

Section 7
Monitoring of Alternative Biocides

Chapter 19

Europe and USA

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19.1 Introduction

Antifouling paints containing active biocides are typically used on the hulls of ships and boats to prevent the growth of fouling organisms. Antifouling paint biocides are therefore released directly into surface waters following their release from painted surfaces or from the inappropriate disposal of paint related waste. The levels of biocides found in surface waters are therefore directly related to the amount released from such surfaces. Once in the water column, antifouling biocides, as with all other contaminants, are subjected to a number of environmental processes that control their environmental fate. Depending on their physico-chemical properties, biocides can partition onto sediments and accumulate in biological material. In order to measure the occurrence of antifouling biocides in water, sediments and biota analytical methods have been developed and applied. This chapter will review the data available on the occurrence of the biocides listed below in surface waters, sediments and biota for Europe and the Americas, including Canada, USA and the Caribbean (Fig. 19.1).

19.2 Irgarol 1051 and Its Metabolite M1

Since 1993, when Irgarol 1051 was reported as an aquatic contaminant (Readman et al. 1993) many studies have been performed to monitor the occurrence of Irgarol 1051 from antifouling inputs (Table 19.1). In Europe many of these studies have been performed in the UK (Boxall et al. 2000; Thomas et al. 2000, 2001, 2002;

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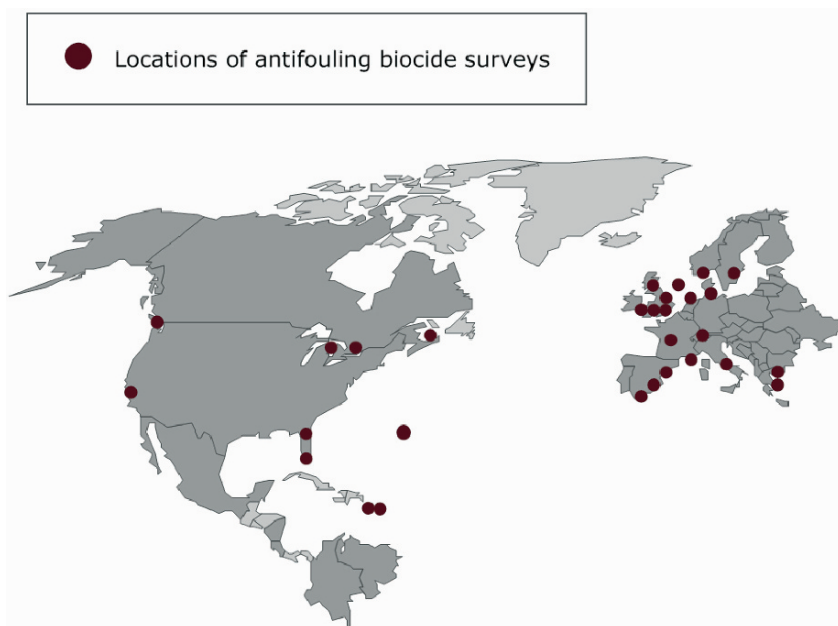


Fig. 19.1 Locations of antifouling paint biocide surveys in Europe and North America

Voulvoulis et al. 2000; Voulvoulis 2006). Early studies performed on the busy yachting areas of the Hamble estuary, UK showed Irgarol 1051 to occur in surface waters and sediments at concentrations of between 12 and 190 ng l⁻¹ and 12 and 132 ng g⁻¹, respectively (Gough et al. 1994). A more widespread study in 1998, funded by the UK Department for the Environment, showed Irgarol 1051 to occur at concentrations of up to 1,421 ng l⁻¹ with the higher concentrations being found early in the season in areas of high boating activity and low water exchange; such as those found in enclosed marinas (Thomas et al. 2001). Surface water concentrations in estuaries and harbours were much lower and these concentrations declined even further during the winter when most boats are removed from the water. These studies from the UK also reported that Irgarol 1051 was detected only in marina sediments where high water levels of Irgarol 1051 were measured (Thomas et al. 2000). It has been suggested that Irgarol 1051 has a low affinity for particulate matter ($\log K_{OC}$ 3.0; $\log K_{OW}$ 3.9) and in most marine waters is mainly associated with the dissolved phase (Tolosa et al. 1996; Ferrer et al. 1997). However, detectable concentrations are present in marina sediments where aqueous concentrations are at their highest and partitioning does occur (Thomas et al. 2000). Other studies on marine waters from the UK during the same period showed similar data, suggesting that Irgarol 1051 is persistent and can accumulate in areas where its release is intense. This was mirrored in data from around Europe where Irgarol 1051 painted boats were to be found (Ferrer et al. 1997; Scarlett et al. 1999; Biselli et al. 2000). Similar concentrations have been reported in other areas of Europe

Table 19.1 Irgarol concentrations in waters and sediments

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹) ^a	Reference
Puerto Rico, Caribbean	9 Marinas/harbours	<1–51		Carbery et al. (2006)
US Virgin Islands	5 Marinas/harbours	<1–1,300		Carbery et al. (2006)
San Diego area, California, USA	4 Marinas/harbours	1–304		Sapozhnikova et al. (2007)
Florida Keys, USA	4 Marinas	10.6–99.7		Owen et al. (2002)
Bermuda, USA	3 Harbours	37.4–294		Owen et al. (2002)
South Florida coastal waters, USA	75 Sites with varying levels of boating activities	<1–182		Gardinali et al. (2004)
Biscayne Bay, Florida, USA	2 Commercial ports	<1–2.24		Gardinali et al. (2002)
Biscayne Bay, Florida, USA	7 Sites on Miami River	<1–60.9		Gardinali et al. (2002)
Biscayne Bay, Florida, USA	11 Marinas	<1–15.2		Gardinali et al. (2002)
Biscayne Bay, Florida, USA	Open bay area	<1		Gardinali et al. (2002)
Canada	Marinas/harbours	<LOD		Liu et al. (1999)
Gulf of Napoli, Italy	7 Marinas	3–22		Di Landa et al. (2006)
Gulf of Napoli, Italy	3 Harbours	3.5–8.2		Di Landa et al. (2006)
Barcelona, Spain	Marinas	<LOD–119	3–57	Ferrer and Barcelo (2001)
Almeria, Spain	Marinas	25–450		Aguera et al. (2000)
Greece	3 Ports	<LOD–14		Albanis et al. (2002)
Greece	8 Marinas	5–338		Albanis et al. (2002)
Piraeus-Elefsina, Greece	Marinas	<LOD–90	<LOD–690	Sakkas et al. (2002b)
Riviera, Monaco	Marinas/harbours	14–640		Tolosa et al. (1996)
Cote d'Azur, France	Marinas/harbours	110–1,700		Readman et al. (1993)
North Sea	6 Marinas/harbours – water samples	11–170	<LOD–14	Biselli et al. (2000)
Baltic Sea	7 Marinas/harbours – water samples	80–440	<4–220	Biselli et al. (2000)

(continued)

Table 19.1 (continued)

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹) ^a	Reference
The Netherlands	7 Marinas	8–90		Lamoree et al. (2002)
Western Scheldt, Netherlands	Estuary location	1.6–37		Steen et al. (1997)
Stockholm, Sweden	Marina	3–130		Haglund et al. (2001)
Stockholm, Sweden	Outside marina	<LOD–6		Haglund et al. (2001)
Fiskebackskil, Sweden	Marina	30–400		Dahl and Blanck (1996)
Southampton Water, UK	Water samples	<LOD–403	<LOD–110	Thomas et al. (2001)
Southampton Water, UK	Sediment samples		0.3–3.5	Thomas et al. (2002)
Hamble Estuary, UK	Estuary location	12–190	12–132	Gough et al. (1994)
North Sea	Sediment samples		<LOD	Thomas et al. (2000)
Conwy Marina, UK	Marina	7–543		Sargent et al. (2000)
UK	3 Marina locations	5.6–61.1		Boxall (2004)
Orwell Estuary, UK	3 Marina locations – summer water samples	24.3–201.4	<10–1,011	Boxall (2004)
Plymouth Sound, UK	Marina location	28–127		Scarlett et al. (1997)
Humber, UK	Marina location	169–682		Zhou et al. (1996)
Blackwater Estuary, UK	Estuary location	150–680	3.3–222	Voulvoulis et al. (2000)
East Anglia, UK	Rivers	<1–1,332		Lambert et al. (2006)
East Anglia, UK	Norfolk Broads	<1–1,220		Lambert et al. (2006)
UK	Coastal waters	<1–36		Cresswell et al. (2006)
UK	Coastal waters	<1–305		Thomas et al. (2002)

^aDry weight.

including the Mediterranean, West Coast of Sweden; Stockholm Archipelago, Sweden; Oslofjord, Norway; Western Scheldt, The Netherlands; Sas van Gent and Schaar van Ouden, The Netherlands; and the Baltic and North Sea marinas of Germany (Table 19.1).

The occurrence of Irgarol 1051 was not restricted to marine waters. Studies also showed that the use of antifouling paints formulated with Irgarol 1051 were common in freshwater lakes and waterways (Tóth et al. 1996; Lambert et al. 2006). Irgarol 1051 was detected in the waters of marinas around Lake Geneva, Switzerland and in the inland waterways of the Norfolk Broads UK. Even though the boating density in inland waterways is not as high as coastal areas concentrations as high as $1,200\text{ ng l}^{-1}$ were reported.

In the Americas, where Irgarol 1051 use is relatively recent, studies show that where Irgarol 1051 is in use, or where boats painted with Irgarol 1051 formulated antifouling paints are used, Irgarol 1051 occurs. An early study from Canada reported concentrations to be below the LOD when paints containing Irgarol 1051 were not in use (Liu and Pacepavicius 1999). Studies from the USA, including US territories in the Caribbean show that marina/harbour concentrations range from <1 to $1,300\text{ ng l}^{-1}$ (Gardinali et al. 2002, 2004; Owen et al. 2002; Sapozhnikova et al. 2007). As expected the highest concentrations are seen in the busiest boating areas such as San Diego, California (Sapozhnikova et al. 2007).

In 2001 the UK restricted the use of Irgarol 1051 in antifouling paints for small vessels ($<25\text{ m}$). The impact of this legislation was that these paints were removed from the marketplace for small boats. Post-restriction surveys performed in 2005 demonstrated a clear reduction in water concentrations of Irgarol 1051 (between 10% and 55% of that found during pre-restriction studies), indicating that legislation appears to have been effective (Cresswell et al. 2006).

19.3 GS26575/M1

The occurrence of the Irgarol 1051 metabolite, 2-methylthio-4-tert-butylamino-6-amino-s-triazine (GS26575 or M1) has also been reported in Irgarol 1051 contaminated surface waters and sediments (Thomas et al. 2000, 2002). Environmental degradation of Irgarol 1051 appears not to be the only source of GS26575 since it has also been reported to occur in Irgarol 1051 paint formulations (Thomas et al. 2003). The occurrence of GS26575 is therefore directly related to that of Irgarol 1051 either being released from painted surfaces with Irgarol 1051 or as a product of environmental degradation. GS26575 has been reported to occur in both surface waters and sediments (Table 19.2). Typically concentrations are lower than those detected for Irgarol 1051 in the same samples and have been reported at up to $4,000\text{ ng l}^{-1}$ (Ferrer et al. 1997). In the UK concentrations of between <1 and 140 ng l^{-1} have been reported for freshwater and <1 and 300 ng l^{-1} for marine samples (Thomas et al. 2002; Lambert et al. 2006). Similar levels have been recorded in both Florida and

Table 19.2 Concentrations of Irgarol 1051's main metabolite M1 in water and sediment

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹)	Reference
San Diego area, California, USA	4 Marinas/harbours	1-68		Sapozhnikova et al. (2007)
South Florida coastal waters, USA	75 Sites with varying levels of boating activities	<3-47		Gardinali et al. (2004)
Barcelona, Spain	Marinas	<LOD-23	0.2-3.3	Ferrer and Barcelo (2001)
Catalonia, Spain	4 Marinas	<LOD-4,000		Marínez et al. (2000)
The Solent, UK	Sediment samples		<LOD-5.7	Thomas et al. (2000)
East Anglia, UK	Rivers	<1-139		Lambert et al. (2006)
East Anglia, UK	Norfolk Broads	<1-231		Lambert et al. (2006)
Southampton Water, UK	Sediment samples		<LOD-0.3	Thomas et al. (2002)
Southampton Water, UK	Water samples	1-59		Thomas et al. (2001)
UK	Coastal waters	<1-59		Thomas et al. (2002)

California in the USA (Gardinali et al. 2002; Owen et al. 2002). GS26575 has also been found in sediments but at much lower concentrations (<1–6 ng g⁻¹) (Thomas et al. 2000)).

19.4 Diuron and Its Metabolites

Diuron, a phenylurea herbicide, has been in use since the 1950s. Predominantly this use has been associated with weed control in non-agricultural applications. Several studies have investigated the impact of non-antifouling use on diuron release into the aquatic environment (Albanis et al. 1995), however, the assessment of inputs from antifouling applications has been restricted to a few studies (Thomas et al. 2000, 2001, 2002; Lamoree et al. 2002; Gatidou et al. 2005, 2007; Lambert et al. 2006). For example Dahl and Blanck (1996) reported diuron concentrations in Swedish marinas of between 10 and 100 ng l⁻¹. A study of marinas on the Spanish Mediterranean coast reported similar concentrations (10–100 ng l⁻¹) whilst a study in the UK reported much higher concentrations in marinas (4–6,742 ng l⁻¹) probably reflecting the level of diuron use in the UK at the time. This study also reported diuron concentrations of between 5 and 226 ng l⁻¹ in water samples collected from estuaries, of between 1 and 45 ng l⁻¹ in coastal waters and <8 ng l⁻¹ off-shore. In freshwater boating areas diuron has been shown to occur at concentrations less than 170 ng l⁻¹ (Lambert et al. 2006) suggesting diuron containing paints are not so extensively used on inland waterways (Table 19.3). The principal metabolites of diuron, 1-(3-chlorophenyl)-3,1-dimethylurea (CPDU), 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichlorophenyl)urea (DCPU) have also all been detected at measurable concentrations in surface water samples collected from the UK (Thomas et al. 2002), albeit at concentrations much lower than diuron itself.

19.5 DCOIT

DCOIT (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one), the active ingredient in SeaNine 211, has been subject to a number of studies in Europe and the Americas, however its occurrence is rarely reported. A season long survey from the UK in the late 1990s reported concentrations < LOD in samples collected from some of the UK's busiest boating areas around Southampton Water (Thomas et al. 2001). Elsewhere in Europe, Steen et al. (2004) detected DCOIT in samples collected from a harbour which contained a ship painted with a SeaNine 211 antifouling paint. Samples collected on a transect away from the ship showed levels to be below 5 ng l⁻¹ within 400 m of the ship. DCOIT has also been detected in water samples collected from marinas in Greece and Spain. DCOIT was detected at concentrations of up to 3,300 ng l⁻¹ in water samples

Table 19.3 Concentrations of Diuron detected in water and sediment samples

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹)	Reference
San Diego area, California, USA	4 Marinas/harbours	<2–12		Sapozhnikova et al. (2007)
Gulf of Napoli, Italy	7 Marinas	12–475		Di Landa et al. (2006)
Gulf of Napoli, Italy	3 Harbours	6.1–51		Di Landa et al. (2006)
Catalonia, Spain	4 Marinas	up to 2,000		Martínez et al. (2000)
Mediterranean Coast, Spain	Marinas/harbours	5–200		Ferrer and Barcelo (1999)
Amvrakikos Gulf, Greece	Wetland areas	Nd–260		Albanis et al. (1995)
Lake Geneva, Switzerland		<0.3–142.5		Tóth et al. (1996)
The Netherlands	7 Marinas	90–1,130		Lamoree et al. (2002)
Sweden	Marinas	10–100		Dahl and Blanck (1996)
Southampton Water, UK	Water samples	<LOD–6,742	<LOD–1,420	Thomas et al. (2001)
Southampton Water, UK	Sediment samples		0.4–6.2	Thomas et al. (2002)
North Sea	Sediment samples		<LOD	Thomas et al. (2000)
Humber rivers, UK	11 River locations	40–8,700		House et al. (1997)
UK	3 Marina locations	10.5–786		Boxall et al. (2000)
Orwell Estuary, UK	3 Marina locations	117–768	<12–395	Boxall et al. (2000)
East Anglia, UK	Rivers	<1–169		Lambert et al. (2006)
East Anglia, UK	Norfolk Broads	<1–249		Lambert et al. (2006)
UK	Coastal waters	16–1,249		Thomas et al. (2002)

collected from marinas along Spain's Catalan coast. Lower concentrations of up to 49 ng l⁻¹ were detected in Greek marinas (Sakkas et al. 2002b), whilst all other studies in Europe and the Americas have failed to detect DCOIT at concentrations > LODs. Overall, the reported occurrence of DCOIT is patchy with studies reporting reasonably high concentrations, whilst other studies report lower than LOD concentrations. DCOIT is predominantly used on large vessels (>25 m) so it is unlikely that it will occur in marinas exclusively used for pleasure craft

Table 19.4 DCOIT concentrations measured in water samples

Location	Description	Concentration range(ng l ⁻¹)	Reference
Puerto Rico, Caribbean	9 Marinas/harbours	<LOD	Carbery et al. (2006)
US Virgin Islands	5 Marinas/harbours	<LOD	Carbery et al. (2006)
Catalonia, Spain	4 Marinas	<LOD–3,300	Martínez et al. (2000)
Greece	Marinas/harbours	<LOD	Albanis et al. (2002)
Greece	Marinas	<LOD–49	Sakkas et al. (2002b)
UK		<LOD	Thomas (1998)
Korsør Harbour, Denmark	Harbour in immediate vicinity of ship	30–72	Steen et al. (2004)
	Harbour 2 m from ship	20–25	

(Table 19.4). In addition DCOIT is reported to rapidly degrade in water (Sakkas et al. 2002a).

19.6 Dichlofluanid and DMSA

Dichlofluanid has been reported to occur in marina surface waters and sediments from Greece and Spain, as well as UK sediments (Voulvoulis et al. 2000; Sakkas et al. 2002a,b; Readman 2006) (Table 19.5). Other extensive studies in areas of intensive boating activity in the UK have reported concentrations below detection limits for both surface waters and sediments. Interestingly the occurrence of dichlofluanid in Greek (and other) surface waters and sediments has been challenged by a study which showed that the dichlofluanid metabolite N-dimethyl-N-phenyl-sulphamide (DMSA) occurs in surface waters and sediments following rapid degradation and 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 GC-MS (Hamwijk et al. 2005; Schouten et al. 2005). The few studies performed in the Americas report dichlofluanid concentrations below LODs.

19.7 Chlorothalonil

Few studies have been performed on the occurrence of chlorothalonil in surface waters arising from antifouling inputs. Recent studies performed in the Caribbean failed to detect chlorothalonil in marina or harbour waters (Table 19.6). These

Table 19.5 Concentrations of diclofluanid and DMSA detected in water and sediment samples

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹)	Reference
Dichlofluanid				
Puerto Rico, Caribbean	9 Marinas/harbours	<LOD		Carbery et al. (2006)
US Virgin Islands	5 Marinas/harbours	<LOD		Carbery et al. (2006)
Greece	3 Marinas	<LOD		Hamwijk et al. (2005)
Piraeus-Elefsina, Greece	Marinas	<LOD–214	12–65	Sakkas et al. (2002b)
Catalonia, Spain	Coastline	<4–600		Martínez et al. (2000)
Catalonia, Spain	Coastline		<1.6–11	Martinez et al. (2001)
Greece	3 Ports	Nd–49		Albanis et al. (2002)
Greece	8 Marinas	4–102		Albanis et al. (2002)
Greece	3 Marinas	20–205		Lambropoulou et al. (2000)
Blackwater Estuary, UK	Estuary location		7.2–688	Voulvoulis et al. (2000)
DMSA				
Greece	3 Marinas		<LOD–36	Hamwijk et al. (2005)

Table 19.6 Chlorothalonil concentrations measured in water and sediment samples

Location	Description	Water concentration (ng l ⁻¹)	Sediment concentration (ng g ⁻¹)	Reference
Puerto Rico, Caribbean	9 Marinas/harbours	<LOD		Carbery et al. (2006)
US Virgin Islands	5 Marinas/harbours	<LOD		Carbery et al. (2006)
Greece	3 Ports	Nd–49		Albanis et al. (2002)
Greece	8 Marinas	Nd–120		Albanis et al. (2002)
Greece	3 Marinas	Nd–37		Lambropoulou et al. (2000)
Greece	Marinas	<LOD–63	<LOD–126	Sakkas et al. (2002b)
Blackwater Estuary, UK	Estuary location	360–1,380	16–34.3	Voulvoulis et al. (2000)

data corroborate an extensive survey for chlorothalonil in UK marinas, estuaries and harbours where all of the samples collected contained < LOD concentrations. Chlorothalonil has been detected at one UK location in both surface waters and sediments at reasonably high concentrations (e.g. 360–1,380 ng l⁻¹ in water) and at lower concentrations in Greek marinas (<LOD – 120 ng l⁻¹) (Voulvoulis et al. 2000; Sakkas et al. 2002).

19.8 Zinc Pyrithione

Zinc pyrithione (ZnPT) has been included in very few monitoring surveys in Europe and the Americas. To date we are aware of only one study whereby ZnPT concentrations were determined in surface waters collected from UK marinas (Thomas et al. 2001). None of the samples contained ZnPT at concentrations greater than the LOD of 20 ng l⁻¹. The samples were analysed by liquid chromatography coupled to APCI mass spectrometry following transchelation to copper pyrithione (CuPT) (Thomas 1999). The only reported occurrence of ZnPT in Europe is from a smaller scale study, also performed in the UK, which reported ZnPT at a concentration of 105 ± 5 nM using differential-pulse cathodic stripping voltametry (Mackie et al. 2004). These data are not surprising since ZnPT is known to rapidly photodegrade (half-life = 15 min) and also to rapidly transchelate with copper which is also commonly used in antifouling paints (Turley et al. 2000). Although ZnPT is used as an active ingredient in antifouling paints it is likely that it transchelates with copper also present in the paint to form CuPT which then acts as a biocide. As far as we are aware there are few studies on the occurrence of CuPT. Recent, unpublished work in our group has shown that ZnPT and CuPT photolysis is reduced with depth when compared to laboratory measurements. Therefore it may be that CuPT is what occurrence studies should be targeting, especially in sediments.

19.9 Summary

Extensive antifouling paint biocide occurrence data are available for Europe. Data are also available for areas of the Americas. Many of the studies performed have focused on Irgarol 1051 and reported its occurrence in marinas, harbours, estuaries and coastal areas. Diuron has also been shown to occur at elevated levels in areas where it is used as a biocide. The occurrence of elevated levels of both Irgarol 1051 and diuron is a direct effect of the large quantities of these substances released from paints and their persistence in the aquatic environment. Occurrence data are also available for other biocides such as DCOIT, dichloflaunil, chlorothalonil and ZnPT. Reported concentrations of these biocides tend to vary from study to study suggesting occurrence is localised and/or short lived. Although a number of these biocides are relatively labile (e.g. ZnPT, dichloflaunil and DCOIT) the quantities

of these biocides used may be less (than Irgarol and diuron); significant changes in the volumes used should be a cause for further assessment.

References

- Aguera A, Piedra L, Hernando MD et al. (2000) Multiresidue method for the analysis of five anti-fouling agents in marine and coastal waters by gas chromatography-mass spectrometry with large volume injection. *J Chromatogr A* 889:261–269.
- Albanis TA, Danis TG, Hela DG (1995) Transportation of pesticides in estuaries of Louros and Arachthos rivers (Amvrakikos Gulf, N. W. Greece). *Sci Total Environ* 171:85–93.
- Albanis TA, Lambropoulou DA, Sakkas VA et al. (2002) Antifouling paint booster biocide contamination in greek marine sediments. *Chemosphere* 48:475.
- Biselli S, Bester K, Huhnerfuss H et al. (2000) Concentrations of the antifouling compound Irgarol 1051 and of organotins in water and sediments of German North and Baltic Sea marinas. *Mar Pollut Bull* 40:233.
- Boxall ABA (2004) Environmental risk assessment of antifouling biocides. *Chimica Oggi* 22:46.
- Boxall ABA, Comber SD, Conrad AU et al. (2000) Inputs, monitoring and fate modelling of antifouling biocides in UK estuaries. *Mar Pollut Bull* 40:898.
- Carbery K, Owen R, Frickers T et al. (2006) Contamination of Caribbean coastal waters by the antifouling herbicide Irgarol 1051. *Mar Pollut Bull* 52:635–644.
- Cresswell T, Richards JP, Glegg GA et al. (2006) The impact of legislation on the usage and environmental concentrations of Irgarol 1051 in UK coastal waters. *Mar Pollut Bull* 52:1169.
- Dahl B, Blanck H (1996) Toxic effects of the antifouling agent Irgarol 1051 on periphyton communities in coastal water microcosms. *Mar Pollut Bull* 32:342–350.
- Di Landa G, Ansanelli G, Ciccoli R et al. (2006) Occurrence of antifouling paint booster biocides in selected harbors and marinas inside the Gulf of Napoli: a preliminary survey. *Mar Pollut Bull* 52:1541.
- Ferrer I, Barceló D (1999) Simultaneous determination of antifouling herbicides in marina water samples by on-line solid-phase extraction followed by liquid chromatography/mass spectrometry. *J Chromatogr A* 854:197–206.
- Ferrer I, Barceló D (2001) Identification of a new degradation product of the antifouling agent Irgarol 1051 in natural samples. *J Chromatogr A* 926:221–228.
- Ferrer I, Ballesteros B, Marco MP et al. (1997) Pilot survey for determination of the antifouling agent Irgarol 1051 in enclosed seawater samples by a direct enzyme-linked immunosorbent assay and solid-phase extraction followed by liquid chromatography-diode array detection. *Environ Sci Technol* 31:3530–3535.
- Gardinali PR, Plasencia M, Mack S et al. (2002) Occurrence of Irgarol 1051 in coastal waters from Biscayne Bay, Florida, USA. *Mar Pollut Bull* 44:781–788.
- Gardinali PR, Plasencia MD, Maxey C (2004) Occurrence and transport of Irgarol 1051 and its major metabolite in coastal waters from South Florida. *Mar Pollut Bull* 49:1072–1083.
- Gatidou G, Kotrikla A, Thomaidis NS et al. (2005) Determination of the antifouling booster biocides irgarol 1051 and diuron and their metabolites in seawater by high performance liquid chromatography-diode array detector. *Anal Chim Acta* 528:89.
- Gatidou G, Thomaidis NS, Zhou JL (2007) Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints. *Environ Int* 33:70.
- Gough MA, Fothergill J, Hendrie JD (1994) A survey of Southern England coastal waters for the s-triazine antifouling compound Irgarol 1051. *Mar Pollut Bull* 28:613–620.
- Haglund K, Petersson A, Peterson M et al. (2001) Seasonal distribution of the antifouling compound Irgarol® 1051 outside a marina in the Stockholm Archipelago. *Bull Environ Contam Toxicol* 66.
- Hamwijk C, Schouten A, Foekema EM et al. (2005) Monitoring of the booster biocide dichlofluanid in water and marine sediment of Greek marinas. *Chemosphere* 60:1316.

- House WA, Leach D, Long JLA et al. (1997) Micro-organic compounds in the Humber rivers. *Sci Total Environ* 194–195:357–371.
- Lambert SJ, Thomas KV, Davy AJ (2006) Assessment of the risk posed by the antifouling booster biocides Irgarol 1051 and diuron to freshwater macrophytes. *Chemosphere* 63:734.
- Lambropoulou DA, Konstantinou IK, Albanis TA (2000) Determination of fungicides in natural waters using solid-phase microextraction and gas chromatography coupled with electron-capture and mass spectrometric detection. *J Chromatogr A* 893:143–156.
- Lamoree MH, Swart CP, Van Der Horst A et al. (2002) Determination of diuron and the anti-fouling paint biocide Irgarol 1051 in Dutch marinas and coastal waters. *J Chromatogr A* 970:183.
- Liu DG, Pacepavicius RJM, Lau Y L et al. (1999) Survey for the occurrence of the new antifouling compound Irgarol 1051 in the aquatic environment. *Water Res* 33:2833–2843.
- Mackie DS, van den Berg CMG, Readman JW (2004) Determination of pyriithione in natural waters by cathodic stripping voltammetry. *Anal Chim Acta* 511:47–53.
- Martínez K, Ferrer I, Barceló D (2000) Part-per-trillion level determination of antifouling pesticides and their byproducts in seawater samples by off-line solid-phase extraction followed by high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry. *J Chromatogr A* 879:27–37.
- Martínez K, Ferrer I, Hernando MD et al. (2001) Occurrence of antifouling biocides in the Spanish Mediterranean marine environment. *Environ Technol* 22:543.
- Owen R, Knap A, Toasperm M et al. (2002) Inhibition of coral photosynthesis by the antifouling herbicide Irgarol 1051. *Mar Pollut Bull* 44:623–632.
- Readman JW (2006) Development, occurrence and regulation of antifouling paint biocides: Historical review and future trends. *Handbook of Environmental Chemistry, Volume 5: Water Pollution*. Springer, Berlin: 1.
- Readman JW, Liong Wee Kwong L, Grondlin D et al. (1993) Coastal water contamination from a triazine herbicide used in antifouling paints. *Environ Sci Technol* 27:1940–1942.
- Sakkas VA, Konstantinou IK, Albanis TA (2002a) Aquatic phototransformation study of the antifouling agent Sea-Nine 211: identification of byproducts and the reaction pathway by gas chromatography-mass spectroscopy. *J Chromatogr A* 959:215.
- Sakkas VA, Konstantinou IK, Lambropoulou DA et al. (2002b) Survey for the occurrence of antifouling paint booster biocides in the aquatic environment of Greece. *Environ Sci Pollut Res* 9:327.
- Sapozhnikova Y, Wirth E, Schiff K et al. (2007) Antifouling pesticides in the coastal waters of Southern California. *Mar Pollut Bull* 54:1972–1978.
- Sargent CJ, Bowman JCZhou JL (2000) Levels of antifoulant Irgarol 1051 in the Conwy Marina, North Wales. *Chemosphere* 41:1755–1760.
- Scarlett A, Donkin ME, Fileman TW et al. (1997) Occurrence of the marine antifouling agent Irgarol 1051 within the Plymouth Sound locality: implications for the Green Macroalga *Enteromorpha intestinalis*. *Mar Pollut Bull* 34:645–651.
- Scarlett A, Donkin P, Fileman TW et al. (1999) Occurrence of the antifouling herbicide, Irgarol 1051, within coastal-water seagrasses from Queensland, Australia. *Mar Pollut Bull* 38:687.
- Schouten A, Mol H, Hamwijk C et al. (2005) Critical aspects in the determination of the antifouling compound dichlofluanid and its metabolite DMSA (N,N-dimethyl-N'-phenylsulfamide) in seawater and marine sediments. *Chromatographia* 62:511.
- Steen RJCA, Leonards PEG, Brinkman UAT et al. (1997) Ultra-trace-level determination of the antifouling agent Irgarol 1051 by gas chromatography with tandem mass spectrometric detection. *J Chromatogr A* 766:153–158.
- Steen RJCA, Ariese F, Hattum BV et al. (2004) Monitoring and evaluation of the environmental dissipation of the marine antifoulant 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in a Danish Harbor. *Chemosphere* 57:513.
- Thomas KV (1998) Determination of selected antifouling booster biocides by high-performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. *J Chromatogr A* 825:29.

- Thomas KV (1999) Determination of the antifouling agent zinc pyrithione in water samples by copper chelate formation and high-performance liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. *J Chromatogr A* 833:105.
- Thomas KV, Blake SJ, Waldock MJ (2000) Antifouling paint booster biocide contamination in UK marine sediments. *Mar Pollut Bull* 40:739.
- Thomas KV, Fileman TW, Readman JW et al. (2001) Antifouling paint booster biocides in the UK coastal environment and potential risks of biological effects. *Mar Pollut Bull* 42:677.
- Thomas KV, McHugh M, Waldock M (2002) Antifouling paint booster biocides in UK coastal waters: inputs, occurrence and environmental fate. *Sci Total Environ* 293:117.
- Thomas KV, McHugh M, Hilton M et al. (2003) Increased persistence of antifouling paint biocides when associated with paint particles. *Environ Pollut* 123:153.
- Tolosa I, Readman JW, Blaevøet A et al. (1996) Contamination of Mediterranean (Cote d'Azur) coastal waters by organotin and Irgarol 1051 used in antifouling paints. *Mar Pollut Bull* 32:335.
- Tóth S, Becker-van Slooten K, Spack L et al. (1996) Irgarol 1051, an antifouling compound in freshwater, sediment, and biota of Lake Geneva. *Bull Environ Contam Toxicol* 57:426–433.
- Turley PA, Fenn RJ, Ritter JC (2000) Pyrithiones as antifoulants: Environmental chemistry and preliminary risk assessment. *Biofouling* 15:175.
- Voulvoulis N (2006) Antifouling paint booster biocides: Occurrence and partitioning in water and sediments. *Handbook of Environmental Chemistry, Volume 5: Water Pollution*. Springer, Berlin: 155.
- Voulvoulis N, Scrimshaw MD, Lester JN (2000) Occurrence of four biocides utilized in antifouling paints, as alternatives to organotin compounds, in waters and sediments of a commercial estuary in the UK. *Mar Pollut Bull* 40:938.
- Zhou L, Fileman TW, Evans S et al. (1996) Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary and Humber coastal zone. *Mar Pollut Bull* 32:599–608.