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Viewpoint

Antifouling strategies: History and regulation, ecological impacts and mitigation

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ABSTRACT

Biofouling increases drag on marine vessels resulting in higher fuel consumption and can also facilitate the transport of harmful non-indigenous species (NIS). Antifouling technologies incorporating biocides (e.g., copper and tributyltin) have been developed to prevent settlement of organisms on vessels, but their widespread use has introduced high levels of contamination into the environment and raised concerns about their toxic effects on marine communities. The recent global ban on tributyltin (1 January 2008) and increasing regulation of copper have prompted research and development of non-toxic paints. This review synthesises existing information regarding the ecological impact of biocides in a wide range of organisms and highlights directions for the management of antifouling paints. We focus particularly on representatives of the recent past (copper and tributyltin) and present (copper and 'booster') biocides. We identify knowledge gaps in antifouling research and provide recommendations relating to the regulation and phasing-out of copper.

1. Introduction

Marine biofouling describes the community of organisms that settle and grow on the external surfaces of submerged or semi-submerged objects, both natural and artificial (Lewis, 1998). Within hours of a structure's submergence, a slime layer develops, which is comprised of microscopic organisms (bacteria and algae) bound within an extracellular matrix of polymeric substances (Steinberg et al., 2002; Zobell and Allen, 1935). This layer facilitates the settlement and attachment of macro-organisms, including larvae of invertebrates such as ascidians, serpulids and barnacles, by providing biochemical cues for settlement and increasing their adherence to the substrate (Zobell and Allen, 1935).

Biofouling is ubiquitous in the marine environment and is a major problem for the shipping industry (Fig. 1). Shipping accounts for approximately 90% of world trade and seaborne trade has quadrupled over the past three decades (ICS&ISF, 2009). Growth of organisms on a vessel hull increases frictional drag which reduces ship speed or requires increased power and fuel consumption to maintain speed (Abbott et al., 2000). Slime films alone can impart powering penalties of 21%, with heavy calcareous biofouling increasing this penalty to 86% (Schultz, 2007). The economic costs of hull fouling have been a driving force behind the development of AF technologies, a global industry that is now worth approximately US$ 4 billion annually (Wright, 2009).

Antifouling measures include the use of coatings on vessel hulls to inhibit the settlement of marine organisms (Table 1). These have traditionally incorporated toxicants including copper and tributyltin into a paint matrix that gradually leaches the biocide from the surface layer to prevent settlement (Table 1) (Fig. 2a–c) (Lewis, 1998). The widespread use of toxicants in AF paints has resulted in high levels of contamination in the environment and raised concerns about their effects on marine communities (Alzieu et al., 1986; Claisse and Alzieu, 1993; Thomas and Brooks, 2010). Some non-toxic silicone-based coatings, known as foul release coatings have been developed (Table 1) (Townsin and Anderson, 2009). These do not prevent settlement of fouling organisms, but reduce the attachment strength such that when the vessel is in motion any accumulated biofouling will slough off as drag increases (Fig. 2d). However, foul release coatings have restricted application as they only self-clean effectively on high speed/high activity vessels. Other non-toxic strategies include incorporating natural antifouling compounds from marine organisms such as algae and sponges into coatings, however these are not yet in commercial production (Table 1). Hence the development of a general use non-toxic AF paint is far from complete (Yebra et al., 2004).

In this paper we review the ecological impacts of AF strategies with reference to the history and regulation of AF technology and provide comment on future regulation to mitigate impacts. Past reviews have tended to focus on (a) economic impacts (Abbott et al., 2000), (b) toxic effects of biocides (Bryan, 1971; Flemming and Trevors, 1989; Hall and Bushong, 1996; Thomas and Brooks, 2010), (c) biological invasion (Piola et al., 2009) or (d) progress in developing non-toxic alternatives (Hellio et al., 2009). Consequently, due to

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Fig. 1. Vessel hull fouling. Marine biofouling describes the community of organisms that settle and grow on the external surfaces of submerged structures. Within hours of a structure's submergence, a slime layer develops. This layer promotes the settlement and attachment of macro-organisms, including larvae of invertebrates such as ascidians, serpulids and barnacles. Photo: J. Lewis.

these multiple but disparate foci, our general understanding of the ecological impacts of various AF strategies is somewhat fragmented. Here we integrate environmental effect information regarding AF strategies and describe current regulations. We consider the future for AF strategies, including the development of non-toxic coatings.

2. Antifouling technology: history and regulation

Antifouling technology has developed in close association with increased maritime transportation of people and cargo (Table 2). The early Phoenicians (1500–300 BC) are credited with the first advance in the form of lead and copper sheets to prevent biofouling on their wooden boats (WHOI, 1952). By the late 18th and into the 19th centuries coatings containing copper, arsenic and mercury were increasingly applied to vessel hulls (WHOI, 1952). Copper was an effective and widely used biocide, however the effectiveness was relatively short-lived so dry dockings of vessels for cleaning and paint reapplication were required frequently (*c.* every 18 months (Lewis, 1998)).

2.1. Tributyltin

With the discovery of the antifouling efficacy of trialkyltins, hull fouling was thought to be a problem of the past (Minchin and Gollasch, 2003). Tributyltin was first used in freshwater systems to eradicate molluscs harbouring the parasitic worm *Schistosoma* and from the early 1960s TBT was introduced as a biocide in marine AF paints (Lewis, 1998). Initially, TBT was incorporated in conventional or 'free association' paints, which relied on passive leaching from a soluble matrix or contact leaching to deliver surface toxicant to inhibit growth (Fig. 2a–b) (Lewis, 1998). Conventional paints had a limited lifetime of around two years and were superseded in the 1970s by self-polishing copolymer (SPC) paints (lifetime > 5 years). In SPC paints the TBT copolymer provides both the biocide and paint matrix, and this hydrolyses in seawater to release the TBT leaving an unstable surface layer that gradually erodes to expose a fresh layer of active paint (Fig. 2c) (Lewis, 1998).

Authorities first became aware of the problems associated with TBT in the early 1980s, when several oyster farms in France experienced major declines due to reduced oyster spatfall, anomalies in larval development, and shell malformation affecting 80–100% of individual oysters (Table 3; Alzieu et al., 1986). TBT use was subsequently prohibited on vessels <25 m in France (Alzieu et al., 1986). This ban targeted mainly recreational vessels as they spend long periods in enclosed marinas and were therefore perceived as the biggest contributor to TBT contamination via passive leaching (Alzieu et al., 1986). Imposex (the development of male characteristics on female gastropods) was soon after identified as another negative effect of TBT contamination (Gibbs and Bryan, 1986). This triggered subsequent TBT restrictions on small vessels in the UK (1987), USA (1988), Canada (1989), Australia (1989) and the EU (1989) (Champ, 2000). Commercial vessels continued to use TBT, although the latter were commonly restricted to using low TBT release SPC systems.

In November 2001 the International Maritime Organisation (IMO) adopted the "AFS Convention", to ban the application of TBT on all vessels after 1 January 2003 and require its absence as an active coating on all vessels after 1 January 2008 (IMO, 2001). The AFS Convention did not become internationally binding until September 2008, twelve months after its ratification by the required 25 states representing at least 25% of the gross tonnage of the world's merchant shipping. However, some anticipatory action was taken in some regions; for example, European Union Regulation (EC) No. 782/2003 banned the application of TBT-paints on all EU-flagged vessels from 1 January 2003 and in Australia the registration of all anti-fouling paints containing TBT was revoked in March 2003. It is likely that TBT continues to be used on domestic vessels in non-signatory countries (Antizar-Ladislao, 2008).

2.2. Copper

Even while TBT dominated the international marketplace, copper continued to be used, both in cheaper paints for small craft or as a co-biocide to boost performance of some TBT paints (Nichols, 1988; Young et al., 1979). Since the ban on TBT, copper has once again become the predominant antifouling biocide, but its use in AF paints is under scrutiny in several countries and has an uncertain future (Table 2). Restrictions on copper release rates have been introduced in Canada and Denmark. Health Canada requires that AF paints containing copper have a release rate of less than 40 $\mu g/cm^2$/day (HC, 1994) and in Denmark AF paints that release copper exceeding a cumulative 200 $\mu g/cm^2$ over the first 14 days are prohibited (DEPA, 2003). Another strategy has been to target particular vessels, ecologically sensitive areas, or highly contaminated environments with restrictions, for example, copper AF paints are no longer in use on small boats on the Baltic Coast of Sweden (KEMI, 2006) and copper input reduction targets have been set for the Shelter Island Yacht Basin in San Diego Bay, California, that will require a transition to non-toxic and less toxic AF paints (CRWQCB, 2005). The US EPA is also reviewing current AF regulations with the likely scenario being restrictions on copper use in the future (Carson et al., 2009).

2.3. 'Booster' biocides

Despite copper's high toxicity to many marine organisms, some algal groups are tolerant (Foster, 1977; Reed and Moffat, 1983). Hence, most copper AF paints are fortified with additional 'booster' biocides to target hull colonisation by micro- and macro-algae (Table 3). Approximately 18 are currently in use worldwide including chlorothalonil, dichlofluanid, Irgarol 1051®, TCMS pyridine, thiocyanatomethylthio-benzothiazole (TCMTB), diuron, dichloro-octyl-isothiazolin (DCOIT, Sea Nine 211®), zinc and copper pyrithione (Zinc and Copper Omadine®) and zineb (Boxall et al., 2000; Thomas, 2009, 2001; Voulvoulis et al., 1999). These are often herbicides (e.g., Irgarol 1051® and diuron) that have negative effects

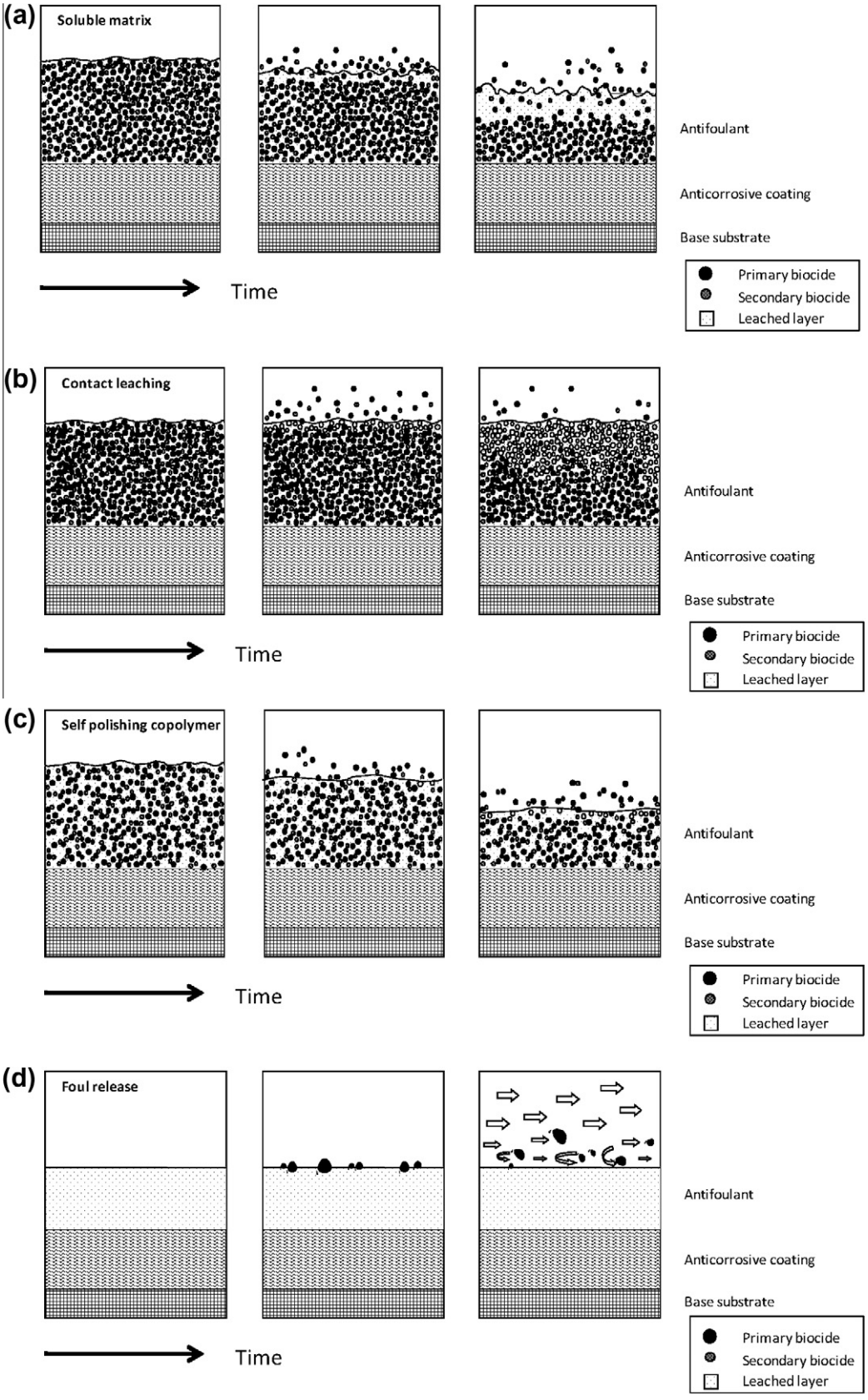

Fig. 2. Diagrammatic representation of (a) soluble matrix, (b) contact leaching, (c) self-polishing copolymer (SPC) and (d) foul-release coatings.

on the growth rate of photosynthetic organisms (Voulvoulis et al., 1999). Legislation now exists in some countries to regulate the use of some 'booster' biocides in AF paints, for example, diuron and Irgarol 1051. In the UK, a review of booster biocides in 2000 resulted in only four biocides gaining approval (dichlofluanid, DCOIT (Trade name: Sea Nine 211), zinc pyrithione and zineb).

Table 1
Description of the major AF strategies past and present.

Anti-fouling system	Mode of action
TBT Self-polishing copolymer (SPC) coatings	TBT biocide chemically bonded in copolymer resin – hydrolysis with seawater results in slow and consistent release of TBT biocide
Tin-free SPC coatings	Cu/Zn/Silyl copolymer resin with Cu particles and booster biocides dispersed through the paint matrix – hydrolysis with seawater results in slow and consistent release of biocide
Tin-free conventional coatings	Cu particles and booster biocides dispersed through soluble or insoluble paint binder – dissolution in seawater results in slow and decreasing release of biocide
Booster biocides	Most often herbicides/pesticides incorporated into Tin-free Conventional and SPC AF paints to increase efficacy against Cu-tolerant algae
Foul-release coatings	Low energy, minimally adhesive surfaces, mostly silicone elastomers and often incorporating silicone oils
Biomimetics	Incorporation of natural AF compounds produced by marine organisms (e.g., secondary metabolites) or surfaces based on natural microtopography

Table 2
Historical development of AF strategies.

Timeline	Major events
1500–300 BC	Use of lead and copper sheets on wooden vessels
1800–1900s	Heavy metals (copper, arsenic, mercury) incorporated into coatings
1800s–present	Continued use of copper in AF coatings
1960s	Development of TBT conventional coatings
1974	Oyster farmers report abnormal shell growth
1977	First foul release AF patent
1980s	Development of TBT SPC coatings allowed control of biocide release rates
1980s	TBT linked to shell abnormalities in oysters (*Crassostrea gigas*) and imposex in dogwhelks (*Nucella lapillus*)
1987–90	TBT coatings prohibited on vessels <25 m in France, UK, USA, Canada, Australia, EU, NZ and Japan
1990s–present	Copper release rate restrictions introduced in Denmark and considered elsewhere e.g. California, USA
2000s	Research into environmentally friendly AF alternatives increases
2001	International Maritime Organisation (IMO) adopts "AFS Convention" to eliminate TBT from AF coatings from vessels through: 2003 – prohibition of further application of TBT 2008 – prohibition of active TBT presence
2008	IMO "AFS Convention" entered-into-force

Approvals of chlorothalonil, diuron and Irgarol 1051 were revoked due to their high toxicity at low concentrations and their persistence in the environment (Cresswell et al., 2006; Thomas, 2009). Irgarol 1051 and diuron are also banned in Denmark (DEPA, 2008), and diuron is banned in the Netherlands (Bannink, 2004). Use of Irgarol 1051 in AF paints is not permitted in Australia as it was not granted approval for use as an AF biocide by the Australian Pesticides and Veterinary Medicines Authority (APVMA) when assessed in the 1990s. Applications for approval have been submitted to the European Union for eleven AF biocides, including copper (II) oxide, copper thiocyanate and Irgarol 1051, but not diuron (Pereira and Ankjaergaard, 2009).

2.4. Non-toxic and "natural" alternatives

Increased awareness of the impacts resulting from the use of toxic AF paints has prompted investment in the research and development of non-toxic alternatives such as foul-release coatings that incorporate silicone elastomers, waxes or silicone oils, and "natural" coatings that source AF compounds from algae and other marine organisms (Table 3; Hellio et al., 2009). Foul-release coatings currently on the market include silicone (e.g., Intersleek 700®, Sealion® and Bioclean®), fluoropolymer (e.g., Intersleek 900®), hybrid (e.g., Phasecoat UFR®) and hydrogel silicone (e.g., Hempasil X3®) coatings (Townsin and Anderson, 2009). "Natural" coatings however are not currently in commercial use due to the difficulties in sourcing a supply of natural AF compounds at a reasonable cost in addition to meeting the requirements of environmental regulation agencies (reviewed by Yebra et al., 2004). Future regulatory decisions in favour of non-toxic alternatives in antifouling paints could shift the balance and force these products into commercial use.

Table 3
Key advantages and disadvantages of past and present AF systems.

Anti-fouling system	Key advantages	Key disadvantages
TBT self-polishing copolymer (SPC) coatings	Most effective broad spectrum AF biocide developed, long lifetime (~5 years)	Impacts on non-target species, human health risks, half life of days in seawater, but months – years in sediments depending on environmental conditions
Tin-free SPC coatings	Effective against range of invertebrate foulers, long lifetime (~5 years)	Cu and booster biocide impacts on non-target species, Cu persistent in marine environment (depends on pH, salinity and dissolved organic matter – also determines toxicity)
Tin-free conventional coatings	Effective against range of invertebrate foulers	Short lifetime (~12–18 months), Cu and booster biocide impacts on non-target species, Cu persistent in marine environment (depends on pH, salinity and dissolved organic matter – also determines toxicity)
Booster biocides	Effective against a range of bacterial, algal and fungal foulers	Impacts on non-target species, e.g., algae, seagrasses, corals, invertebrates, some persistent in marine environment
Foul-release coatings	Effective at reducing strength of fouling attachment, do not leach, no or low toxicity, potential long life (~10 years)	Only self-clean on high speed (>15 knots)/high activity vessels, or otherwise require regular cleaning, susceptible to abrasion damage
Biomimetics	Natural alternatives "environmentally friendly"	Not commercially available yet, difficult to source adequate supply of compound

3. Environmental impacts of anti-fouling paints

The widespread use of toxic biocides in AF paints has introduced high levels of contamination into the environment and raised concerns about their toxic effects on marine communities (Table 4). Marine organisms directly accumulate AF contaminants through a variety of active and passive mechanisms. The transfer of contaminants to higher trophic levels is also of major concern, especially when the organism in question is an important human food source (Antizar-Ladislao, 2008). If the uptake of the contaminant exceeds the organism's ability for excretion and detoxification, this can reduce normal metabolic functioning (Rainbow, 2007).

Table 4
Selected maximum concentrations of anti-fouling biocides reported from sea water (μg/L) and sediments (μg/g).

Biocide	Location	Water (μg/L)	Year	References	Sediments (μg/g)	Year	References
Tributyltin	**North America**						
	USA	0.93	1983–1985	Valkirs et al. (1986)	0.909	1993–1994	Wade et al. (2004)
	Asia						
	Australia	0.012	2006	Reitsema (2008)	89	2006	Reitsema (2008)
	Japan	0.002	2007	Eguchi et al. (2010)	0.011	2007	Eguchi et al. (2010)
	Korea	0.16	2001–2005	Choi et al. (2009)	9.58	2001–2005	Choi et al. (2009)
	Hong Kong	1.05	1988–1989	Lau Wong (1991)	53	1994	Ko et al. (1995)
	Singapore	3.2	2000	Basheer et al. (2002)			
	India	0.037	2007–2008	Meena et al. (2009)	16.82	2000–2002	Bhosle et al. (2006)
	Europe						
	UK	1.06	1984–1986	Cleary and Stebbing (1987)	3.9	1990	Dowson et al. (1992)
	France	1.5	1986–1987	Alzieu et al. (1989)	8.163	1996–1997	Amouroux et al. (2000)
	Spain	2.8	1996	Prego and Cobelo-Garcia (2003)	13.3	2000	Arambarri et al. (2003)
	Portugal	0.071	1999–2000	Díez et al. (2005)	0.003	1999–2000	Díez et al. (2005)
	North Africa						
	Egypt	0.083	1994	Abd-Allah (1995)	2.07	1999	Barakat et al. (2001)
Copper	**North America**						
	USA	5.7	1997	BCI Engineering and Scientists (2001)	162	2006–2007	Trefry et al. (2008)
	Asia						
	Australia	5.7	2006	Reitsema (2008)	17.9	2006	Reitsema (2008)
	Europe						
	France	10	1980s	Carruesco et al. (1986)			
	Greece	20.7	1993	Dassenakis et al. (1996)	80.4	1993	Dassenakis et al. (1996)
	Middle East						
	Israel				41	1984–1987	Hornung et al. (1989)
Irgarol 1051	**Asia**						
	Australia	0.006	2006	Reitsema (2008)	1.34	2006	Reitsema (2008)
	Japan	0.018	2007	Eguchi et al. (2010)	0.01	2007	Eguchi et al. (2010)
	Europe						
	UK	1.4	1998	Thomas (2001)	1.011	1998–1999	Boxall et al. (2000)
	Netherlands	0.09	2000	Lamoree et al. (2002)	< 1	1998	Thomas et al. (2000)
	Spain	1	1990s	Hernando et al. (2001)	0.088	2000	Martinez and Barcelo (2001)
	Greece	0.09	1999–2000	Sakkas et al. (2002)	0.69	1999–2000	Sakkas et al. (2002)
Diuron	**Asia**						
	Australia	2.16	2006	Reitsema (2008)	0.555	2006	Reitsema (2008)
	Japan	0.257	2007	Eguchi et al. (2010)	0.012	2007	Eguchi et al. (2010)
	Europe						
	UK	6.7	1998	Thomas (2001)	1.42	1998	Thomas et al. (2000)
	Netherlands	1.13	2000	Lamoree et al. (2002)	<0.1	1998	Thomas et al. (2000)
	Spain	2	1999	Martinez et al. (2000)	0.136	2000	Martinez and Barcelo (2001)

Toxicity is related to the properties of the contaminant as well as its bioavailability in the marine environment. For example, organotins such as TBT are highly toxic because of their increased fat solubility (compared to inorganic tin), which allows them to penetrate biological membranes, and their mode of action as a potent endocrine disruptor within the cell (Champ and Pugh, 1987). Toxicity will increase if a contaminant is more bioavailable and this is related to local environmental conditions (e.g., temperature and pH) as well as the partitioning behaviour or binding strength of the contaminant to sediment (Burton et al., 2004). Therefore when contaminants occur in the water column, they are often found in their most toxic dissolved form whilst sediments tend to act as a contaminant sink (Eggleton and Thomas, 2004). The remobilisation of sediments by natural (e.g., storms and bioturbation) or anthropogenic events (e.g., dredging) can be a major source of heavy metal contaminants but has received comparatively little attention (but see Eggleton and Thomas, 2004; Knott et al., 2009).

3.1. Tributyltin

Ecological effects of TBT on growth, development, reproduction and survival have been reported in organisms ranging from bacteria to fish and mammals (Antizar-Ladislao, 2008). Laboratory studies indicate TBT exposure as low as 0.002 μg/L causes shell abnormalities in oysters by inhibiting calcification (Chagot et al., 1990), and >0.73 μg/L results in reduced oyster growth (Valkirs et al., 1987). Water column TBT concentrations recorded along the French coastline were up to 1.5 μg/L before the 1980s when TBT was prohibited on vessels <25 m (Alzieu et al., 1989). During this period, it became apparent that some gastropod populations were also declining in areas of high vessel activity and TBT was identified as the primary cause behind their disappearance (Bryan et al., 1986). Tributyltin causes a hormonal imbalance in gastropod females which induces the development of male sex organs, a condition known as imposex (Matthiessen and Gibbs, 1998; Smith, 1981). It should be noted that recent research has suggested that imposex may also be a response to other stress stimuli such as polychlorinated biphenyls (Garaventa et al., 2008, 2006), but TBT is still widely recognised as the primary cause. Imposex manifests in stages, initially with the development of a rudimentary penis and vas deferens in the female. This is followed by penis enlargement and the completion of the vas deferens which blocks the oviduct, preventing the release of eggs and potentially causing death (Gibbs and Bryan, 1986). Tributyltin levels in the water column as

low as 0.02 μg/L will readily induce imposex (Gibbs and Bryan, 1986) and between 1.2 and 5.6 μg/L can induce irregular swimming behaviour of gastropod larvae (Horiguchi et al., 1998).

Marinas and commercial ports in developed countries were identified as hotspots of TBT contamination with concentrations in the surface water and sediments correlating to the level of shipping or boating intensity (Batley et al., 1989; Cleary and Stebbing, 1987; Maguire et al., 1982; Valkirs et al., 1986). Recreational marinas have recorded TBT concentrations up to 0.93 μg/L in San Diego Bay (Valkirs et al., 1986), up to 1.06 μg/L in SW England (Cleary and Stebbing, 1987) and 1.05 μg/L in Hong Kong (Lau Wong, 1991). Less heavily impacted areas included SE Australia with TBT concentrations in the water column up to 0.19 μg/L in Sydney Harbour (Batley et al., 1989). Following the implementation of TBT regulations for vessels <25 m, contamination became largely restricted to commercial vessel areas (Choi et al., 2009; de Mora et al., 1995; Díez et al., 2002; Gibson and Wilson, 2003; Harino et al., 1998). In coastal areas of Korea TBT contamination is greatest in areas of intense commercial shipping, up to 0.16 μg/L (Choi et al., 2009), and in Japan up to 0.04 μg/L in the Port of Osaka (Harino et al., 1998). Some developing countries where TBT remains unregulated have also experienced high levels of contamination (Barakat et al., 2001; Rilov et al., 2000; Sudaryanto et al., 2004).

Tributyltin contamination extends into deep sediments and along major shipping lanes (0.019 μg/g (Strand et al., 2003)) and in 'pristine' marine environments, including Antarctica (2.2 μg/g (Negri et al., 2004)) and the Great Barrier Reef World Heritage Area; at ship grounding sites up to 340 μg/g (Haynes and Loong, 2002; Negri et al., 2002)). Long range passive transport has exposed organisms not inhabiting point source areas to TBT. For example, deep sea fish collected between 1000–1800 m depth in the Mediterranean had comparable levels of TBT to coastal fish (Borghi and Porte, 2002). The effects of TBT contamination also have the potential to extend to higher organisms through consumption (Antizar-Ladislao, 2008). Both mammals and seabirds have been found to harbour high TBT concentrations (e.g., cetaceans in Norway (Berge et al., 2004), Poland (Kannan and Falandysz, 1997), Japan (Iwata et al., 1995) and the Mediterranean (Kannan et al., 1996) and river otters in the USA (Kannan et al., 1999)). Tributyltin in human blood and liver has raised concerns about the trophic transfer of TBT via human consumption of seafood (Antizar-Ladislao, 2008). Tolerable daily intake values for TBT of 0.25 μg/kg of body weight per day are recommended and there is evidence that these could be exceeded from some seafood in fish markets (reviewed by Antizar-Ladislao, 2008). Consumption rates are not likely to be high enough to be damaging in most people, but for some specific groups (e.g., fishers), in certain localities, TBT contaminated seafood may pose a health risk.

Since the introduction of TBT restrictions, there is some evidence of recovery in marine ecosystems. For example, imposex has declined in dogwhelks in the UK (Evans et al., 1991; Morton, 2009) and Canada (Tester and Ellis, 1995) and in dogwinkles in Australia (Rees et al., 2001). Oyster populations have recovered from TBT contamination in Australia (Batley et al., 1992) and in France (Ruiz et al., 1996). However, in some areas imposex persists (e.g., Gibbs, 2009) and despite restrictions, TBT contamination in the water column remains high (Dafforn et al., 2009). Even a brief exposure to TBT can result in shell deformities and significant bioaccumulation in oysters (Scammell et al., 1991). If a few vessels are illicitly coated with TBT this might explain the persistence of impacts. However, a more likely scenario relates to the environmental persistence of TBT. Tributyltin has a half-life of ~20 days in the water column, but can persist in sediments for months (reviewed by Clark et al., 1988) and potentially much longer if deposited as paint flakes or in an oligotrophic environment (Michel and Averty, 1999). If there is no ongoing illegal use of TBT, then detectable levels of TBT in the water column are likely to result from TBT desorption from bottom sediments either by resuspension, for example, during shipping movements or coastal developments such as dredging (Knott et al., 2009; Tolhurst et al., 2007).

The long-term effects of contaminated sediments on marine systems remain relatively unknown. Recreational marinas are of particular concern as they are often sheltered and poorly flushed (Floerl and Inglis, 2003) making it less likely that contaminants accumulating in the sediment will be dispersed. Enclosed ports and marinas suffer additional contamination from deposited antifouling paint particles, which until recently have remained relatively unstudied, but could increase the persistence and long-term bioavailability of contaminants (Turner, 2010). This has implications for infauna that ingest and burrow into the contaminated sediments. Field data suggests that TBT sediment concentrations between 0.1 and 1 μg/g will have adverse effects on infaunal species (Langston and Burt, 1991) and in areas of intense shipping activities, concentrations greatly exceed this (up to 5.48 μg/g in Spain (Arambarri et al., 2003) and up to 16.82 μg/g in India (Bhosle et al., 2006). While TBT remains bound to the sediments, impacts are likely to remain confined to the resident infaunal community, but remobilisation of contaminated sediments can also become a problem for epifaunal species (Hedge et al., 2009).

3.2. Copper

Copper is found naturally in the marine environment and is an essential element in the enzyme activity necessary for healthy metabolic functioning as well as the growth and metamorphosis of many organisms (Lewis and Cave, 1982). Copper becomes toxic when, in a bioavailable form, it exceeds the threshold of the organism's tolerance, and this has been shown to vary widely between life stages (Xie et al., 2005) and even between species within the same taxonomical group (Han et al., 2008; Piola and Johnston, 2006). Copper toxicity is also strongly influenced by environmental factors that govern copper speciation and hence its bioavailability (Srinivasan and Swain, 2007). Various models have been developed to predict metal toxicity including the Biotic Ligand Model (BLM), which utilises water chemistry and has become a useful tool in water quality monitoring, for example, US EPA (Arnold et al., 2005; Paquin et al., 2002; Toro et al., 2001), and the Free Ion Activity Model (FIAM) based on the chemical reactivity of the metal (Morel, 1983; Parent and Campbell, 1994).

Natural background concentrations of copper in seawater are estimated at between 0.5 and 3 μg/L, but concentrations up to 21 μg/L Cu have been found in contaminated areas (Brooks and Waldock, 2009). A recent risk assessment on the use of copper as a biocide in AF paints considered the concentration, speciation and effects of copper in the coastal marine environment, and inputs from AF paints (Brooks and Waldock, 2009). They concluded that copper toxicity was a potential problem in isolated water bodies, such as enclosed marinas and harbours with little water exchange and high levels of boating activity and recommended ongoing development of improved and environmentally friendly AF products that would reduce copper usage.

To identify ecologically significant levels of copper and advise water quality guidelines, a number of lethal and sublethal effects of copper have been documented. Most often, experimental studies are used to assess the toxic effect of copper on a particular species (Hall et al., 1998; Rivera-Duarte et al., 2005), e.g., 1.2 μg/L Cu reduces the filtration rate of a marine bivalve (Hall et al., 1998) and 20 μg/L Cu impairs or inhibits the settlement of coral larvae (Reichelt-Brushett and Harrison, 2000). Diatoms exhibit reduced growth (50% at 100 μg/L Cu) (Cid et al., 1995) and oxidative stress upon exposure to copper, which can result in cell abnormalities (Rijstenbil et al., 1994).

Copper can be rapidly bound to sediments where its toxic effects impact on infaunal communities by reducing benthic recruitment (Olsgard, 1999). Field monitoring in Antarctica found sediments contaminated with 30 μg/g Cu were associated with reduced infaunal diversity (Stark et al., 2003), and experimental spiking of sediments above background levels in temperate regions also resulted in reduced abundances of infaunal species (Hall and Frid, 1995; Morrisey et al., 1996). Similarly, Norwegian communities were less diverse where copper exceeded 200 μg/g (Rygg, 1985) and sediment spiked with 300 μg/g Cu reduced the re-colonisation success of several polychaete species, a bivalve and brittle star in Norway (Olsgard, 1999). When these studies are considered in the context of potential estuarine contamination levels (between 1000 and 2400 μg/g Bryan and Langston, 1992; Irvine and Birch, 1998; Rygg, 1985), the continued use of copper can be viewed as a major threat to soft sediment communities.

3.3. 'Booster' biocides

Macroalgae have a relatively high tolerance to copper and 'booster' biocides initially were introduced to AF paints to improve their efficacy against these photosynthetic organisms (Voulvoulis et al., 1999). Four of the most widely used and studied 'booster' biocides are reviewed here (Table 5).

Irgarol 1051 (2-methylthio-4-tert-butylamino-6-cyclopropylamino-*S*-triazine) is an effective photoinhibitor and prevents algal fouling by decreasing electron transport within chloroplasts of photosystem II (Hall and Gardinali, 2004), but its effects have been found to extend to non-target species such as corals, mangroves and seagrasses, even at very low concentrations (Carbery et al., 2006). These effects are exacerbated by the continued persistence of Irgarol 1051 in the marine environment [half-life of around 100 days in seawater (Konstantinou and Albanis, 2004)], and because several degradation products (e.g., M1 and M3) demonstrate even greater toxicity than the parent compound and longer persistence in the environment (Okamura et al., 2000).

Irgarol 1051 has been detected in estuaries worldwide and hotspots of contamination are linked to vessel activity (Carbery et al., 2006; Konstantinou and Albanis, 2004; Readman et al., 1993; Sargent et al., 2000). van Wezel and van Vlaardingen (2004) derived environmental risk limits (ERLs) from the ecotoxicology and environmental chemistry of several booster biocides. Irgarol 1051 presents a potential ecological risk to 95% of organisms in the water column at levels above 0.024 μg/L and this value has already been exceeded in many areas worldwide, e.g., the Caribbean (1.3 μg/L (Carbery et al., 2006)), Sweden (0.4 μg/L (Dahl and Blanck, 1996)), the United Kingdom (0.13 μg/L (Scarlett et al., 1997)), France (1.7 μg/L (Readman et al., 1993)) and the United States (0.3 μg/L (Sapozhnikova et al., 2007)). Sediment resuspension has recently been highlighted as a source of ongoing Irgarol 1051 contamination; resulting in concentrations up to 0.23 μg/L with negative effects on the photosynthetic activity of the green alga *Ulva intestinalis* (Tolhurst et al., 2007).

Comparatively less is known about the other main 'booster' biocides; diuron, copper/zinc pyrithione or DCOIT. Diuron is used as an algaecide in AF paints and inhibits photosynthesis by blocking the electron transfer in photosystem II (Giacomazzi and Cochet, 2004). Diuron persists in the marine environment anywhere from between a month to a year (Giacomazzi and Cochet, 2004). However, significant contamination is more likely attributable to agricultural run-off rather than AF usage (Haynes et al., 2000). Pyrithiones have a broad spectrum of antimicrobial activity and have been widely used as bactericides, fungicides and algaecides due to their low water solubility and favourable environmental chemistry (Turley et al., 2000). The compounds are active against fungal cell walls, associated membranes and bacterial transport processes (Dinning, 1998). They also rapidly degrade in the water column to less toxic compounds, with a reported half-life of <24 h (Turley et al., 2000). DCOIT is currently considered to have low environmental risk among 'booster' biocides because of rapid degradation (Thomas, 2009). The compound has potential effects against a wide range of bacteria, fungi and algae and also rapidly degrades to compounds of negligible toxicity when released to the environment (estimated half-life of less than 24 h (Jacobson and Willingham, 2000)).

'Boosters' have sometimes been assumed as environmentally sound, but their effects are poorly understood. Accumulations of 'booster' biocides can reduce the germination and growth of non-target algae such as *Hormosira banksii* (e.g., diuron, zineb, DCOIT and zinc pyrithione Myers et al., 2006) and seagrasses such as

Table 5
Description of key booster biocides currently in use including their mode of action.

Common name	Chemical name	Chemical class	Application	Mode of action	Persistence
Chlorothalonil	2,4,5,6-Tetrachloroisophthalonitrile	Organochlorine	Fungicide	Inhibitor of mitochondrial electron transport	<2 d (seawater), <2 h (sediment)
Copper pyrithione (CuPT)	Copper 2-pyridinethiol-1-oxide	Organometallic salt	Microbiocide	Multi-site inhibitor (metabolic processes)	<1 h (seawater)
Dichlofluanid	*N*-Dichlorofluoromethylthio-*N*′,*N*′-dimethyl-*N*-phenylsulfamide	Organochlorine	Fungicide	Inhibitor of PS II electron transport	<1 d (seawater), <10 h (sediment)
DCOIT (Sea-Nine 211®)	(4,5-Dichloro-2-*n*-octyl-4-isothiazolin-3-one)	Isothiazolone	Herbicide	Inhibitor of PS II electron transport	<1 d (seawater), <12 h (sediment)
Diuron	3-(3,4-Dichlorophenyl)1,1-dimethylurea	Phenylurea	Herbicide	Inhibitor of PS II electron transport	1 months–1 year (seawater), 14 d (sediment)
Irgarol 1051®	2-Methylthio-4-Butylamino-6-Cyclopropylamine-s-triazine	*s*-Triazine	Herbicide	Inhibitor of PS II electron transport	100–350 d (seawater), 100–200 d (sediment)
TCMS pyridine	2,3,5,6-Tetrachloro-4-(methylsulfonyl) pyridine	Pyridine	Fungicide	Inhibitor of mitochondrial electron transport	Unknown
TCMTB	(2-Thiocyanomethylthio) benzothiazole	Benzothiazol	Fungicide	Inhibitor of mitochondrial electron transport	31–36 d (seawater), 1.5 d (sediment)
Thiram	Bis(dimethylthiocarbamoyl)disulfide	Dithiocarbamate	Fungicide	Multi-site inhibitor (metabolic processes)	<1.6 d (seawater), <1.6 d (sediment)
Zinc pyrithione (ZnPT)	Zinc 2-pyridinethiol-1-oxide	Organometallic salt	Microbiocide	Multi-site inhibitor (metabolic processes)	<1 d (seawater), <15 d (sediment)
Zineb	Zinc ethylene bisdithiocarbamate	Dithiocarbamate	Fungicide	Multi-site inhibitor (metabolic processes)	<20 d (seawater), <33 d (sediments)

Zostera marina (e.g., Irgarol 1051 and diuron Chesworth et al., 2004), reduce the photosynthetic efficiency of symbiotic algae in corals (e.g., Irgarol 1051; Carbery et al., 2006) and are toxic to sea urchin eggs and embryos (e.g., DCOIT, zinc and copper pyrithione Kobayashi and Okamura, 2002). However, knowledge gaps still exist regarding the interactive effects of different biocides (but see Arrhenius et al., 2006; Chesworth et al., 2004; Fernández-Alba et al., 2002; Manzo et al., 2008 for discussion of the more commonly used 'booster' biocides, e.g. diuron and Irgarol 1051), their occurrence, degradation, bioaccumulation and transport leading many researchers to recommend the precautionary principle when dealing with the regulation of these chemicals (Thomas, 2001).

3.4. Antifouling paints and the transfer and establishment of non-indigenous species (NIS)

Heavy metals in the marine environment are recognised as important selection agents acting on aquatic organisms (reviewed by Klerks and Weis, 1987). The use and accumulation of AF paints may in fact have facilitated the invasion of some metal tolerant NIS, by enabling their settlement and survival on vessel hulls, and also their establishment in polluted harbours (Piola and Johnston, 2008a).

Tributyltin is widely recognised as the most effective biocide and therefore transport of NIS on TBT-coated vessel hulls has likely been minimal (Minchin and Gollasch, 2003). Bacteria (e.g., *Vibrio, Alteromonas* and *Bacillus* sp.) and microalgae (e.g., diatoms *Achnanthes, Amphora* and *Amphiprora*) are the only organisms to display tolerance (Suzuki and Fukagawa, 1995; Suzuki et al., 1992; Wuertz et al., 1991) and to colonise TBT paints (Callow, 1986; Cassé and Swain, 2006; Thomas and Robinson, 1987). However, fouling species may have also colonised "niche areas" on vessels (unpainted or damaged parts of the hull, e.g., sea chests (Coutts and Dodgshun, 2007)). TBT paints afforded longer docking cycles, which may have facilitated establishment and reproductive maturation of fouling communities harbouring NIS in these unpainted areas.

Minchin and Gollasch (2003) suggest that the accumulation of TBT in estuaries has largely prevented the establishment of NIS due to its high toxicity, and prohibition of TBT use might result in greater opportunities for invaders. Recent incursions of the serpulid tubeworm *Hydroides sanctaecrucis* and the Asian green mussel *Perna viridis* into northern Australia may reflect this scenario (Lewis et al., 2006; Stafford et al., 2007). Other examples include the barnacle *Amphibalanus variegatus*, which was introduced to Japan in 1936, but after 1970 the barnacle was not found again until a 2004 survey (Horikoshi and Okamoto, 2005). This timeline closely parallels the introduction of TBT in the 1960s and its gradual phasing out. One possible scenario is that elevated levels of TBT in Japanese harbours during TBT use resulted in its disappearance (Dafforn et al., 2009) and reductions in TBT contamination since prohibition have enabled its re-colonisation.

Copper paints are highly effective after application; however when release rates drop below a critical level, tolerant species may recruit. Threshold toxic concentrations appear in general to be higher for marine invaders than for more sensitive endemic species (Allen, 1953; Dafforn et al., 2008; Piola and Johnston, 2008a; Wisely, 1963). Uncoated surfaces or areas where the AF coating is damaged on the hull will experience reduced exposure to leached copper and are likely to be colonized by tolerant species (Piola and Johnston, 2008b). Natural marine bacteria (Vaccaro et al., 1977) and algae (e.g., *Fucus vesiculosus* (Bryan and Gibbs, 1983) and *Chlorella vulgaris* (Butler et al., 1980; Foster, 1977)) develop resistant populations when exposed to copper contaminant, which makes them likely colonizers of copper paints. Copper tolerance has also been associated with the transport of ship fouling algae, e.g., *Ulva* (*Enteromorpha*) *compressa* (Reed and Moffat, 1983) and *Ectocarpus siliculosus* (Russell and Morris, 1972) and the establishment of the more tolerant alien *Ulva armoricana* over the native *Ulva pertusa* in polluted Korean estuaries (Trefry et al., 2008). Among the invertebrate foulers, attention has focused on several copper-tolerant species. The bryozoan *Watersipora subtorquata* can attach to copper-painted hulls and provide a toxic barrier, allowing less tolerant organisms to recruit (Fig. 3 (Allen, 1953; Floerl et al., 2004)). The cosmopolitan serpulid *Hydroides elegans* is also highly tolerant of copper (Allen, 1953; Dafforn et al., 2008, 2009; Piola and Johnston, 2008a), and its spread around the world is thought to have occurred primarily through biofouling on vessel hulls (Pettengill et al., 2007). Similarly, *H. sanctaecrucis* was first discovered in Australia on the hull of a vessel with depleted copper paint (Lewis et al., 2006).

Fig. 3. Positive interactions between fouling species. The non-indigenous bryozoan *Watersipora subtorquata* is shown growing directly onto a vessel hull coated with copper AF paint and facilitating algal recruitment. Photo: J. Lewis.

The use and accumulation of 'booster' biocides has also resulted in the development of tolerance in marine communities. High concentrations of zinc pyrithione increased growth of tolerant microbial species (Petersen et al., 2004), and exposure to diuron (Molander and Blanck, 1992) or Irgarol 1051 (Blanck et al., 2009) select for tolerant species of marine diatom. Similarly, exposure of microbial communities to DCOIT resulted in a loss of diversity with those species remaining able to tolerate the toxicant (Larsen et al., 2003). The continued use of 'booster' biocides in AF paints increases the likelihood that microbial communities may develop increased tolerance and therefore reduce their effectiveness at preventing biofouling and the transport of NIS.

4. Future directions for anti-fouling paints and the management of their impact

We argue that the way forward is to phase-out metals and organic biocides from AF paints and to adopt non-toxic alternatives (Carson et al., 2009; Piola et al., 2009). However, we call for caution in the timeframe for making these changes. Some effective alternative paints are now commercially available, but not well suited to all vessels, and the ecological benefits of banning toxic biocides have to be weighed up against the ecological impacts of greater fuel consumption and NIS transfer. Ecological impacts of greater fuel consumption include increased emission of greenhouse gases; for example, use of TBT in AF paints was estimated to have reduced carbon dioxide emissions by 23 million tonnes annually (Abbott et al., 2000). The ecological impacts of NIS transfer include competition with native species, predation and habitat modification

(Byers, 2000; Didham et al., 2005; Ross et al., 2004). In economic terms, little data exists on the global costs of marine introductions, although in the United States costs associated with harmful NIS are estimated at US$138 billion annually (Pimentel et al., 2000). Unless other AF coatings prove to be highly effective, restricting the use of copper might increase both operating costs for the shipping industry and the invasion opportunities for 'high risk' NIS (e.g., the invasive mussels *Perna viridis* or *Mytilopsis sallei*) on less effective AF coatings.

We propose a strategy to reduce biocidal contamination beginning with the regulation of release rates and stricter regulation of dry dock facilities, similar to the regulations that preceded the elimination of TBT from AF paints. Initial restrictions on TBT usage limited TBT release rates from AF paints to <4 or 5 $\mu g/cm^2$/day and resulted in the removal of the more harmful conventional paints from the market, leaving only SPC paints with more controlled release rates (Evans, 1999). Conventional copper-based paints are still the most widely used by recreational vessel owners due to their affordability, but these also have greater polluting potential than SPCs and other new technology coatings (Valkirs et al., 2003). Therefore we suggest initially imposing restrictions on copper release rates that would reduce, then eliminate the usage of conventional paints. This should be accompanied by monitoring to identify the effects of this form of regulation on copper loads in polluted hotspots.

Despite recent TBT regulations, commercial ports and recreational marinas continue to experience exhibit TBT contamination (Gibson and Wilson, 2003). Given the uncertainty surrounding TBT persistence in the environment (Clark et al., 1988), remediation of contaminated areas seems a logical next step. Possible fixes include in situ remediation using resistant organisms, e.g., bacteria or microalgae to degrade organotins in sediments and reduce their availability through bioaccumulation (Dowson et al., 1996; Gadd, 2000). Other alternatives could involve the removal or containment of contaminated material through dredging and disposal or capping of sediments. However, the implementation of any remediation technique requires the integration of different considerations, including the chemical behaviour of the target contaminant as well as local environmental conditions and resident biota (Simpson et al., 2002; Wang et al., 2004). Moreover, the process of remediation could prove to be both lengthy (Dubey and Roy, 2003), and costly raising the question of liability (Champ, 2003).

The environmental impacts of biocides have driven research in an environmentally friendly direction, with a particular focus on foul-release technology and natural marine compounds to inhibit biofouling. Foul-release coatings rely on silicone technology which does not prevent settlement, but reduces the strength of attachment of settling organisms. Although promising, these coatings are best suited to fast moving vessels as they generally require a speed of 20 knots or more to dislodge biofouling (Srinivasan and Swain, 2007). Application is costly and frequent cleaning would be necessary to prevent build up of biofouling on vessels that do not have the activity or speed to self-clean (Carson et al., 2009). However, these coatings do not leach and could prove to be more durable than copper-based paints for some vessel applications (Carson et al., 2009). From the successful first vessel trials of a foul release coating in 1987, and full vessel application in 1993, a foul release coating was formally introduced for the rapidly expanding fast ferry market in 1996 and many of the world's leading fast ferry operators now use foul-release coatings (Townsin and Anderson, 2009). Products were subsequently targeted at the high activity, high speed (>15 knot) scheduled ship sector, including container ships, gas carriers and cruise liners. Sales of foul-release coatings rose significantly following the adoption of the IMO AFS Convention in 2003, then further increased in subsequent years when the price of fuel rose dramatically and the prospect of reduced fuel consumption further attracted ship owners and operators to the technology (Townsin and Anderson, 2009). However, total sales of foul-release coatings have risen to no more than 10% by volume for commercial shipping and remain at less than 1% in the yacht sector (C.D. Anderson, pers. comm.).

Although still in the early stages of development, paints containing naturally-produced compounds isolated from marine organisms also show promise as an environmentally friendly alternative to biocides (Hellio et al., 2009). Sources of natural AF compounds include the metabolites produced by sessile organisms such as cnidarians, ascidians, sponges, algae and seagrasses. Halogenated furanones extracted from the red alga *Delisea pulchra* have proved the most effective natural product in deterring barnacle settlement (De Nys et al., 1995). Bacteria isolated from organisms in the marine environment are also a possible source of natural AF compounds. For example, *Pseudoalteromonas tunicata* isolated from the tunic of the ascidian *Ciona intestinalis* produces five compounds that inhibit a range of organisms (Burgess et al., 2003), and bacterial strains isolated from the surface of the seaweed *Fucus serratus* and the nudibranch *Archidoris pseudoargus* were found to inhibit settlement by other micro-organisms (Armstrong et al., 2000). If these compounds can be incorporated into effective coatings, there is the potential to disrupt the early stages of biofilm development and therefore inhibit the settlement of some macrofauna (Burgess et al., 2003). Difficulties in this approach lie in the identification of compounds that inhibit a wide range of fouling organisms and the subsequent integration of these compounds into a coating that can be applied to a vessel hull (Yebra et al., 2004). "Natural" anti-fouling compounds also face the same regulatory hurdles to approval as any other new anti-fouling biocides with the estimated cost of assembling data packages on efficacy and environmental fate and effects many millions of dollars, and the timeline for the approval process of approximately 10 years (Rittschof, 2000).

5. Conclusion

Decisions regarding the use and regulation of AF paints in the marine environment are complex and require the integration of information regarding the economic and ecological costs and benefits of different strategies. Bans on TBT were primarily based on the economic costs to the oyster industry, but also because of ecological impacts on non-commercial species, bioaccumulation by a range of organisms, and potential human health risks. The subsequent shift to copper paints containing 'booster' biocides may still result in environmental impacts, toxicity to non-target marine organisms and the spread of tolerant NIS.

An ideal situation would allow the complete elimination of toxic biocides from AF paints, however, in reality this poses the question of what do we replace them with? We currently do not have a viable option for widespread replacement of copper in AF paints (although foul-release and natural compounds show some potential). Without an effective replacement, the ecological costs of increased bioinvasions and the economic costs of increased drag, may outweigh the impacts of current AF strategies. Therefore we would advise caution in regulating copper and the gradual introduction of increased restrictions, similar to the TBT strategy, to allow time for the development and implementation of more environmentally-friendly alternatives.

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