from marinas, harbours,

Box 12.1 Examples of booster biocides used or promoted as agents in antifouling paints

- 2-methylthio-4-tertiary-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051)
- 1-(3,4-dichlorophenyl)-3,3-dimethylurea (diuron)
- 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Sea-Nine 211)
- N-dichlorofluoromethylthio-N', N'-dimethyl-N-phenylsulphamide (dichlofluanid)
- 2,4,5,6-tetrachloro isophthalonitrile (chlorothalonil)
- bis(1hydroxy-2(1H)-pyridethionato-O,S)-T-4zinc (zinc pyrithione)
- 2-(thiocyanomethylthio)benzthiazole (TCMBT)
- 2,3,5,6-tetrachloro-4-(methyl sulphonyl) pyridine (TCMS pyridine)
- cuprous thiocyanate
- 4-chloro-meta-cresol
- arsenic trioxide
- cis1-(3-chloroallyl)-3,5,7-triaza-1-azonia adamantanechloride
- zineb
- folpet
- thiram
- oxy tetracycline hydrochloride
- ziram
- maneb

estuaries and coastal waters, covering diverse European coastal systems (ACE, 2002; Readman, 2006). Of the major booster biocides, diuron was found in the greatest mean concentrations, with the highest levels in north-western Europe. Irgarol 1051 was present at lower mean concentrations than diuron, with Mediterranean coastal environments the most contaminated. Chlorothalonil, dichlofluanid and Sea-Nine 211 were sporadically encountered, primarily in the Mediterranean. In isolated cases, however, high concentrations were recorded. Measurable concentrations of the degradation products of Irgarol 1051 and diuron were also recorded, albeit at lower levels than the parent compounds.

Globally, data for the most common biocides (diuron, Irgarol 1051 and Sea-Nine 211) are available for Europe, North America and Japan, while negligible data are available for other regions. Konstantinou and Albanis (2004) summarise data on Irgarol 1051 levels in water and sediment samples reported in the literature. More recently, booster biocides have been detected in the remotest part of the Indian Ocean, although at negligible concentrations. Indeed, of the substances sought, only Irgarol 1051 was detected. Moreover, it was only encountered in two of the 31 samples analysed, at concentrations of 2 ng/L and 8 ng/L (Guitart et al., 2007).

12.3 Early warnings: the science on antifouling agents

12.3.1 Persistence and toxicity

Concerns about the potential environmental impacts of booster biocides arose because of the high concentrations reported at an increasing number of areas, coupled with findings regarding their toxicity to periphyton (at equivalent concentrations). The high concentrations in coastal environments are maintained by leaching from vessels, although dilution and degradation act to reduce concentrations (see below). While some antifouling biocides have other uses (e.g. as agrochemicals), in marinas and harbours antifouling use normally dominates the total input (Konstantinou and Albanis, 2004). Compounds can be removed from the water column through, for example, biotic degradation, photo-degradation, chemical hydrolysis, attachment to particulates followed by sedimentation, volatilisation or bioaccumulation (Readman, 2006).

The MAM-PEC model (van Hattum et al., 1999) was developed to predict environmental concentrations of antifouling agents in the marine environment. It has been validated using the data set collected during the ACE project and can now be applied to predict future concentrations.

The half-lives of booster biocide compounds vary and can be considerable. The abiotic and biotic half-lives for these booster biocide agents, examined in laboratory studies and under controlled field conditions, indicated that diuron and Irgarol 1051 were substantially resistant to degradation in comparison with other agents. Thomas et al. (2002) and Thomas and Brooks (2010) have reported the following highly variable half-lives for booster biocides:

- Irgarol 1051: 100 days;
- dichlofluanid: 18 hours;
- chlorothalonil: 1.8 days;
- Sea-Nine 211: < 24 hours;
- zincpyrithione: < 24 hours;
- TCMTB: 740 hours;
- zineb: 96 hours;
- diuron: no degradation over 42 days in seawater when associated with antifouling paint particles (without this particle association it has a 14-day half-life).

More worrying still were the toxic effects that scientists were beginning to identify, reviewed in studies such as Jones (2005), Yamada (2006) and more recently by Thomas and Brooks (2010). The herbicidal properties of most antifoulants mean that marine plants appear to be particularly vulnerable to many of these biocides. As noted above, the first published study on the herbicidal properties of booster biocides was by Dahl and Blanck (1996), addressing the toxicity of Irgarol 1051 to periphyton communities. Long-term effects were detected at 0.25–1 nM (63–250 ng/L), which is within the range of concentrations reported for coastal waters. Later studies (Okamura et al., 2003; Jacobson and Willingham, 2000; Fernandez-Alba et al., 2002) have confirmed the vulnerability of algae/phytoplankton to booster biocides.

Using natural populations of phytoplankton, Readman et al. (2004) reported toxic effects of Irgarol 1051 at low concentrations with a 72-hour half maximal effective concentration (EC50) of

70 ng/L ([2]). The endpoint used in this study was the selective reduction in 19'-hexanoyloxyfucoxanthin. Again, this concentration is well within the range of concentrations reported in coastal waters.

Devilla et al. (2005) provide some insights into relative susceptibilities to a range of booster biocides. Growth inhibition results following 72 hours of exposure indicated that *Synechococcus* sp. was more tolerant to zinc pyrithione (NOEC ([3]) of 1 000 ng/L) and Sea-Nine 211 (NOEC of 900 ng/L) than *E. huxleyi* (EC50 of 540 and EC50 of 350 ng/L, respectively). In contrast, *Synechococcus* sp. was more sensitive to diuron (EC50 of 550 ng/L) than *E. huxleyi* (EC50 of 2 260 ng/L), whereas exposure to Irgarol 1051 similarly impacted both species (EC50 of 160 and 250 ng/L, respectively).

Endocrine disruption was also assessed within the ACE Project. None of the antifoulants evaluated (Irgarol 1051, Sea-Nine, chlorothalonil, diuron, dichlofluanid, maneb and ziram) showed a strong estrogenic response. Thomas et al. (2001) identified persistence and toxicity as critical features in the risk evaluation of booster biocides.

Despite accumulating substantial information, Voulvoulis et al. (2002) considered that additional data would still be required to properly evaluate the risks associated with widespread use of the booster biocides Irgarol 1051, diuron, Sea-Nine 211 and chlorothalonil. They cautioned against the use of TCMS pyridine, TCMTB and dichlofluanid, although again identified a lack of appropriate data. And in their initial risk evaluation, zinc pyrithione and zineb appeared to be the least hazardous options for the aquatic environment. However, analytical constraints for these latter booster biocide compounds render environmental assessment difficult.

12.3.2 Adverse ecological effects on corals

The herbicidal (chlorophyll photosystem II-inhibiting) mode of action of Irgarol 1051 also raises concerns regarding the potential impact on zooxanthellae — the symbiotic microalgae that live within warm water corals to the mutual benefit of both the coral polyps and the algae. This has important implications for the growth, survival and health of corals, already rendered vulnerable by events such as the 1998 coral bleaching episode in the Indian Ocean. That event arose from exceptional seawater warming in 1997–1998 and led to massive coral mortality. Most island archipelagos were severely affected, with mortality of over 90 % to considerable depths in the Maldives, Seychelles and Chagos (Sheppard et al., 2002).

During bleaching events coral expel, to a greater or lesser extent, their symbiotic algae known as zooxanthellae. In extreme events, as occurred in 1998, zooxanthellae are totally evicted from their host. All that remains is dead white coral skeletons or, worse still, rubble and debris — something very different from a vibrant, living reef attached firmly to the seabed (see Price, 2009). Recent publications have shown that Irgarol 1051 inhibits the photosynthesis of both zooxanthellae isolated from the coral tissues and also zooxanthellae still within the host (coral) tissues (i.e. in symbio) at environmentally relevant concentrations (as low as 60 ng/L) (Owen et al., 2002; Owen et al., 2003; Jones, 2005). Studies at many harbours in the world report concentrations of Irgarol 1051 at or above this level (Konstantinou and Albanis, 2004). This creates the possibility that antifouling agents will disperse to offshore sites, including coral reefs.

'Coral bleaching' — the dissociation of symbiosis between corals and algae — is a common but significant sub-lethal stress response requiring many months to recover. It is generally considered to be caused by elevated water temperatures but diuron and Irgarol 1051 will also cause bleaching and, like warm water bleaching, they may operate by affecting algal/zooxanthellae photosynthesis (Jones, 2005). The notion that Irgarol and diuron contamination could exacerbate bleaching caused by elevated water temperatures has not yet been tested.

Jones (2005) points out that at low levels and over short exposure periods, the coral-bleaching effects of herbicides can be reversible (i.e. when corals are returned to clean seawater) and vary according to type of herbicide. However, on exposure to higher concentrations in the light or over longer exposure periods, sustained long-term reduction of the photochemical efficiency of the algae (symptomatic of chronic photo-inhibition) follows.

Corals and reefs in European waters lack symbiotic microalgae, meaning that booster biocide toxicity

([2]) The EC50 is the concentration of a toxicant that induces a response halfway between the baseline and maximum after a specified exposure time.

([3]) NOEC denotes 'no observable effect concentration'.

to coral microalgae is not directly relevant within the EU. However, several European countries have dependent territories with significant coral reefs. In some cases (e.g. France, the Netherlands and some UK dependent territories), the environmental legislation of the dependent territories is closely allied to that of the European country. In others, such as Chagos, British Indian Ocean Territory, environmental legislation is more independent.

Chagos happens to lie in the remotest part of the Indian Ocean and studies more than 10 years ago revealed that these atolls and islands were virtually pristine and contaminant free (Everaarts et al., 1999; Readman et al., 1999), despite the fact that the biggest atoll and island, Diego Garcia, is an important military base. Booster biocide concentrations from the atolls of Chagos were determined during early 2006 as part of an international environmental research effort (Guitart et al., 2007). This has provided a useful international baseline or standard, against which biocide concentrations in European waters and elsewhere could be compared. More generally, studies have recently highlighted the scientific importance of Chagos as a 'clean' control site for monitoring environmental change (SOFI, 2009; Sheppard et al., 2009). Environmental monitoring is also an important requirement of national, European and international agreements to which the British Indian Ocean Territory is party.

12.4 The lessons drawn

12.4.1 Permitted agents

Controls and legislation have been developed to address the accumulation of booster biocides in the marine environment and the marked toxicity of certain agents. The booster biocides permitted in European waters and the legislative situation, as of 2002, are listed in Tables 12.2 and 12.3. This shows that several agents previously permitted for small craft in the United Kingdom, including diuron and Irgarol 1051, are now prohibited. In the United Kingdom, only three organic booster biocides are permitted. In Sweden there is even greater restriction. In the Netherlands, France, Greece and Spain, a greater number of agents are permissible. In the Netherlands, files for antifouling agents are being reviewed. In Denmark, diuron and Irgarol 1051 were banned for use on pleasure craft in 2000. Results from an environmental risk analysis of Sea-Nine 211 and zinc pyrithione in Danish waters demonstrated that, in most cases examined, the PEC/PNEC (predicted environmental concentration/predicted no effect concentration) ratio was less than 1, indicating an acceptable risk.

The Biocidal Products Directive (98/8/EC) provides for the authorisation of biocidal products within the European Union. The Directive harmonises the data requirements for existing and new biocides within the EU, including antifouling agents (product type 21). Any company seeking to register an antifouling agent was required to submit a notification in 2002 and provide a base set of data. Time scales for submitting additional necessary data have not been established.

National legislative positions on antifoulings are presented in IYP (2008) and Thomas and Brooks (2010) provide a review of the current legislative position.

Experiences in Bermuda provide insights that may have useful applications elsewhere. Within a period of 10 years, harmful booster biocides were identified in some harbour areas and, because of their potential harm to corals, were banned in the entire territory (Box 12.2).

Box 12.2 Case study — Bermuda

In June 1995, Readman visited Bermuda and analysed seawater samples for antifouling agents including booster biocides. Levels of Irgarol were high in some harbour areas and sparked fears of damage to coral endosymbiotic algae (Readman, 1996). Extended data were later published (Connelly et al., 2001).

The Bermuda Government (Ministry of the Environment) funded toxicological studies at the Bermuda Biological Station for Research that demonstrated the vulnerability of the corals (Owen et al., 2002 and 2003). On 1 July 2005, Irgarol- and diuron-based antifouling paints were banned in Bermuda by amendment to the Bermuda Statutory Instrument BR 20/1989 Fisheries (Anti-Fouling Paints Prohibition) Regulations 1989.

Table 12.2 Use of metallic antifoulants and organic booster biocides on yachts < 25 m in European waters

	United Kingdom	France (a)	Greece (a)	Spain (a)	Sweden	Denmark (b)	Netherlands (b)
Copper(I) oxide	+	+	+	+	+ (c)	+	+
Copper thiocyanate	+	+	–	–	+ (c)	+	+
Cu powder	–	–	–	–	+ (c)	+	–
Chromium trioxide	–	–	–	–	–	–	+
Diuron	–	+	+	+	–	–	+
Irgarol 1051	–	+	+	+	+	–	+
Zinc pyrithione	+	+	+	+	–	+	
Dichlofluanid	+	+	+	+	–	–	+
TCMTB	–	–	–	–	–	–	–
Chlorothalonil	–	+	+	–	–	–	–
TCMS pyridine	–	–	–	–	–	–	–
SeaNine 211	–	–	–	+	–	+ (d)	–
Ziram	–	–	+	–	–	–	+
Zineb	+	–	–	–	–	–	+
Folpet	–	–	+	–	–	–	–
Total (booster biocides)	3	5 (a)	7 (a)	5 (a)	1	2	5

Note: (+) Agent permitted.
(–) Agent not permitted.
(a) Very limited/no approval scheme (in principle, all can be used).
(b) Regulations currently under debate.
(c) Leach rate regulated on west coast; banned on east coast.
(d) Although approved, product not used on pleasure craft.

Source: ACE, 2002, cited in Readman, 2006.

Table 12.3 Legislative position of EU Member States, October 2008 update

European Union Member States	Antifoulings applied in EU Member States must be notified or authorised for use. Products sold in Austria, Belgium, Finland, Ireland, Malta, the Netherlands, Sweden and the United Kingdom must be registered under national pesticide laws. The Biocidal Products Directive (98/8/EC) is now in force and a review of all antifouling biocides submitted for approval is well under way. Decisions on the acceptability of these biocides are expected shortly. If a biocide is deemed 'acceptable' under the directive, EU Member States will then re-review the antifouling products containing biocides that are on the market. If acceptable, a product registration will be issued allowing sale and application of the product. Products deemed 'unacceptable' will be removed from the EU market. In the interim period before all products on the market are reviewed, the directive has required manufacturers of antifouling paints to notify details of antifouling products on the market in each EU Member State.
Restrictions	Application of TBT antifoulings to all vessels is forbidden in all EU Member States under the Marketing and Use Directive (76/769/EEC). Under Regulation (EC) No 782/2003, application of TBT antifoulings on all ships and boats flying flags of EU countries are also banned and those with active TBT antifoulings are forbidden from entering European ports and harbours. Ships over 400 gross tonnage flying flags of EU Member States must be surveyed and carry certificates of compliance with the Regulation. Ships over 24 m in length and less than 400 gross tonnage must self-certify as compliant.
Sweden	Use of antifouling products is evaluated on a case-by-case basis using risk assessment to determine if the paint's use is acceptable.
Denmark	Import, marketing and use of biocidal antifouling paint with release of copper exceeding 200 µg Cu/cm^2 after the first 14 days and 350 µg copper/cm^2 after the first 30 days are banned for pleasure crafts of 200 kg and above that are mainly used in saltwater. Import, marketing and use of biocidal antifouling paint for use on pleasure crafts less than 200 kg and mainly used in salt water is banned. This does not apply for wooden boats and it does not apply for pleasure craft belonging to harbours classified as A or B for insurance purposes. Use of Irgarol 1051 and diuron in antifoulings applied to pleasure craft is banned.
United Kingdom	Use of the organic biocides Irgarol 1051 and diuron in antifoulings is banned.
Netherlands	Use of diuron in antifoulings is banned.

Source: IYP, 2008.

12.4.2 *Effects of banning selected booster biocide agents*

While the positive impact of banning TBT has been well demonstrated in European waters and elsewhere, the effectiveness of legislation outlawing specific booster biocides has been determined only recently. The following summarises key findings of a study by Cresswell et al. (2006).

In 2001, the United Kingdom introduced legislative measures restricting the antifouling agents that could be used in paints for small (< 25 m) vessels to three substances: dichlofluanid, zinc pyrithione and zineb. This removed the previously popular booster biocides diuron and Irgarol 1051 from the market (for small vessels) on the grounds of environmental concerns. To investigate the impact of this legislation, water samples were taken from locations where previous biocide levels were well documented. Results from analyses demonstrate a clear reduction in water concentrations of Irgarol 1051 (by 10–55 % of levels in pre-restriction studies), indicating that the legislation appears to have been effective (Cresswell et al., 2006). No comparable data were reported for diuron. Although other booster biocides were screened for (chlorothalonil, dichlofluanid and Sea-Nine 211), they were below the limits of detection (< 1 ng/L) in all samples. It is unclear whether the Irgarol 1051 remaining resulted from some ongoing use, continued presence on pre-painted hulls, continued use on non-UK vessels entering UK ports or simply persistence of the chemical in the environment, even after use stopped completely. It is likely to be a combination of all these factors.

The reduced concentrations are attributed to changes regulating the distribution, advertising, sale and use of the booster biocide. A survey of antifouling paint retailers revealed that small amounts of Irgarol 1051-based paints were still being sold and that there was no routine monitoring of retailers. However, by regulating the production and distribution of Irgarol 1051 at the manufacturer level, the UK Health and Safety Executive has been successful in reducing environmental concentrations of the compound to below the proposed Environmental Quality Standard, EQS, of 24 ng/L. The survey of chandlers and discussions with legislative authorities supports these results and concurs with removing Irgarol 1051-based paints from the market using simple regulations targeted at manufacturers (Cresswell et al., 2006).

12.4.3 *History repeats itself?*

The development and use of booster biocides has followed a very similar pattern to the evolution and demise of organotin and earlier antifoulants:

- identification of new antifouling agents to replace older supposedly more toxic or less effective products (although the relative efficacy and toxicity of antifouling paints can only be determined by subsequent monitoring to establish whether initial suppositions/hypotheses were correct);
- monitoring of distribution, accumulation and toxicity of the new agent(s) to determine whether the initial supposition or hypotheses about the net benefits of new products were correct;
- concern, debate and review of the new antifouling agent(s);
- banning of the most harmful agents;
- search for less toxic solutions to the problem of biofouling communities on hulls of small craft and ships.

Detailed toxicity tests have not been undertaken for all booster biocides. There is evidence, however, for example for diuron and Irgarol 1051, that non-target organisms are exposed and potentially vulnerable. Concern arises because, as noted above, photosynthesis can be affected by booster biocides at extraordinarily low concentrations, i.e. in the 'parts per trillion' (ng/L) range. Effects may be reversible over short exposures, but higher concentrations and long-term exposure can lead to reduced photochemical efficiency of algae (Jones, 2005). In corals this may lead to breakdown of the coral-zooxanthellae symbiosis (bleaching), demanding lengthy recovery times. This has certainly been the case following coral bleaching induced by seawater warming, for example in 1998. Hence, booster biocides can impact the base of food chains, which are linked to seafood production and many other ecosystem services.

A particularly significant aspect of booster biocides is that the most popular ones act herbicidally. Both diuron and Irgarol 1051 act at the herbicide binding site (by definition) of PSII, affecting the primary photochemical reactions of photosynthesis via the QB binding site on the D1 protein. This is a remarkably conserved area (the amino acid sequence of D1 has a 98 % homology between different higher plants and 85–90 % between PSII containing species). This conservation, and the fact that it is the base of the food chain, means that, like TBT, booster biocides can potentially have far-reaching consequences. Whereas TBT acted quite specifically in causing imposex and shell abnormalities, through endocrine disruption, the booster biocides that replaced TBT have more broad-spectrum impacts.

The wider ecological impacts of the above finding and the transition to booster biocides remain poorly understood but of considerable potential concern. The message is clear: there is a need to develop and apply non-toxic and less toxic solutions to the problem of biofouling on vessel hulls.

12.4.4 Why monitoring should continue

Monitoring should continue for several reasons: the legacy of TBT, our understanding now that booster biocides are far from 'risk free', and the recognition that developing non-toxic alternatives may take years or decades. One key lesson is that there is a need to monitor at least selected constituents of the newer antifouling agents. Both the chemical and ecological aspects are, and will remain, an important marine and environmental indicator within European waters. Monitoring design will need to be sufficiently robust to identify, and quantify, temporal and spatial trends with an appropriate degree of precaution. This is necessary to ensure that any 'clean bill of health' given to existing and new booster biocides is environmentally warranted. And while several booster biocides have already been banned in parts of Europe, monitoring of both banned and permitted antifouling agents will help determine whether further legislation is needed as an additional measure of precaution.

The present report's chapter on methyl mercury pollution in Minamata Bay, Japan, demonstrates that it is not always easy to identify pollution-free sites to serve as an 'international baseline'. For booster biocides, one possible reference area has recently been established in Chagos (Guitart et al., 2007), one of the world's essentially pristine and remotest marine areas. In Chagos, concentrations of Irgarol 1051 and other booster biocides screened for were extremely low. Over the coming years, monitoring of these antifouling agents will be necessary in both affected and reference or 'control' areas.

Price and Readman (2006) outlined an approach for establishing a monitoring procedure and an indicator for booster biocides in European waters. Essentially this could be a scaled down version of the ACE project (ACE, 2002). Sampling is recommended in sites in the regions of Norway and the Faroe Islands, the Baltic, the North Sea, the Mediterranean (north and south), the Black Sea, the Barents Sea, the English Channel, the Celtic region and Irish Sea, and the Iberian Peninsula.

Monitoring efforts should focus initially on Irgarol 1051, in view of its widespread use, marked toxicity and other factors. Extensive data are available for Irgarol 1051 and it can be traced to antifouling paints since it is not used as a herbicide (unlike diuron). The 800 samples collected and analysed during the ACE project represent a valuable resource, providing baseline data that should help determine temporal and spatial patterns in booster biocide accumulation and toxicity. Sampling from one of the world's least contaminated ocean areas (Guitart et al., 2007) might provide a valuable international standard or benchmark to determine the contamination of other marine and coastal areas.

Any future monitoring programme should be firmly linked to an action plan and catalyse management activities if contaminant levels or other metrics of ecosystem health fall to some predetermined threshold level(s). Otherwise, monitoring can easily become an essentially scientific or academic pursuit. For example, physical, chemical, ecological and visual criteria have been developed to determine when (if at all) to begin and when to end oil spill clean-up. Monitoring therefore informs clean-up, by helping determine environmental situations in which clean-up is and is not appropriate. Similar considerations may be needed for regulating and controlling biocides. On the other hand, the detection of imposex at least partly resulted from initially academic work, rather than monitoring of toxic effects. Academic activities may thus play a role, not least in identifying possible emerging issues.

12.4.5 New-age antifouling: is there a non-toxic way?

Given the undeniable (and necessarily) toxic nature of biocidal antifouling agents, there is a case for further research and fast-track development of more environmentally benign solutions. The controlled, slow release of agents regulated through polymer design (Readman, 2006) is seen as one approach. However, this represents only a 'stop-gap' and far from an optimal environmental solution given the undesirability of releasing toxic substances into the water column and environment, even slowly. Arguably, it might be better for these substances to be retained permanently in the paint, assuming they could still be sufficiently effective, to enable recovery and disposal on land.

An alternative strategy makes use of natural products (or synthesised analogues). These compounds normally act enzymatically by interfering with the metabolism of fouling organisms or dissolving their adhesive materials. Structures include terpenoids, steroids, heterocyclics, alkaloids and polyphenolics. This approach to preventing fouling has not, however, been commercially exploited (Readman, 2006). Although not all natural products are hazard-free — strychnine and aflatoxins are two examples that are not used in antifouling preparations — the release and occurrence of natural antifoulant compounds derived from marine organisms is not perceived to pose a serious environmental threat by the general public.

Non-stick fouling-residue coatings that prevent adhesion by fouling organisms are another approach. At present the choice of materials is restricted to fluoro-polymers and silicones (Readman, 2006). From an environmental perspective, this option is appealing. Results from performance tests for currently available coatings indicate modest performance, requiring relatively high speeds to remove fouling organisms. A number of such formulations are already on the market and in use for some classes of vessels. Coupled with expense, however, poor adhesion qualities to the hull and susceptibility to damage mean that widespread commercial application seems unlikely without further advances in technology (Readman, 2006).

The Biocidal Products Directive (98/8/EC) and other legal instruments give consideration to substitutes and alternatives. However, it is normally existing manufacturers of antifouling products that seek to innovate in response to such instruments and they tend to devise solutions with which they are familiar — typically more biocide. The result is incremental change, such as the shift to booster biocides after TBT use was outlawed. As noted, relatively undeveloped alternatives exist, such as non-stick coatings and polishing robots, but the companies that could develop more innovative solutions are generally unaware of the emerging market.

12.4.6 Hindsight, foresight and conclusions

Table 12.4 provides a summary of the historical use of antifouling agents and the main early environmental warnings and actions. TBT, now in demise, has been a highly effective antifouling agent but is among the most toxic synthetic compounds ever produced. Use on small crafts was banned in European waters in the late 1980s and early 1990s. Prohibition has taken longer on ships. Through an international convention, and European legislation linked to this, a total ban has come into force.

For technical and socioeconomic reasons, the extent of TBT hazards was initially underestimated. Many of the warnings serve as important reminders for booster biocides, in terms of the value of early recognition of potential environmental hazards, protocols for monitoring and appropriate regulatory measures. Uncertainties regarding the geographical scale of the problem of TBT (e.g. the limited sensitivity of analytical methods and imperfect baseline data) do not constrain understanding of antifouling residues as they did twenty or more years ago.

Recent research has demonstrated the significant toxicity of booster biocides at extremely low concentrations. Of the major booster biocides, diuron has been encountered in the highest mean concentrations, particularly in north-western Europe (ACE, 2002). Irgarol 1051 has normally been identified at lower mean concentrations, with most contamination in Mediterranean coastal environments. Globally, data are available for the biocides most commonly used in Europe, North America and Japan (i.e. diuron, Irgarol 1051 and Sea-Nine 211), while negligible data are available for other biocides. Significant endocrine disruption, the major problem associated with TBT, was not found for booster biocides (ACE, 2002). Instead, booster biocides are often photosystem II inhibitors; by impairing photosynthesis they can impact the base of food chains and their dependencies (e.g. symbiotic algae and host corals).

Despite accumulating substantial information on adverse environmental side effects, some experts (Voulvoulis et al., 2002) consider that additional data are needed to evaluate properly the risks of widespread use of Irgarol 1051, diuron, Sea-Nine 211 and chlorothalonil. They caution against using TCMS pyridine, TCMTB and dichlofluanid, again identifying a lack of appropriate data. In their initial risk evaluation, zinc pyrithione and zineb appeared the least hazardous options for the aquatic environment.

Like several other countries, the United Kingdom has taken precautionary action, introducing legislation in 2001 to restrict the use of antifouling agents in paints on small (< 25 m) vessel to dichlofluanid, zinc pyrithione and zineb. The previously popular booster biocides diuron and Irgarol 1051 were banned. Recent research (Cresswell et al., 2006) indicates that this legislation appears to have been effective in reducing environmental concentrations.

Even for prohibited (but still used) toxic substances, it is fair to assume that a release into the environment is often inevitable. The preference should always be for non-toxic, competitively priced alternative approaches, rather than adding toxic contaminants to the environment.

Booster biocides must be monitored to gather more data on accumulation, toxicity and the impact of legislation. Given the undeniable (and necessarily) toxic nature of antifouling agents, however, there appears to be a strong case and market demand for further research and fast-track development of more environmentally benign solutions to biofouling, such as natural products and non-stick coatings.

Thomas and Brooks (2010) indicate that even today DDT is used in China as an antifoulant. Meanwhile, novel compounds, such as phenylborane pyridine, Econea, capsaicin and medetomidine, are almost uninvestigated, with very little information available on them in the public domain.

In conclusion, booster biocide antifouling agents threaten a variety of habitats — from coral reefs and seagrass beds to open moorings — within the EU and globally. Their primarily herbicidal properties mean that coral zooxanthellae, phytoplankton and periphyton are particularly vulnerable. Compared to TBT — an antifouling agent with a quite specific action — booster biocides have more broad-spectrum impacts. The wider ecological effect of shifting to booster biocides remain poorly understood but of considerable concern because they may affect the base of marine food chains.

For policymakers, the challenge is to protect non-target biological communities from selective change resulting from booster biocide use. Policy has proven effective in, for example, Bermuda and the United Kingdom, where banning selected agents lowered concentrations and limited adverse ecological impacts. Clearly persistence, bioaccumulative and toxic (PBT) criteria can be used to evaluate the relative potential impact from the available biocides, and consequently target appropriate legislation. Nevertheless, lateral thinking, aiming to identify novel materials and strategies to address antifouling, could pay dividends in the future.

Table 12.4 Early warnings and actions

Early maritime to late-1600s ~ 2–3 thousand years	Ancient Greece: lead sheathing and copper nails caused no environmental concern
~ 800 AD	Arab ships: lime and mutton fat coating caused no environmental concern
Late 1400s	Columbus: pitch and tallow coating caused no environmental concern
1600s	UK navy: tar, grease, sulphur pitch coating caused no environmental concern
Late 1700s	Copper sheathing caused no environmental concern
Mid 1800s →	Copper paints caused no or limited environmental concern
Mid 1900s	Copper, arsenic and mercury paints caused no or limited environmental concern
Late 1950s/early 1960s–1990s	Organotin compounds such as tributyl tin (TBT) caused increasing environmental warnings and actions (see EEA, 2001, Ch. 13)
1989	EC Directive 89/677/EEC bans TBT on small boats (< 25 m), triggering the development and use of booster biocides
1993	First report of booster biocides in coastal waters (Irgarol 1051)
1996	First report on the toxicity of booster biocides at environmental levels (Dahl and Blanck, 1996)
1997	Previous events trigger expanded environmental research
1999	European Commission funds ACE Project (ACE, 2002)
2000	Under the Biocidal Products Directive (98/8/EC) the European Commission began reviewing all biocides used in all biocidal products, including antifouling paints. It entered into force on 14 May 2000
2000	UK Health and Safety Executive began phasing out all booster biocides except dichlofluanid, zinc pyrithione and zineb for small vessels (< 25 m)
2002–2005	Concern raised over toxicity of booster biocides to coral zooxanthellae at extremely low concentrations (e.g. Owen et al., 2002, 2003; Jones, 2005) leading to bans on specific agents in several countries
Today	Development of new technologies/non-toxic alternatives: • potential for natural products (disturbing foulant metabolism or dissolving foulant adhesives) • potential for fluoro-polymers and silicones (non-stick coatings)

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