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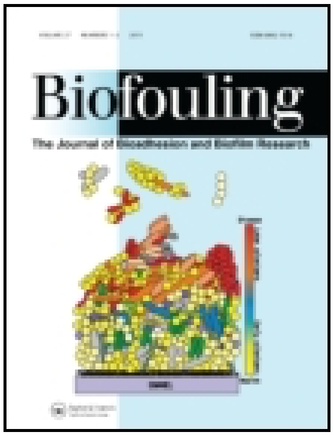

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MINI REVIEW

The environmental fate and effects of antifouling paint biocides

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Antifouling (AF) biocides are the active ingredients in AF paints that prevent the settlement, adhesion and growth of organisms to a painted surface. A wide range of chemicals are used as AF biocides, which have very different physico-chemical properties and therefore differing environmental fates, behaviour and effects. Copper has been used as an antifoulant for centuries and extensive research has been performed to understand how copper speciation influences bioavailability and toxicity. For biocides that have been widely used over a number of decades, for example Irgarol 1051 and diuron, there are a large amount of environmental data in the public domain, including for their respective metabolites, that allows their environmental safety and potential risk to the environment to be assessed. For other biocides such as dichlofluanid, DCOIT (SeaNine 211) and zinc/copper pyrithione, there is a good understanding of their fate and effects. However, few monitoring studies have been performed and not so much is known about the fate and effects of their metabolites. There are also new or candidate biocides such as triphenylborane pyridine, Econea, capsaicin and medetomidine for which there is very little information in the public domain. This review provides an overview of the environmental fate and occurrence data that are in the public domain for AF biocides and provides some insight into the effects of these compounds on non-target organisms.

Keywords: antifouling paint; biocides; copper; environmental fate; fouling

Introduction

Colonisation by fouling organisms is a problem for any structure placed in the aquatic environment and can be controlled through both chemical biocides and non-biocidal technologies. In spite of the large number of publications reporting research on diverse non-biocidal technologies (eg Schumacher et al. 2007; Beigbeder et al. 2008; Perez-Roa et al. 2008, 2009; McMaster et al. 2009) and an increase in the commercial use of fouling-release coatings, the majority of vessels are protected by antifouling (AF) paint containing biocides. The journal *Biofouling* published its last review on the environmental fate and behaviour of biocides used in AF paints in 2001 (Thomas 2001). At that time, it was clear from the broad range of environmental properties shown by AF paint biocides that their fate and behaviour would differ widely. It was also notable that data were available for the biocides most commonly used in Europe and North America (ie Irgarol 1051, DCOIT (SeaNine 211) and zinc pyrithione), whilst very little or no data were available for many other biocides. Data limitations regarding a number of key environmental fate processes such as equilibrium partition coefficients meant that predicting environmental concentrations was difficult and very few data were available for biocide transformation products. Data gaps were also evident regarding the uptake of biocides by organisms and the fate of biocidal compounds associated with paint waste. These significant gaps meant that in order to underpin environmental risk assessments of biocidal products, further data were required.

Since 2001, a number of national and international projects have resulted in a significant improvement in understanding of the occurrence, fate and effects of AF biocides. During this period, the use of certain biocides has been restricted by some countries and in Europe a large amount of data have been gathered as part of the Biocidal Products Directive (BPD, 98/8/EC). Additionally, new biocides have become of interest over the last few years such as the emergence of triphenylborane pyridine (TPBP) in Japan, Econea in the US, capsaicin in China and novel biocides such as medetomidine in Sweden.

The key properties of a good AF biocide with respect to the environment is one that is effective in preventing fouling of the painted surface without persisting at concentrations greater than those that can cause detrimental environmental effects. This can be achieved through rapid transformation following release from the surface or possibly a very specific mode of action. In this updated review, an overview of

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the biocides currently used globally is presented. Knowledge prior to 2001 is summarised and the significant peer reviewed articles are reviewed that have improved understanding of biocide occurrence, and their fate and effects over the last 8–9 years.

Review of published data

Antifouling biocides and their key environmental properties

The key environmental properties of the most predominantly used biocides are presented in Table 1. Irgarol 1051 (2-(*tert*-butylamino)-4-(cyclopropylamino)-6-(methylthio)-*s*-triazine) is a widely used triazine-based biocide that functions through inhibiting photosynthesis through blocking the electron transport at photosystem II. Irgarol 1051 and diuron have been extensively used in AF paints as restrictions were placed on the use of tributyltin. Diuron also works through the inhibition of photosystem II and along with Irgarol 1051 has been shown to accumulate in areas where there is intense boating activity. This is predominantly due to the fact that both biocides are relatively persistent in seawater and do not extensively partition into other environmental compartments such as sediments. Other biocides, for example dichlofluanid, have been reported to occur in sediments, whereas the occurrence of DCOIT and the pyrithione salts of copper and zinc have rarely been reported. Understanding the processes which control the release of AF biocides into the environment and their behaviour is essential in helping to understand whether they have any effect on the environment. Table 1 lists data associated with easily identifying the biocide by its IUPAC and trade names as well as chemical abstract services (CAS) number. In addition, it provides key information on the environmental data that essentially control their fate in terms of partition and degradation. The data presented are the octanol–water partition coefficient K_{OW}, degradation half-life ($t½$) and principal degradation mechanism, as well as the known primary metabolites. Where data are unavailable this is made clear. These data, as well as other important environmental data, are discussed further in the following sections.

Use in AF paints and leaching studies

Globally, a wide range of chemicals is used as AF biocides with differing degrees of regulation. For example, in China dichlorodiphenyltrichloroethane (DDT) is recognised as an AF biocide whilst in Europe the use of chemicals as AF biocides will soon be restricted to those approved by the EUs BPD. Globally, there is currently a wide range of chemicals used as AF biocides. Copper, copper pyrithione, zinc pyrithione, TPBP, diuron, SeaNine 211 (DCOIT), Iragrol 1051, chlorothalonil, cichlofluanid, cuprous thiocyanate, ziram, zineb, trichlorophenyl maleimide, Densil S-100, naphthenic acid copper salts, thiram, tolyfluanid, Econea, DDT and capsaicin are just a few of the antifoulants in use. A summary of biocide use and restrictions is presented in Table 2. In Europe, ahead of the BPD, all biocides used in the UK, Sweden, Finland, The Netherlands, Eire, Belgium, Austria and Malta must be registered under existing pesticide laws. In both the UK and Denmark, diuron and Irgarol 1051 are prohibited for use on pleasure craft. The use of diuron is also restricted in The Netherlands. Copper use is restricted in the Baltic by both Sweden and Denmark. Copper use is forbidden on pleasure boats that operate in the Swedish Baltic Sea; the copper release rate from all other vessels operating in the Baltic must be $<55\ \mu g\ cm^{-2}\ day^{-1}$. In Denmark, the regulation of copper is such that the use of copper containing paints with a cumulative copper release rate $>200\ \mu g\ cm^{-2}$ after 14 days and $350\ \mu g\ cm^{-2}$ after 30 days are prohibited on boats <25 m in length. Outside Europe biocides must be registered for use with a regulatory authority. For example, in North America biocides must be registered for use by the United States EPA and Health Canada. Likewise in Australia and New Zealand, whereas in Japan there is no specific AF regulation.

Biocide release rates (or leaching rates) are very important factors when models are used to predict environmental concentrations. Over the past 8 years, very few studies have been reported on the release of AF biocides from painted surfaces. It is possible to determine the standard laboratory release rate of a biocide using standard protocols provided by American Society for Testing and Materials (ASTM) and International Standards Organisation (ISO). However, published release rate data are scarce. As discussed in the last review (Thomas 2001), there are concerns that standard laboratory methods do not replicate what occurs in the environment and are, therefore, not representative (Valkirs et al. 2003; Hastbeck and Ellor 2005). To this end, various modelling approaches have been considered as suitable alternatives to laboratory measurements (Kiil et al. 2002a,b, 2003; Yebra et al. 2006a,b,c). Modelling approaches offer the opportunity to estimate the amount of a biocide released during the lifetime of a paint based upon the biocidal content of the paint. The release of a biocide is very specific to the type of paint and to the biocide (Thomas et al. 1999; Thomas 2001). Alternative developing technologies such as nanotechnology appear to offer promise. For example, absorption or microencapsulation of biocides into nanoparticles to control the release of biocides and prevent premature leaching,

Table 1. Key environmental properties of the main antifouling biocides currently in use.

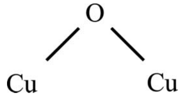
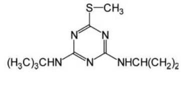
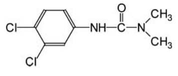
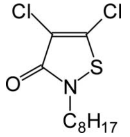
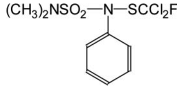
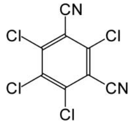
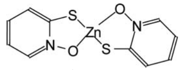
Name	Copper oxide	Irgarol 1051 (2-*N*-tert-butyl-4-*N*-cyclopropyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine)	Diuron (1-(3,4-dichlorophenyl)-3,3-dimethylurea)	DCOIT SeaNine 211 (4,5-dichloro-2-*n*-octyl-3-(2*H*)-isothiazolin-3-one)	Dichlofluanid (*N*′-dimethyl-*N*-phenylsulphamide)	Chlorothalonil (2,4,5,6-tetrachloro-isophthalonitrile)	Zinc/Copper pyrithione (bis(1 hydroxy-2(1*H*)-pyridethionato-O,S)-T-4 zinc)/(bis (1hydroxy-2(1*H*)-pyridethionato-O,S)-T-4 copper)
Structure							 
Molecular weight	143.1	253.367	233.09	282.227	253.367	265.89	317.69/315.85
CAS No.	1317-39-1	28159-98-0	330-54-1	64359-81-5	28159-98-0	1897-45-6	154592-20-8
Log K_{OW}		2.8	2.8	2.8	2.8	2.64–4.38	0.97
Degradation	<24 h	$t\frac{1}{2} = 100–250$ days in eawater, persistent in sediments	Persistent in seawater, $t\frac{1}{2} = 14$ days in marine sediment (biotic degradation)	<24 h (Biotic degradation)	18 h	1.8–8 days in seawater (biotic degradation)	<24 h in seawater (photolysis)
Metabolites	Cu^+, Cu^{2+}, Cu-organic ligand, Cu-inorganic ligand	2-methylthio-4-tert-butylamino-6-amino-*s*-triazine (M1/GS26575) M2 (3-[4-tert butylamino-6-methylthiol-s-triazin-2-ylamino]-propionaldehyde (the *N*-propional dehyde derivative of M1) and M3, *N*′-di-*tert*-butyl-6-methylthiol-*s*-triazine-2,4-diamine	1-(3-chlorophenyl)-3,1-dimethylurea (CPDU), 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichloro phenyl)urea (DCPU)	*N*-octyl oxamic acid, 4,5 dichloro-thiazole and *N*-octyl carbamic acid	*N*′-dimethyl-*N*-phenyl-sulphamide (DMSA)	4-hydroxy-2,5,6-trichlorisophthalo nitrile, 5-cyano-4,6,7-trichloro-2*H*-1,2-benzisothiazol-3-one	2-pyridine sulphonic acid

Table 2. Summary of biocide use/restrictions.

Substance	IUPAC name	CAS	Use/known restrictions	Application submitted to BPD
Tolylfluanid	1,1-dichloro-*N*-(dimethylsulfamoyl)-1-fluoro-*N*-(4-methylphenyl)methanes			
ulfenamide	731-27-1	Not currently registered in UK	✓	
Dichlofluanid	*N*-dichlorofluoromethylthio-*N*′,*N*′-dimethyl-*N*-phenylsulfamide	1085-98-9	None	✓
Copper thiocyanate		1111-67-7	Inport, sale and use of paints with a cumulative copper release rate >200 $\mu g\,cm^{-2}$ after 14 days and 350 $\mu g\,cm^{-2}$ after 30 days on boats <25 m in length are prohibited in Denmark. Not permitted for use in the Swedish Baltic	✓
Dicopper oxide		1317-39-1		✓
Zineb	zinc-ethylene (dithiocarbamate)	12122-67-7	No known global restrictions	✓
Zinc pyrithione	bis(2-pyridylthio)zinc 1,1′-dioxide	236-671-3	No known global restrictions. Approved in US and for pleasure boats in UK	✓
Copper pyrithione	bis(2-pyridylthio)copper 1,1′-dioxide	238-984-0	No known global restrictions	✓
Irgarol 1051	2-*N*-*tert*-butyl-4-*N*-cyclopropyl-6-methylsulfanyl-1,3,5-triazine-2			
4-diamine	28159-98-0	Restricted use in UK and Denmark	✓	
DCOIT	4,5-dichloro-2-*n*-octyl-3-(2*H*)-*iso*thiazolin-3-one)	64359-81-5	Widely used following professional application only	✓
Econea	4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)- 1*H*-pyrrole-3-carbonitrile	122454-29-9	Registered with the U.S. EPA for formulating use, and is listed on the chemical inventories in US, South Korea, New Zealand and China. Paints reported to be available from late 2009	✓
Medetomidine	(*RS*)-4-[1-(2,3-dimethylphenyl)ethyl]-3*H*-imidazole	106807-72-1	Not currently used but undergoing assessment as part of the BPD	✓
Diuron	(1-(3,4-dichlorophenyl)-3,3-dimethylurea)	330-54-1	Prohibited for use in UK and the Netherlands and on pleasure boats in Denmark	
Triphenylborane pyridine	Pyridine-triphenylborane	971-66-4	Reported to be used in Japan	
Capsaicin		8023-77-6	No known use at present	
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane	50-29-3	Only known use is in China. Controlled by the Stockholm Convention on Persistent Organic Pollutants	

Table prepared with the information available in June 2009.
BPD, Biocidal Products Directive.

appears to offer a superior control mechanism for biocide release, which would result in reduced environmental loadings (Shtykova et al. 2009).

Key environmental effects

Environmental effects data are very important in the overall assessment of the risks AF biocides pose to the aquatic environment. Such data are used to derive predicted no-effect concentrations (PNEC) which are estimated from the toxicity data available for each compound along with a safety factor based upon the amount and type of data available.

Copper oxide

The speciation of copper is essential for understanding its bioavailability and subsequent toxicity to aquatic organisms. The free copper ions (Cu^+, Cu^{2+}) are the most bioavailable with inorganic-copper being bioavailable to a lesser extent, whereas copper bound to organic matter is widely thought to be non-bioavailable and therefore non-toxic (Arnold et al. 2005; Brooks (unpublished data); Brooks et al. 2007). The effects of dissolved organic carbon (DOC) on reducing copper toxicity have been reported in fish (Playle et al. 1993a,b), bivalves (Brooks et al. 2007), echinoderms (Lorenzo et al. 2006), macroalgae (Brooks et al. 2008) and unicellular algae (Florence and Stauber 1986). In each case, DOC binding of the free copper ion was responsible for reducing the bioavailability of the metal causing the reduction in copper toxicity.

There have been a plethora of ecotoxicity tests that have been conducted over the last 50 years on copper. However, many of the earlier tests and some recent ones have quoted only nominal copper concentrations. Because of the importance of copper speciation in determining its toxicity, only studies that have reported measured copper concentrations have been considered for this review. *In vivo* toxicity data for the main taxonomic groups and life stages have been compiled by the United States Environmental Protection Agency (US EPA), which have been summarised by Brooks and Waldock (2009). The embryo/larval stages of the mussel, oyster and sea urchin were found to be sensitive, with total dissolved copper EC50 concentrations of 6.8, 12.1 and 14.3 $\mu g\ l^{-1}$, respectively. Overall, fish were the most tolerant group to copper exposure with EC/LC50 concentrations ranging between 0.12 and 1.5 mg l^{-1} total dissolved copper. Of all species tested, cyanobacteria have been found to be the most sensitive group of organisms to copper exposure, with growth effects reported at 0.2 $\mu g\ l^{-1}$ total dissolved copper (0.63 ng l^{-1} free copper) (Moffett and Brand 1996). However, since these values are significantly below the natural background concentrations for copper in coastal waters (1–2 $\mu g\ l^{-1}$), there is an argument amongst regulators and scientist whether it is unrealistic for cyanobacteria to be included in current risk guidelines for these coastal water bodies.

Organic biocides

To complement the environmental fate studies performed on AF biocides, a large number of studies have been performed on their toxicity to non-target organisms. This review does not provide a summary of such data as recent reviews are available (eg Mochida and Fujii 2009).

It is unsurprising that the herbicides Irgarol 1051 and diuron, which inhibit photosynthesis, are much more toxic to phytoplankton species than other aquatic animals (Figure 1). Irgarol 1051 appears to be especially toxic to the freshwater diatom (*Navicula pelliculosa*; (5 day EC50 0.136 $\mu g\ l^{-1}$) (Hall et al. 1999) and the freshwater macrophytes *Chara vulgaris* (14 day EC50 0.017 ng l^{-1}) and *Apium nodiflorum* (14 day EC50 0.014 ng l^{-1}) (Lambert et al. 2006). These are important data in light of the fact that AF biocide use is not confined to the marine environment and that freshwater boating areas are often areas of limited water exchange. Toxicity data are also available for the Irgarol 1051 metabolite M1, which tends to be less toxic to phytoplankton but of similar toxicity to other aquatic animals (Hall et al. 1999; Gatidou et al. 2007). The metabolites of diuron have also been shown to be less toxic to phytoplankton than diuron itself (Gatidou et al. 2007).

DCOIT shows toxic effects at concentrations between 2.7 and 32 $\mu g\ l^{-1}$, which is very similar to that of the pyrithione biocdes CuPT and ZnPT (Mochida and Fujii 2009). Although many data are available for the effects of AF biocides on target and

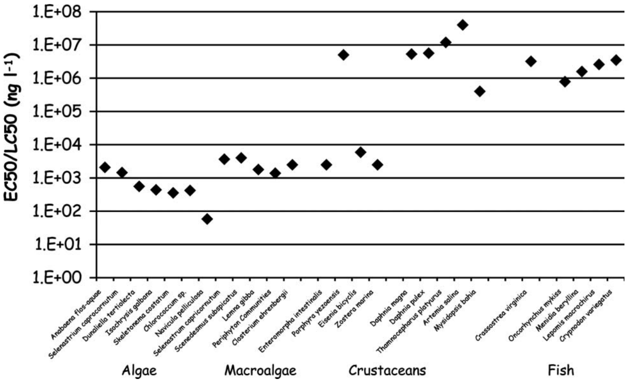


Figure 1. Comparative toxicity (EC50/LC50) of Irgarol 1051 to algae, macroalgae, crustaceans and fish.

non-target species, few data are available in the open literature on the toxic effects of biocide transformation products, ie the products of biocide degradation. Of the newer biocides, few data are available for TPBP. TPBP has a reported 14 day LC50 of 61 μg l^{-1} to juvenile rainbow trout (*Oncorhynchus mykiss*) (Okamura et al. 2002), a 48 h EC50 of 130 μg l^{-1} to the crustacean, *Artemia salina* and a 72 h EC50 of 2.2 μg l^{-1} to the diatom *Skeletonema costatum* (Okamura et al. 2009). TPBP transformation products were much less toxic when tested with the same species (Okamura et al. 2009).

Even though medetomidine, which is targeted against barnacles and inhibits cyprid settlement at nanomolar concentrations, has yet to be registered as an AF biocide, a number of studies have been published on its effects on non-target organisms. Medetomidine has been reported to reduce the pheromone induced mate search of the amphipod *Corophium volutator* at 10 μg l^{-1} (Krång and Dahlström 2006), and to cause a significant decrease in the burrowing response and sediment reworking activity of the bivavlve *Abra nitida* with an EC50 of 86 μg l^{-1} and 0.9 μg l^{-1}, respectively (Bellas et al. 2006). Other sub-lethal effects that have been reported include effects on respiration frequency and oxygen consumption of juvenile turbot (*Psetta maxima*) (Hilvarsson et al. 2007) and on cytochrome P4501A (CYP1A) activity in rainbow trout (*Oncorhynchus mykiss*), turbot (*Psetta maxima*) and Atlantic cod (*Gadus morhua*) (Lennquist et al. 2008).

Environmental fate

There are a number of key processes that control the environmental fate of any chemical released into the environment. For AF biocides, the processes that control the persistence and eventual sinks are very important because biocides are deliberately released into the water column. Understanding of biocides (and other contaminants in general) has shown that when biocides do not undergo rapid degradation once released into the water column they can persist resulting in elevated concentrations. The key processes that are important in understanding the fate of AF biocides are degradation, including the specific mechanism, partition onto sediments and uptake into organisms. Compounds with a half-life >50 days are considered to be persistent whereas those with a log $K_{\mathrm{OW}} > 3$ are considered to bioaccumulate. The sediment-specific equilibrium sorption constant, K_{d}, describes the distribution of a compound between sediment and water. The values range from 10^5 for compounds such as DDT and polychlorinated biphenyls (PCBs) that bind strongly to sediments to <1 for compounds that are weakly sorbed and soluble in water.

Copper oxide

Copper oxide leaches from the boat surface and enters the water as a free copper ion (Cu^+), which is immediately oxidised to Cu^{2+} and forms complexes with inorganic and organic ligands. The process is thought to occur within the first few micrometers of the painted surface. The presence of a biofilm on the vessel surface can act as a source of DOC, which can bind the free copper. In the dissolved phase, the proportion of copper existing as the free ion, inorganic or organic complexed copper, varies greatly with respect to water properties, such as DOC, pH, hardness and salinity (Arnold et al. 2005). Labile copper (free and inorganically complexed) has been found to make up between 10 and 30% of the total dissolved copper concentration in marinas and harbours around the UK coastline (Jones and Bolam 2007). However, this proportion can be reduced to as little as 0.1% when only the free copper ion is considered (HSE 1999).

Copper has a tendency to adsorb to suspended particulate matter (SPM), which will eventually settle and accumulate in the sediment. As a result, copper concentrations are often two to three orders of magnitude higher in the sediment than in the water column, which is confirmed from coastal monitoring programs (eg Brooks (unpublished data); Jones and Bolam 2007). In aerobic sediments, copper is mainly bound to metal oxides and high-molecular-weight organic matter, with around 5% of the copper easily exchangeable between water and sediment (Roper 1990). However, a recent study found $>15\%$ of copper existing in an exchangeable form, available to contribute to the copper concentration of the water column (Choi et al. 2006). In anaerobic sediments, copper is bound strongly to sulphides reducing their bioavailability. However, for both aerobic and anaerobic conditions, sediment disturbance events, such as dredging and storms can significantly increase the copper input into the water column from the underlying sediment. In areas of high sediment copper concentrations, such as harbours and marinas, resuspension of the sediment can release bioavailable copper into the water, thereby increasing the risk to aquatic life.

Irgarol 1051

Irgarol 1051 does not easily degrade in water which may explain its persistence once released from painted surfaces (Table 1) (Scarlett et al. 1999). In natural seawater, Irgarol 1051 has a half-life ($t½$) of between

100 and 350 days (Hall et al. 1999; Scarlett et al. 1999; Thomas et al. 2002) whilst being very persistent in anaerobic sediments (Thomas et al. 2003). 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (M1/GS26575) is the principal transformation product of Irgarol 1051, produced through n-dealkylation following biodegradation (Liu et al. 1997), photodegradation (Okamura et al. 1999) or chemical hydrolysis (Liu et al. 1999) (Figure 2). Other transformation products of Irgarol 1051 include M2 (3-[4-*tert*butylamino-6-methylthiol-*s*-triazin-2-ylamino]-propionaldehyde (the *N*-propionaldehyde derivative of M1) (Lam et al. 2005) and M3, *N'*-di-*tert*-butyl-6-methylthiol-*s*-triazine-2,4-diamine. All metabolites have been shown to occur in the environment (Lam et al. 2005). The persistence of the metabolites is largely unknown. However, GS26575 is relatively stable in water ($t\frac{1}{2} = >200$ days) and sediment ($t\frac{1}{2} = 260$ days) (Okamura 2002; Thomas et al. 2002).

Water-sediment partitioning coefficients suggest that Irgarol 1051 will be mainly associated with the dissolved phase and modelled estimations suggest that around 4% of Irgarol 1051 in marina waters will partition to sediments (Rogers et al. 1996). This is confirmed by a reported K_d of between 142 and 3100 kg l^{-1} and a K_{OC} of between 251 and 63095 kg l^{-1} for marine sediments (Tolosa et al. 1996; Biselli et al. 2000, Thomas et al. 2002). Indeed, Irgarol 1051 occurs in sediments with reports from the UK ($<$10–132 ng g^{-1}, $<$1–30 ng g^{-1}) (Gough et al. 1994; Thomas 1999, 2001; Thomas et al. 2002); Switzerland (2.5–8 ng g^{-1}) (Tóth 1996), Sweden ($<$10 ng g^{-1}) (Haglund et al. 2001) and Germany ($<$1–220 ng g^{-1}) (Biselli et al. 2000). A few studies have also reported the occurrence of M1 in sediments at concentrations of between $<$0.4 and 10 ng g^{-1} suggesting that it can partition onto sediments, albeit to a lesser degree than Irgarol 1051 (Hall et al. 1999; Thomas et al. 2000). All AF paint biocides can enter the environment associated with paint particles following the scrubbing of boat hulls. Irgarol 1051 is persistent in sediments whether adsorbed to sediment particles or associated with paint particles (Thomas et al. 2003). Little is known about the bioavailabilty of Irgarol 1051 present in sediments. It has been shown that the resuspension of sediments contaminated with Irgarol 1051 can result in release of bioavailable Irgarol 1051 into the water column (Tolhurst et al. 2007).

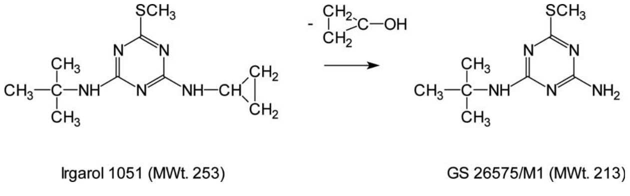


Figure 2. Degradation pathway of Irgarol 1051.

Diuron

Diuron also persists in seawater, but is less persistent in marine sediments with a half-life of 14 days (Callow and Finlay 1995; Thomas et al. 2002). The aerobic degradation of diuron results in the transformation of diuron to 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichlorophenyl)urea (DCPU). Anaerobic degradation in sediments results in the formation of 1-(3-chlorophenyl)-3,1-dimethylurea (CPDU) (Figure 3) (Ellis and Camper 1982). Diuron is relatively soluble in water (35 mg l^{-1}) and has a reported log K_{OW} of 2.8. Diuron is reported to have a K_d of 8.9 ± 13.4 kg l^{-1} in freshwater (House et al. 1997) and 4 ± 1 kg l^{-1} in seawater, which when normalised to organic carbon gives a K_{OC} of around 250 kg l^{-1} (Thomas et al. 2002). These data suggest that diuron will predominantly be found in the dissolved phase and only weakly sorbed to sediments which is in line with reported environmental concentrations. For example, although diuron has been reported to be present at high concentrations in marina surface waters it has only been detected at low concentrations in sediments (Thomas et al. 2000; Lamoree et al. 2002). Concentrations as high as 1.4 μg g^{-1} have been reported in sediments collected from an enclosed marina in the UK. However, these high concentrations are likely to be due to the contamination

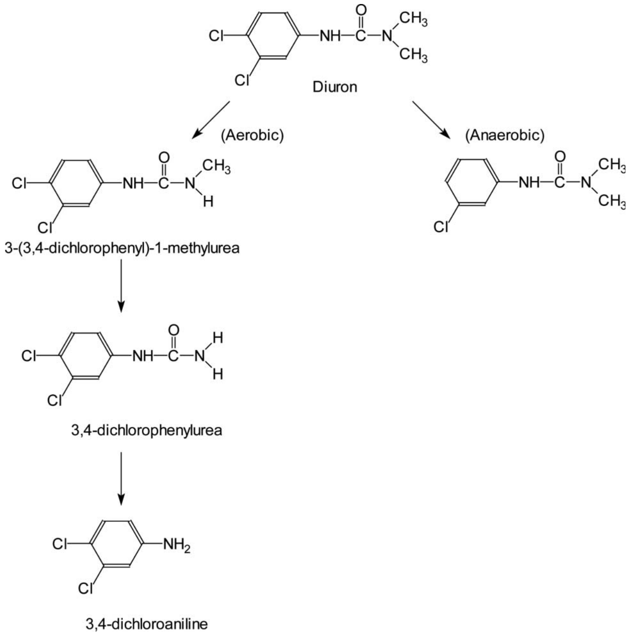


Figure 3. Proposed degradation pathway for diuron under aerobic and anaerobic conditions.

of marina sediments with AF paint particles that are washed into the water following shore-side scrubbing of boat hulls on hard standings (Thomas et al. 2000). Although relatively persistent in seawater, diuron is thought to undergo degradation under anaerobic conditions to form CPDU ($t½ = 14$ days) (Thomas et al. 2003). When associated with AF paint particles, this transformation is significantly reduced with very little degradation seen over 42 days.

DCOIT

DCOIT is reported to be a relatively labile compound compared to the above biocides and degrades rapidly in natural seawater ($t½ < 24$ h) and sediment (Callow and Willingham 1996; Jacobson and Willingham 2000; Thomas et al. 2002, 2003). DCOIT predominantly undergoes biotic degradation under both aerobic and anaerobic conditions with biological degradation over 200 times faster than hydrolysis or photolysis (Callow and Willingham 1996; Jacobson and Willingham 2000). Biodegradation of DCOIT involves the cleavage of the isothiazolone ring and subsequent oxidation of the alkyl metabolites formed primarily resulting in the formation of *N*-octyl oxamic acid, 4,5 dichloro-thiazole and *N*-octyl carbamic acid (Figure 4). DCOIT has a log K_{OW} of 2.8, an aqueous solubility of 14 mg l^{-1} and a K_d of between 250 and 625 kg l^{-1}. It has a K_{OC} of around 1.6×10^4 kg l^{-1} for aquatic sediments, which suggest that DCOIT will bind strongly and essentially irreversibly to sediment (Jacobson and Willingham 2000; Thomas 2001). DCOIT degrades rapidly in sediments with a half-life of <12 h. However, as with other AF biocides it is much more persistent when present in sediments associated with paint particles ($t½ = 10$ days) (Thomas et al. 2003).

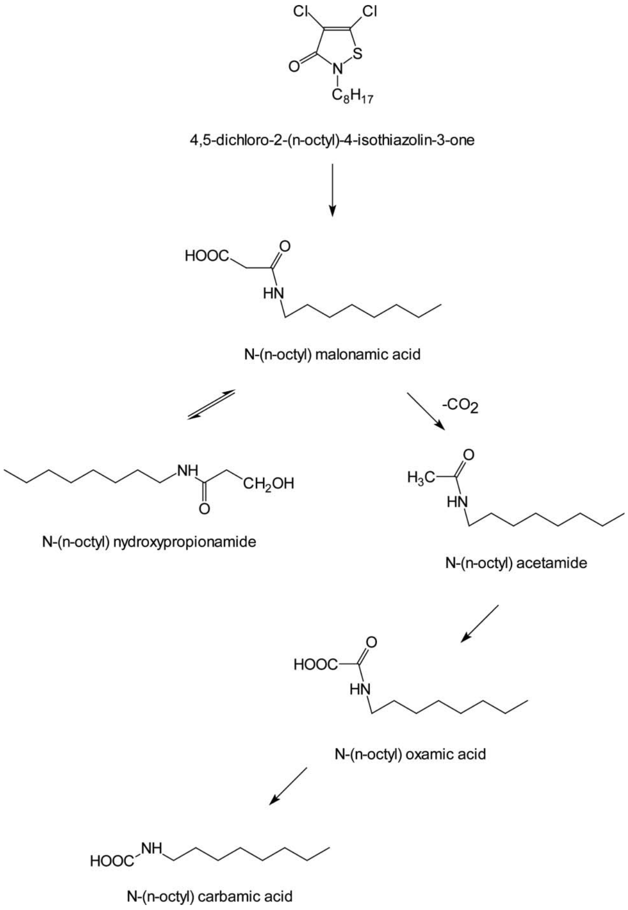


Figure 4. Proposed metabolic pathway for DECOIT (SeaNine 211) under aerobic conditions.

Dichlofluanid

In water, dichlofluanid is thought to rapidly undergo hydrolysis to form *N*′-dimethyl-*N*-phenyl-sulphamide (DMSA) (Hamwijk et al. 2005) with a half-life in seawater of <20 h (Callow and Finlay 1995; Thomas et al. 2002). Dichlofluanid is also known to undergo photolysis with the presence of humic and fluvic acids known to inhibit photodegradation (Sakkas et al. 2001). Very few data are available on the partitioning of dichlofluanid to sediments. This may be due to the rapid transformation of dichlofluanid to DMSA, although dichlofluanid has been reported to occur in marine sediments (Voulvoulis et al. 2000). Any dichlofluanid which absorbs to sediments will be rapidly removed with a published half-life of <10 h in marine sediments. Even when present in sediments associated with paint particles, dichlofluanid has been found to rapidly degrade ($t½ = 1.4$ days) (Thomas et al. 2003). Dichlofluanid degrades to form DMSA, dichlorofluoromethane, *n*-dichlorofluoromethylthionaniline and aniline (Figure 5) (Thomas et al. 2002, 2003).

Chlorothalonil

Chlorothalonil has been shown to rapidly degrade in both fresh and estuarine waters with a $t½$ of between 4 and 150 h in natural fresh water (Davies 1987) and 1.8 and 8 days in a natural estuarine/sediment test system (Walker et al. 1988). The hydrolysis of chlorothalonil is thought to be insignificant (Caux et al. 1996) whereas degradation in sunlight is rapid with a photolysis half-life of between 1 and 48 h reported dependent on water type (Sakkas et al. 2002a,b). Photolysis results in the production of chloro-1,3-dicyanobenzene, dichloro-1,3-dicyanobenzene, trichloro-1,3-dicyanobenzene and benzamide. A much longer half-life of ~8 weeks was reported for chlorothalonil in seawater

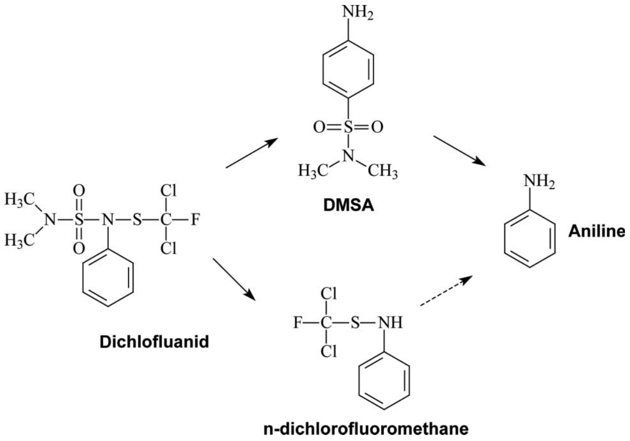


Figure 5. Degradation pathway for dichlofluanid.

at 25°C using a bioassay system to measure degradation (Callow and Finlay 1995; Callow and Willingham 1996).

Zinc pyrithione and copper pyrithione

Zinc and copper pyrithione are considered together for the purpose of this review as zinc pyrithione (ZnPT) can rapidly transchelate to copper pyrithione (CuPT) in the presence of Cu^{2+} (Thomas 1999; Doose et al. 2004; Grunnet and Dahllof 2005), which is also present as CuO in many AF paint formulations and therefore present in waters likely to contain pyrithione AF biocides (Jones and Bolam 2007). ZnPT photodegrades rapidly in natural seawater to 2-pyridine sulfonic acid with a published half-life of <24 h, whereas copper pyrithione (CuPT) has a similar short half-life ($t½ = 0.5$ h) (Turley et al. 2000). ZnPT and CuPT are both very sensitive to light with extremely rapid photolytic degradation under natural sunlight ($t_{½} < 1$ h). By contrast, hydrolysis half-lives range from 96 to 120 days (Turley et al. 2000). Various field experiments have shown that the half-life of ZnPT and CuPT can be affected by reduced sunlight underwater. CuPT degradation has shown to be significantly reduced below 1 m (Grunnet and Dahllof 2005) with much longer ZnPT (and CuPT) half-lives being reported at depths >25 m (Thomas, unpublished data). Bacterial degradation of CuPT has also been reported to be very rapid with a reported biotic half-life in seawater of approximately 4 days (Turley et al. 2000; Harino et al. 2005a,b). Pyrithiones degrade to form 2-pyridine sulfonic acid with Zn^{2+}/Cu^{2} released into the aqueous phase.

ZnPT has been shown to bind strongly to sediments and it may be that due to its short half-life, the influence of partition on the fate of ZnPT/CuPT may be insignificant (Turley et al. 2000). However, since recent data have shown increased persistence at depth near the sediment/water interface, it may be that pyrithione biocides in the form of CuPT or more stable chelates (eg Mn^{2+}) may accumulate in marina and harbour sediments especially if released in the form of paint particles. Further experimental and/or monitoring data are required to substantiate this hypothesis.

TPBP

Being a relatively new AF biocide few data are available for TPBP. Biotic degradation of TPBP has been shown to occur in buffer solutions of different pH (pH 5, 7 and 9) and natural and artificial seawater. TPBP was reported to show degradation by hydrolysis and UV-A irradiation leading to the formation of diphenylborane hydroxide (DPB) and phenylborane dihydroxide (MPB), benzene, phenol and biphenyl (Zhou et al. 2007; Okamura et al. 2009). A photolysis half-life of 6.6 h has been determined for TPBP in natural seawater (Zhou et al. 2007), which has been shown to increase with depth as sunlight is reduced (Thomas, unpublished data).

Zinc ethylenebisdithiocarbamate

Zinc ethylenebisdithiocarbamate (zineb) in Guillard's F2 marine culture medium has been shown to rapidly form 5,6-dihydro-3*H*-imidazo (2,1-c)- 1,2,4-dithiazole-3-thione (DIDT) and ethylene thiourea (ETU) (Hunter and Evans 1991). Although very few data are specifically available for zineb, some data are available for its sister compound (manganese ethylenebisdithiocarbamate (maneb). It is clear that both compounds rapidly undergo hydrolysis and photolysis to form ETU and ethyleneurea (EU). ETU is a relatively polar molecule with a reported log K_{OW} of 0.66 (Vershueren 1996). ETU is relatively stable to hydrolysis but is thought to undergo photolysis to EU.

Capsaicin, Econea and medetomidine

Capsaicin, Econea and medetomidine can be collectively termed as 'emerging' biocides. Each compound is being supported through registration in various parts of the globe and online searches reveal marketing information supporting their use as AF chemicals. What is apparent for these biocides is that little or no scientific data have been published, let alone in the peer reviewed arena. Capsaicin (8-methyl-*n*-vanillyl-6-nonenamide; CAS: 404-86-4) is a compound that may emerge as an AF biocide in the future and has even been evaluated as a marine antifoulant (Xu et al. 2005).

Capsaicin has a log K_{OW} of 3.04 and a soil-sorption coefficient of 1.1 × 10^3. As an emerging biocide very little data are publicly available on the environmental fate and effects of capsaicin but an initial assessment suggests that based on its K_{OW} and K_{OC} it will bind to sediments.

Econea (2-(*p*-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole; CAS 122454-29-9) is being marketed as a metal-free biocidal additive replacement for copper. Econea is described by its manufacturer, as having a short-hydrolytic half-life in seawater of 3 h but this must be viewed with caution as no experimental details are given to support this (www.econea.com). However, these data suggest that Econea will not be persistent following its release from painted surfaces.

Medetomidine (4-[1-(2,3-dimethylphenyl)ethyl]-3*H*-imidazole; CAS: 86347-14-0) is a neuroactive catemine which has been shown to be effective in preventing barnacle cyprid settlement by interfering with the regulation of cement production (Dahlström et al. 2004). Medetomidine is not currently used as an AF biocide, but it has been submitted for evaluation by the BPD in the UK.

Occurrence

Copper

Copper is an essential metal ion that occurs naturally in the environment. Natural background concentrations of copper within estuarine and coastal seawater typically range between 0.5 and 3 μg l^{-1}, with the major source of copper input being from land runoff. For example, significantly elevated concentrations have been found downstream from existing and historical mining activities (2400 mg kg^{-1} Cu in Restronguet Creek, UK (Bryan and Gibbs 1983).

Copper concentrations can potentially build-up in the marine environment around enclosed harbours and marinas with little water mixing and high boat densities. For example, elevated concentrations of copper up to 21 μg l^{-1} were measured in the surface waters of San Diego Bay, California (Schiff et al. 2007). High berth densities and limited water exchange were thought to be the reasons for such high concentrations, which were up to four times above the Environmental Quality Standard (EQS) of 5 μg l^{-1}. Despite the projected problem in these high risk areas, there has been very little monitoring work carried out. Those that have been performed have reported copper concentrations exceeding water quality thresholds (Zirino et al. 1998; Noblet et al. 2002; Schiff et al. 2007).

Most monitoring studies that report on copper concentrations in the marine environment measure total dissolved copper concentration, which fails to provide information on the bioavailability of the metal. As will be mentioned in a later section, the speciation of copper is fundamental to its bioavailability and toxicity, with the free ion considered as the most toxic form. A recent study of UK coastal waters measured copper speciation as total dissolved and labile copper (free ion and inorganic copper) in seawater samples collected from a series of marinas, harbours and ports around the UK. Total dissolved copper ranged from 0.30 to 6.68 μg l^{-1}, with only one concentration above the EQS of 5 μg l^{-1}. Also in this case, elevated concentrations were found in an enclosed marina with little to no water exchange. The labile copper concentrations for the same water samples ranged from 0.02 to 2.69 μg l^{-1}, with labile copper contributing 10–30% of the total dissolved copper concentration (Jones and Bolam 2007). Despite elevated concentrations of total dissolved copper at some marinas, the labile copper concentration remained stable. This stability was believed to be due to the natural buffering capacity of the environment, mainly due to the presence of DOC.

A similar monitoring survey of measured copper speciation was carried out in a Finnish marina with respect to season (Brooks (unpublished data)). Total dissolved copper concentrations ranged between 0.62 and 3.89 μg l^{-1}, with the highest concentrations found in the summer months due to increased boating activity. In contrast, labile copper concentrations tended to remain within a narrow range below 1 μg l^{-1} and high levels of DOC were believed to be responsible for buffering the labile copper concentrations.

Irgarol 1051 and GS26575/M1

Irgarol 1051 is possibly the most studied of the organic AF biocides with a large number of reports on its environmental occurrence. Irgarol 1051 was first reported as an aquatic contaminant in 1993 in the Mediterranean (Readman et al. 1993) with its occurrence subsequently reported in Europe, the US, Caribbean, Asia and Australia (Tolosa et al. 1996; Scarlett et al. 1999; Biselli et al. 2000, Lamoree et al. 2002; Bowman et al. 2003, Harino et al. 2005a,b, 2007, 2008; Lambert et al. 2006; Cassi et al. 2008). From the studies published to date it has been established that Irgarol 1051 occurs in areas where there are boats coated with AF paint that contains Irgarol 1051. This is also true for freshwater environments where intensive boating activity combined with limited water exchange can lead to extremely high aqueous concentrations of Irgarol 1051 (Toth et al. 1996; Lambert et al. 2006). In certain countries, such as the UK, Denmark and Sweden, the use of Irgarol 1051 has been prohibited (Thomas et al. 2002). In the UK, this has been demonstrated to have had a positive effect in reducing the levels of Irgarol 1051 found in areas frequented by boats (Cresswell et al. 2006; Zhou 2008). Irgarol 1051 is predominantly found in the water phase with a weak affinity for sediments (Thomas 2001, 2002) and a number of studies have reported its presence in marina and harbour sediments at a wide range of concentrations with the highest being attributed to the presence of AF paint particles containing Irgarol 1051 (Biselli et al. 2000, Thomas et al. 2000; Carrasco et al. 2003, Cassi et al. 2008).

One area where there has been a significantly improved understanding is of the occurrence of the Irgarol 1051 metabolite, 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (GS26575 or M1). M1 has been reported in Irgarol 1051 contaminated surface waters and sediments (Thomas et al. 2000, 2001) although the degradation of Irgarol 1051 to M1 in the environment is not the sole pathway into the environment since it has also can be found in Irgarol 1051 containing paints (Thomas et al. 2003). GS26575 occurs in both surface waters and sediments at concentrations which are typically lower than Irgarol 1051 (Table 1).

Diuron and its metabolites

Diuron is used for both AF and non-AF (agricultural) applications. Compared to Irgarol 1051, few studies have assessed the inputs of diuron bearing in mind that where used it can be found at high concentrations (Thomas et al. 2000, 2001, 2002; Comber et al. 2002; Lamoree et al. 2002; Harino et al. 2005a,b, 2006a,b, 2007, 2008; Lambert et al. 2006; Sapozhnikova et al. 2007, 2008). The occurrence of diuron in coastal areas where it is used is well established. However, as with Irgarol 1051, it has recently been shown that elevated concentrations can also occur in inland waterways used for pleasure boating (Lambert et al. 2006). Very few studies have assessed the occurrence of the transformation products of diuron, *viz* 1-(3-chlorophenyl)-3, 1-dimethylurea (CPDU), 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichlorophenyl)urea (DCPU) (Thomas et al. 2002). These metabolites have been shown to occur in surface waters and sediments, albeit at concentrations much lower than diuron itself (Thomas et al. 2002; Lambert et al. 2006; Gatidou et al. 2007).

DCOIT

Few monitoring studies have included DCOIT (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) and even few have reported elevated concentrations of DCOIT (Thomas 2001; Martinez et al. 2001; Lambropoulou et al. 2002; Steen et al. 2004; Cassi et al. 2008; Langford and Thomas 2008). For example, a major survey in the UK in the late 1990s failed to detect DCOIT in the busiest boating areas in the UK (Thomas et al. 2001), which may be due to the absence of boats painted with DCOIT containing paints. A study which targeted a ship known to be painted with DCOIT showed concentrations to quickly fall below 5 ng l^{-1} within 400 m of the ship (Steen et al. 2004). The presence of DCOIT has been reported in surface water samples collected from marinas in Greece and Spain (Martinez et al. 2001; Sakkas et al. 2002a,b) and Asian ports (Harino et al. 2005a,b, 2006a,b, 2007, 2008). From the available data it is difficult to clearly state that DCOIT occurs at elevated concentrations in areas frequented by ships and boats since there are insufficient data available.

Dichlofluanid and DMSA

It is unclear as to whether dichlofuanid occurs in areas with boating activity. The first studies performed in Europe showed both the occurrence and absence of dichlofluanid in marina and harbour sediments and surface waters (Thomas et al. 2000, 2001, 2002; Voulvoulis et al. 2000; Sakkas et al. 2002a,b). The occurence of dichlofluanid in Greek and other sediments and surface waters (Albanis et al. 2002) has been challenged by a repeat study which showed the occurrence of the dichlofluanid transformation product *N*-dimethyl-*N*-phenyl-sulphamide (DMSA) following rapid degradation (Hamwijk et al. 2005; Schouten et al. 2005). These studies suggest that previous reports of dichlofluanid may be the result of 'false positives' arising from the use of non-specific detectors or inappropriate confirmation ions when using gas chromatography-mass spectrometry (Hamwijk et al. 2005; Schouten et al. 2005). Monitoring studies to include dichlofluanid failed to detect dichlofluanid in sediments collected from Mediterranean and Caribbean marinas (Carbery et al. 2006; Cassi et al. 2008). However, studies in Japan show the presence of dichlofluanid (Harino et al. 2005a,b, 2007).

Chlorothalonil

Chlrothalonil appears not to occur in boating areas. The few studies that have included chlorothalonil in the monitoring of marinas, harbours, ports and estuaries have generally shown that concentrations are below that which can be detected (Thomas et al. 2001; Carbery et al. 2006; Cassi et al. 2008). For example recent studies performed in the Caribbean and Mediterranean failed to detect chorothalonil in marina or harbour waters or sediments. Chlorothalonil has been detected at one UK location in both surface waters and sediments at moderately high concentrations (Voulvoulis et al. 2000) and at lower concentrations in Greek marinas (Sakkas et al. 2002a,b).

Pyrithione biocides (copper and zinc)

Zinc and copper pyrithione biocides are widely used AF biocides about which very little is known regarding their environmental occurrence. To date, only a few monitoring studies have included zinc and/or copper pyrithione (Thomas et al. 2001; Harino et al. 2007). Both zinc and copper pyrithione are very difficult to analyse and the only reported occurrence of zinc pyrithione is a small scale study performed in the UK using differential-pulse cathodic stripping voltametry where a concentration of 105 ± 5 nM was measured (Mackie et al. 2004). In Japan, copper pyrithione has been detected in certain harbour sediments (Harino et al. 2007). The paucity of data is not only linked to the difficulties associated with analysing zinc and copper pyrithione but also to its instability in seawater being very sensitive to sunlight.

Triphenylborane pyridine and medetomidine

TPBP is predominantly used in Japan and no published data are available on its occurrence. Medetomidine is a novel biocide that has yet to be approved for use in Europe. However, it shows considerable promise as being effective against barnacles (Hilvarsson et al. 2007).

Bioaccumulation

Outside the regulatory testing area there have been very few reported studies relating to the biological uptake and bioaccumulation of AF biocides. Bioconcentration factors (BCFs) are available for certain biocides in specific tissues and represent the concentration of a biocide in tissue per concentration of the biocide in water ($\mathrm{l\ kg^{-1}}$). Irgarol 1051 is known to occur in fresh water macrophytes (Tóth 1996) with reported BCFs of up to 30,000 $\mathrm{l\ kg^{-1}}$. Similarly, Irgarol 1051 has been reported to occur within marine macrophytes (Scarlett et al. 1999). Dyer et al. (2006) showed that Irgarol 1051 bioaccumulated in the green alga *Tetraselmis suecica* under laboratory conditions with reported BCFs of up to 150,000 $\mathrm{ml\ g^{-1}}$. There are no reports of the bioaccumulation of diuron with predicted BCFs of 75 and 22 $\mathrm{l\ kg^{-1}}$ suggesting that its accumulation in aquatic organisms is unlikely (Kenaga 1980). DCOIT has been shown to bioaccumulate in fish at very low levels following exposure to radiolabelled DCOIT (Jacobson and Willingham 2000). Because of the rapid metabolism of DCOIT in fish it was shown that $<1\%$ was present as the parent compound and that the metabolites were associated with proteins. Whole body accumulation of zineb in trout (*Salmo gairdneri*) is reported to be low with a BCF $<100\ \mathrm{l\ kg^{-1}}$. No pertinent data were available for any of the other biocides.

Unlike the other biocides mentioned, copper is an essential metal, which is actively regulated within animal cells to maintain optimum concentrations for cellular mechanisms. This means that animals actively accumulate the metal in copper deficient waters and excrete excess metal in copper rich waters. Because of this active regulation of copper, bioaccumulation is not directly related to the environmental concentration. Indeed, an inverse relation has been found between water and animal metal concentration (Brix and de Forest 2000). For this reason, bioconcentration factors are considered unsuitable for describing copper bioaccumulation.

Conclusions

There are extensive data available on the environmental occurrence, fate and effects of many of the chemicals used as AF biocides. As would be expected, those biocides that have been commonly used globally have received the greatest attention and good data are available regarding the environmental occurrence, fate and effects of copper, Irgarol 1051, its metabolite M1 and diuron. For other biocides, such as DCOIT, CuPT/ZnPT and dichlofluanid there are either no or few available occurrence data or the available data are conflicting. The environmental fate of these compounds is generally well understood, although some uncertainties exist. For example, the absence of CuPT/ZnPT monitoring data mean that experimental data have yet to be confirmed in the field and some uncertainty exists as to whether CuPT/ZnPT are as rapidly removed from the environment as predicted. For other biocides (and candidate biocides), such as TPBP, Econea and capsaicin, which have limited international use, there is a paucity of data compared to other biocides. Zineb, although approved for use on amateur products in the UK, appears to be a very poorly studied biocide when the available public domain data are considered. In common with many classes of organic contaminant, the significant gap in the available data for AF biocides is in the absence of fate and effects data for their products of transformation. Such data are to some extent available for Irgarol 1051 and diuron and with time it is expected that data will be forthcoming from studies in these areas. What is also absent are studies relating to the improper use and removal of AF paints that result in biocides entering the environment by means of a scenario that is different to that which has been used to assess the environmental risk posed by a biocide. For example, in the form of paint particles at point sources in much higher concentrations and in a different form to that released from the painted hull of a ship. An environmentally safe biocide is one that poses little risk to the environment even when it is misused. In conclusion, fully understanding the fate, behaviour and effects of biocides allow a thorough assessment of environmental risk. Such a process is currently underway in Europe where the outcome of the BDP assessment of AF biocides is awaited.

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