Coastal Marine Science 29(1): 28–39, 2004

Review

Occurrence and degradation of representative TBT free-antifouling biocides in aquatic environment

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» Received 5 January 2004; Accepted 7 March 2004

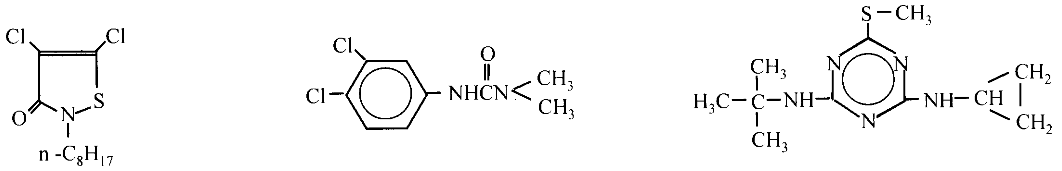
Abstract—The physico-chemical characterization, distribution, degradation and cross media partitioning in aquatic environment of eight species of booster biocides were reviewed. The physico-chemical characterizations of these booster biocides varied. Generally, low water/sediment partitioning, low bioconcentration factor and non volatilization were assumed from physico-chemical properties. The survey of booster biocides were carried out in somewhere of the world. Sea-Nine 211, Diuron, Irgarol 1051, Chlorothalonil and Dichlofluanid in water were detected in the range of <0.001–$3.7\,\mu g\,l^{-1}$, <0.0007–$6.742\,\mu g\,l^{-1}$, <0.001–$1.7\,\mu g\,l^{-1}$, <0.001–$1.38\,\mu g\,l^{-1}$ and <0.001–$0.76\,\mu g\,l^{-1}$, respectively. Concentrations of Sea-Nine 211, Diuron, Irgarol 1051, Chlorothalonil and Dichlofluanid in sediment ranged of <0.1–$2.35\,\mu g\,kg^{-1}$ dry, <0.1–$1350\,\mu g\,kg^{-1}$ dry, 0.007–$222.3\,\mu g\,kg^{-1}$ dry, <0.1–$46.5\,\mu g\,kg^{-1}$ dry and <0.1–$688.2\,\mu g\,kg^{-1}$ dry, respectively. While, there are no report concerning of Copper pyrithione, Zinc pyrithione and Pyridine triphenylboron. Sea-Nine 211, Dichlofluanid, Copper pyrithione, Zinc pyrithione and Pyridine triphenyl boron were degraded easily by sunlight and bacteria. Further Copper pyrithione, Zinc pyrithione and Pyridine triphenyl boron were hydrolyzed in seawater. As a consequence, these compounds therefore produced various degradation products.

Key words: Sea-Nine 211, Irgarol 1051, Diuron, Copper pyrithione, Zinc pyrithione, Chlorothalonil, Dichlofluanide, Pyridine triphenylboron

Introduction

Antifouling products contain biocides which were developed to prevent the progressive built up of bacteria, macro algae, mussels, barnacles and other invertebrates on under water surfaces. Up to date, organotin (Ot) compounds have been used as an effective antifouling biocide. However, non-target marine organisms have been damaged by leaching of Ots into water column from coatings applied to boat hulls (Alizieu et al., 1986, Gibbs and Bryan, 1986). Further the marine environment has been contaminated widely with Ots (Harino et al., 1998, Chau et al., 1997). As a consequence, the International Martine Organization (IMO) adopted the International Convention on the Control of Harmful Antifouling Systems (AFS Convention) which will prohibit the use of Ots as active ingredients in antifouling systems on ships in October 2001, Following international restrictions on the use of Ot based antifoulants, paint manufacturers have developed many products. In Japan, chemical substances more than 20 species were proposed and used as booster compounds. Here, booster biocides means a group of compounds normally induced in addition to copper in antifouling formulations. It is well known that copper exhibits antifouling activities against organisms such as barnacles, tube worms and the majority of algal fouling species. However, several algal species show a marked physiological tolerance to copper. Therefore, booster compounds were added to antifouling paint with copper. By addition of booster compounds, efficacy of antifouling paint was enhanced against a broader spectrum of fouling organisms than that achieved with copper alone. Booster biocide used the self-polishing copolymers by bonding copper, silicon, zinc or oligomer groups with its carboxylate side chain (Omae, 2003). Self-polishing copolymers are made of acrylic or methacrylic polymer and these polymers are easily hydrolyzed in seawater. Aquatic organisms which attached on ship-hull are eliminated together with the copolymer film which is decomposed by the hydrolysis of the copolymer. At the same time, the biocidal effect is occurred.

The booster biocides which were released to the aquatic environment are occurred, transported, degradated, accumulated to sediment and concentrated in aquatic orgamisms in aquatic environment. However, because the behaviour of these



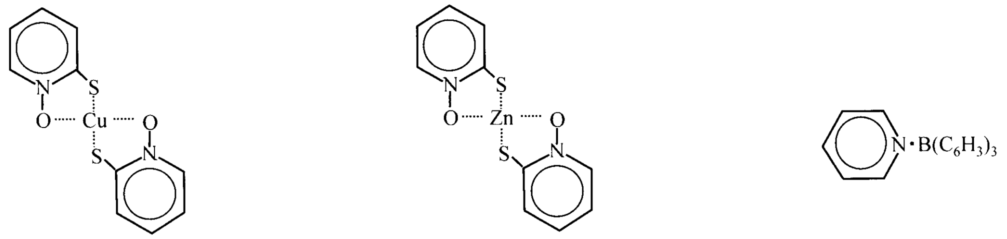
4,5-Dichloro-2-(n-octyl)-4-isothiazoline-3-one
(Sea Nine -211)

N,N'-Dimethyl-N'-(3,4-dichlorophenyl)urea
(Diuron)

2-(Tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5-triazine
(Irgarol 1051)

2,4,5,6-Tetrachloroisopthalonitrile
(Chlorothalonil)

N,N'-Dimethyl-N'-phenyl-N'-((fluorodichloromethyl)thio)sulfamide
(Dichlofluanid)



Copper 2-pyridinethiol-1-oxide
(Copper pyrithione)

Zinc 2-pyridinethiol-1-oxide
(Zinc pyrithione)

Pyridine triphenyl boron
(PK)

Fig. 1. The structure of representative antifouling biocides.

compounds is still no clear, little is known about the effect for aquatic organism of each biocide. The review will focus on the eight booster biocides in common use (Fig. 1) and the occurrence, degradation and water-sediment partitioning of these compounds are discussed in aquatic environment.

General Information and Physico-Chemical Properties

Most of booster biocides have been used as pesticides. Therefore, physico-chemical properties of these compounds were reported. Because Sea-Nine 211, Copper pyrithione and Pyridine triphenylboron were produced as antifouling biocides, there were a few available data. Physico-chemical properties of these representative biocides are shown in Table 1. These booster biocides have various physico-chemical properties.

Sea-Nine 211 was produced for registration purposes with the US Environmental Protection Agency (EPA) by the manufacturers Rohm and Haas Ltd. Sea Nine 211 is a member of a group of 3(2H)-isothiazolones which show high activity against a wide range of bacteria, fungi, algae and marine invertebrates. Though water solubility was high slightly among these biocides, log Pow ranged of 2.8–6.4, indicating that Sea-Nine 211 has possible to be absorbed to particle matter.

Diuron has been used as a selective herbicide to control germination broadleaf and grass weeds in numerous crops such as sugarcane, pineapple, alfalfa, grapes, cotton and peppermint. Higher water solubility and lower log Pow indicate that this compound is dissolved in water. Further, lower vapour pressure shows novolatalization.

Irgarol 1051 has been used as a s-triazine herbicide, which exhibits high activity against algae. It has been registered for use in antifouling paints for a known herbicide which has been in widespread agricultural use for around 40 years. Irgarol 1051 has been used in antifouling paints to control algal fouling for a few years. Irgarol 1051 was slightly soluble in water and moderately lipophilic compound and the vapour pressure was low, indicating that volatilization from water is negligible. Biselli et al. (2000) reported that water solubility of 7 $mg\,l^{-1}$ implied a higher affinity to particle matter than the corresponding atrazine which exhibit higher water solubility (33 $mg\,l^{-1}$).

Chlorothalonil has been used as a fungicide against a

Table 1. Physico-chemical properties of common antifouling paint booster biocides.[1)]

	CAS No.	Molecular weight	Solubility	Log Pow	Henry's law constant	Vapour pressure
Sea-Nine 211	64359-81-5	282.2	6 mg l^{-1}	2.8, 6.4	–	0.98 mPa (25°C)
Diuron	330-54-1	233.1	42 mg l^{-1}	2.86	6×10^{-6} m^3 mol^{-1}	0.41 mPa (50°C)
Irgarol 1051	28159-98-0	253.36	7, 9 mg l^{-1}	2.8	–	0.089 mPa
Chlorothalonil	1897-45-6	265.9	0.9 mg l^{-1} (25°C)	2.64–4.34	2.2×10^{-1} m^3 mol^{-1}	0.076 mPa (25°C)
Dichlofluanid	1085-98-9	333.2	1.3 mg l^{-1} (20°C)	3.7	4.1×10^{-3} m^3 mol^{-1}	0.016 mPa (20°C)
Zinc pyrithione	13463-41-7	317.68	6 mg l^{-1}	0.9	–	–
Copper pyrithione	14915-37-8	315.9	<1 mg l^{-1}	0.9	–	–
Pyridine triphenylboron	971-66-4	321.23	1 mg l^{-1}	–	–	<133 mPa (20°C)

1) Bisseli et al., 2000, Caux et al.,1996, Hall et al.,1999, Omae, 2003, Takahashi et al., 2002, USEPA, 1989, Thomas, 2001a.

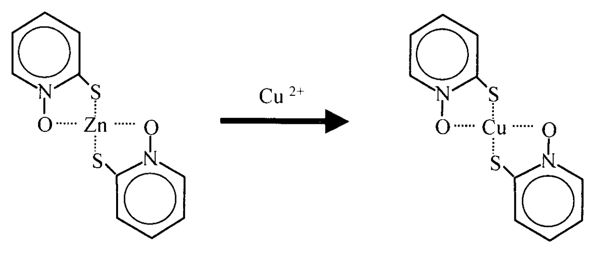
broad spectrum of plant pathogens for around 25 years. Its use in antifouling paints as a broad spectrum antifouling biocide was limited, although it was registered in a number of countries. In spite of lower water solubility of Chlorothalonil in comparison with Sea-Nine 211, Diuron and Irgarol 1051, log Pow was similar level to them. It is presumed that this compound is associated with sediment and suspended particle.

Dichlofluanid has been used as an acaricide and fugicide in agriculture. In spite of lower water solubility, log Pow is 3.7 as well as Chlorothalonil. In judging from physico-chemical data, dichlofluanid has possibility to be associated particle matters.

Zinc pyrithione was effectiveness compounds as a bactericide, fungicide and algicide and this compound has been widely used as an anti-dandruff additive in shampoos. Zinc pyrithione was known to have the potential for chemical transformation, because ZPT was the zinc chelate of 2-pyridinethiol-1-oxide. It has been reported that ZPT can transchelate with other cationic metals such as Cu^{2+} (Fig. 2). Thus, ZPT is unstable compound in water. Water solubility of 6 mg l^{-1} and log Pow of 0.9 indicated no absorption with suspended particles. On the other hand, Galvin et al. (1998) reports that it may accumulate in sediments as copper and manganese complexes, because ZPT undergo transchelation with copper and possibly manganese.

Copper pyrithione was also chelate compounds and the chelate formation constant of the 1 : 1 Cu^{2+} complex of pyrithione was much greater than those of the Zn^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} complexes. Namely, copper complex was so stable (Nakajima et al., 1990). In spite of lower water solubility, log Pow was low. It was difficult to estimate the behaviour of Copper pyrithione from phisico-chemical property, because of organometallic compounds.

Triarylboron-amine adducts have been known since the early 1960s to show a wide variety of biological acitivity including antibacterial, antifungal and marine anti-fouling applications. Pyridine triphenyl boron which was produced by Hokko Chemical Industry, was induced commercially as an antifouling additive in Japan in 1993. Little physico-chemical data was available for this compound. Water solubility was low, presuming the presence in water.



Zinc 2-pyridinethiol-1-oxide
(Zinc pyrithione)

Copper 2-pyridinethiol-1-oxide
(Copper pyrithione)

Fig. 2. Chemical transformation between Copper pyrithione and Zinc pyrithione (Turley et al., 2000).

Occurrence

Concentration

This review was focused on the concentrations of booster biocides in water and sediment, because there was a few reports concerning of those in biological samples. The researches on booster compounds have been carried out since early 1990. Table 2 and 3 shows the concentration of booster biocides in water and sediment.

There a few paper concerning to Sea-Nine 211 in water. A study by Thomas et al. (2001b) did not detect Sea-Nine 211 in water and sediment from marinas on the South coast of the UK in 1998. Martinez et al. (2001) reported that Sea-Nine 211 was detected in the range of 2.6 to 3.7 $\mu g l^{-1}$ in water from Mediterranean sea, Spanish. In coastal area of Greece, concentrations of Sea-Nine 211 were <0.0063–0.049 $\mu g l^{-1}$ (Sakkas et al., 2002a). Harino et al. (2004) reported that concentrations of Sea-Nine 211 in water and sediment ranged of

Table 2. The concentrations of antifouling biocides in water from various countries.

Biocide	Location	Date	Concentration	Average	Reference
Sea-Nine 211	Mediterranean sea, Spanish	Mar.1999–Feb.2000	2.6–3.7		Martinez et al., 2001
	Southampton, England	Summer, 2000	<0.001	<0.001	Thomas et al., 2002
	Coastal area, Greece	Oct. 1999–Sep. 2000	<0.0063–0.049		Sakkas et al., 2002a
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	<0.0003–0.004	0.002	Harino et al., 2004
Diuron	Hamble estuary, England	Sep. 1998–Feb. 1999		0.123	Boxall et al., 2000
	Owell estuary, England	Sep. 1998–Feb. 1999		0.208	Boxall et al., 2000
	Crouch estuary, England	Apr. 1998–Oct. 1998	<0.001–6.742	0.085	Thomas et al., 2001b
	Crouch estuary, England	Jan. 1998	0.6–0.117	0.021	Thomas et al., 2001b
	Southampton, England	Jan. 1998	<0.001–0.101	0.008	Thomas et al., 2001b
	Southampton, England	Apr. 1998–Oct.1998	0.005–0.305	0.036	Thomas et al., 2001b
	Southampton, England	Summer, 2000	<0.016–1.249	0.309	Thomas et al., 2002
	Sutton harbour, England	Jan. 1998	<0.001–0.025	0.011	Thomas et al., 2001b
	Sutton harbour, England	Apr. 1998–Oct. 1998	0.001–0.334	0.065	Thomas et al., 2001b
	Mediterranean sea, Spanish	Mar. 1999–Feb. 2000	0.002–1.030		Martinez et al., 2001
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	<0.0007–1.54	0.126	Harino et al., 2004
Irgarol 1051	Corwy marina, England	Jan. 1999–Mar. 1999	0.007–0.543	0.126	Sargent et al., 2000
	Humble estuarine, England	July 1993–Oct. 1993	0.012–0.19	0.084	Gough et al., 1994
	Hamble estuary, England	Sep. 1998–Feb. 1999		0.025	Boxall et al., 2000
	Owell estuary, England	Sep. 1998–Feb. 1999		0.048	Boxall et al., 2000
	Crouch estuary, England	Jan. 1998	<0.001–0.015	0.009	Thomas et al., 2001b
	Crouch estuary, England	Apr. 1998–Oct. 1998	<0.001–0.404	0.023	Thomas et al., 2001b
	The solent and English Channel	July 1993–Oct. 1993	0.002–0.011	0.005	Gough et al., 1994
	Southampton, England	Jan. 1998	<0.001–1.421	0.105	Thomas et al., 2001b
	Southampton, England	Apr. 1998–Oct. 1998	<0.001–0.049	0.009	Thomas et al., 2001b
	Southampton, England	Summer, 2000	<0.001–0.305	0.036	Thomas et al., 2002
	Sutton harbour, England	Jan. 1998	0.011–0.08	0.054	Thomas et al., 2001b
	Sutton harbour, England	Apr. 1998–Oct. 1998	<0.001–0.084	0.0085	Thomas et al., 2001b
	Brighton marina, England	Nov. 1999–Jan. 2001	<0.001–0.964	0.032	Bowman et al., 2003
	Blackwater estuary, England	Oct. 1998–June 1999	<0.050–0.68	0.148	Voulvoulis et al., 2000
	Medway estuarine, UK	July 1993–Oct. 1993	0.004–0.018	0.011	Gough et al., 1994
	Plymouth sound, England	<1997	<0.001–0.127	0.04	Scarlett et al., 1999
	Lake Geneva, Switzerland	Aug. 1994–Apr. 1995	0.0025–0.145		Toth et al., 1996
	Coastal area, Greece	Oct. 1999–Sep. 2000	<0.0022–0.9	0.016	Sakkas et al., 2002a
	North Sea, German	July 1997–Sep. 1997	0.011–0.17	0.051	Bisslli et al., 2000
	Baltic Sea, German	Aug.1997	0.060–0.44	0.266	Bisslli et al., 2000
	Mediterranean sea, Spanish	Mar. 1999–Feb. 2000	<0.02–0.665		Martinez et al, 2001
	Mediterranean sea, (Cote d'Azur), Monaco	May. 1995–Jun. 1995	<0.0015–0.640	0.296	Tolosa., et al., 1996
	Mediterranean sea, (Cote d'Azur), Monaco	<1993	<0.005–1.7	0.369	Readman et al., 1993
	Florida (Biscayne Bay), USA	Mar. 1999–Sep. 2000	<0.001–0.0609	0.0052	Gardinali et al., 2002
	Hamilton harbour, Bermuda	Jun. 1995	0.01–0.59	0.112	Connelly et al., 2001
	Seto Inland Sea, Japan	1998	<0.005–0.142	0.029	Okamura et al., 2000
	Seto Inland Sea, Japan	Sep. 1996–Aur. 1997	<0.005–0.264	0.019	Liu et al., 1999a
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	<0.0008–0.267	0.013	Harino et al., 2004
Chlorothalonil	Southampton, England	Summer, 2000	<0.001	<0.001	Thomas et al., 2002
	Blackwater estuary, England	Oct. 1998–June 1999	<0.20–1.38	0.252	Voulvoulis et al., 2000
Dichlofluanid	Coastal area, Greece	Oct. 1999–Sep. 2000	<0.0052–0.055	0.021	Sakkas et al., 2002a
	Mediterranean sea, Spanish	Mar. 1999–Feb. 2000	<0.02		Martinez et al., 2001
	Southampton, England	Summer, 2000	<0.001	<0.001	Thomas et al., 2002
	Blackwater estuary, England	Oct. 1998–June 1999	<0.24	<0.24	Voulvoulis et al., 2000
	Coastal area, Greece	Oct. 1999–Sep. 2000	<0.001–0.284	0.075	Sakkas et al., 2002a
	Mediterranean sea, Spanish	Mar. 1999–Feb. 2000	<0.02–0.76		Martinez et al., 2001

$(\mu g\, l^{-1})$

Table 3. The concentrations of antifouling biocides in sediment from various countries.

Biocide	Location	Date	Concentration	Average	Reference
Sea-Nine 211	Southampton, England	Summer, 2000	<0.1	<0.1	Thomas et al., 2002
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	<0.2–2.35	0.516	Harino et al., 2004
Diuron	Hamble estuary, England	Sep. 1998–Feb. 1999		7.8	Boxall et al., 2000
	Owell estuary, England	Sep. 1998–Feb. 1999		105	Boxall et al., 2000
	Southampton, England	The end of the 1998	<0.1–1.42	101	Thomas et al., 2000
	Southampton, England	Summer, 2000	0.4–1.249	187	Thomas et al., 2002
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	0.637–1350	39.4	Harino et al., 2004
Irgarol 1051	Hamble estuary, England	Sep. 1993	<10–132	40	Gough et al., 1994
	Hamble estuary, England	Sep. 1998–Feb. 1999		6.3	Boxall et al., 2000
	Owell estuary, England	Sep. 1998–Feb. 1999		257	Boxall et al., 2000
	Southampton, England	The end of the 1998	<1–11	8.2	Thomas et al., 2000
	Southampton, England	Summer, 2000	300–3500	880	Thomas et al., 2002
	Blackwater estuary, England	Oct. 1998–June 1999	<03.1–222.3	145	Voulvoulis et al., 2000
	Lake Geneva, Switzerland	Aug. 1994–Apr. 1995	<0.2–8		Toth et al., 1996
	North Sea, German	July 1997–Sep. 1997	3–25	12.5	Bisslli et al., 2000
	Baltic Sea, German	Aug. 1997	4–220	67.8	Bisslli et al., 2000
	The Port of Osaka, Japan	Jan. 2002–Oct. 2003	7–816	641	Harino et al., 2004
Chlorothalonil	Southampton, England	Summer, 2000	<0.1	<0.1	Thomas et al., 2002
	Blackwater estuary, England	Oct. 1998–June 1999	<4.1–46.5	14.6	Voulvoulis et al., 2000
Dichlofluanide	Southampton, England	Summer, 2000	<0.1	<0.1	Thomas et al., 2002
	Blackwater estuary, England	Oct. 1998–June 1999	<4.9–688.2	567	Voulvoulis et al., 2000

(μg kg^{-1} dry)

<0.0003–0.004 μg l^{-1} and <0.2–2.35 μg l^{-1} dry, respectively.

Several researches have been made on Diuron in coastal areas of England. The concentrations of Diuron were various in water from each area and maximum concentration was 6.742 μg l^{-1}. Generally, the concentrations of Diuron ranged from 10^{-2}–10^{-1} μg l^{-1} in water from England. The level of Diuron was also reported in Spanish. Concentration of Diuron in Spanish is similar level to England. Studies on Diuron in sediment by Thomas et al. (2002) and Boxall et al. (2000) showed that the concentration of Diuron was around 0. 1 μg kg^{-1} dry. In Japan, maximum concentration of Diuron was over 1000 μg kg^{-1} dry (Harino et al., 2004).

The presence of Irgarol 1051 in the surface waters of marinas on the Cote d' Azur, France was reported at concentrations of up to 1.7 μg l^{-1} in 1993 by Readman et al. (1993). Since 1993, the occurrence of Irgarol 1051 has been reported in a number of other European countries and Japan. Mean concentrations of Irgarol 1051 in water from each coastal area of England, Greece. German, Monaco, USA, Bermuda and Japan were ranged of 0.005–0.148, 0.016, 0.051–0.226, 0.296–0.369, 0.005, 0.112 and 0.019–0.029 μg l^{-1}, respectively. Irgarol 1051 was detected in the range of 0.0025–0.145 μg l^{-1} in water from Spanish. Maximum concentration in water from Spanish was 0.665 μg l^{-1}. At these levels found in the esturary, it is possible that non-target photosynthetic inhibition could occur (Sargent et al., 2000).

Irgarol 1051 was also detected in sediment. Means concentration in England range from 6 to 880 μg kg^{-1} dry and maximum concentration of 3500 mg kg^{-1} dry was detected in Southanpton, England. The concentrations of Irgarol 1051 in sediment from Switzerland, German and Japan were in the range of <0.2–8 μg kg^{-1} dry, 3–220 μg kg^{-1} dry and 7–816 μg kg^{-1} dry, respectively.

Boxall et al. (2000) researched the concentration of Irgarol 1051 and Diuron. In marina of England, the rank concentration were Diuron>Irgarol 1051. Harino et al. (2004) reported that the Port of Osaka, Japan showed the similar pattern to marina of England.

Chlorothalonil was not detected in water from Southampton, England and Mediterranean sea, Spanish. However mean concentration from Blackwater estuary, England was 0.252 μg l^{-1}. Chlorothalonil was also detected in sediment from Blackwater estuary at 146 μg kg^{-1} dry.

There were a few papers concerning of concentration of dichlofluanid in water. Dichlofluanid was not detected in water from most of coastal areas. Dichlofluanid was determined in the coastal water from the Greece and Spanish in the ranging of <0.001–0.284 and <0.02–0.76 μg l^{-1}. The mean concentration of Dichlofluanid in sediment from Blackwater, England was 567 μg kg^{-1} dry.

No literature has been found about the concentration of Pyrithione (Zinc pyrithione and Copper pyritrhione) and Pyridine triphenyl boron.

Geological distribution

The geological distribution of booster biocide was reviewed. Sargent et al. (2000) reported the the concentrations of Irgarol 1051 were not found to be influenced by salinity, pH or temperature, although there was a strong correlation between an average concentrations of Irgarol 1051 and the density of boating activity. Concentrations of Diuron and Irgarol 1051 in the lock marina were highest and concentrations in the open marina were lowest (Boxall et al., 2000). Lock marina was directly adjacent to the slipway where paint particles from pressure-washing and paint scraping may well have entered the marina. Detectable concentrations of both Irgarol 1051 and Diuron were determined in areas of high yachting activity such as mooring areas and marina (Thomas et al., 2001b).

Seasonal variation

Comber et al. (2000) carried out the survey of Diuron and Irgarol 1051 in water from the Hamble and Orwell estuaries during the summer and winter months. Concentrations of Diuron and Irgarol 1051 in water were significantly higher in summer compared with winter. The variation between summer and winter can be attributed to decreased boat density in the winter. Bisselli et al. (2000) reported that a seasonal depnendence of Irgarol 1051 concentrations was found both in the water and sediment samples, with maxima during the periods March–May/July–September, while during the winter period December–January low values were encountered though measurable amounts remained in the sediment. Albanis et al. (2002) monitored Irgarol 1051, Chlorothalonil and Dichlofluanid in sediment. Maximum values during the period June-September and minimum value during the winter period (December–February) were observed.

Degradation

One of conditions for ideal booster biocide is to be degraded rapidly in aquatic environment. Therefore, degradation products of booster biocides are of concern. Degradation products are made clear in some of booster compounds. The half-life of booster compounds in water and it's degradation products were reviewed (Table 4).

Though Sea-Nine 211 was stable in sterile water at pH7, Isothiazolone which Sea-Nine 211 had, was undergone chemical hydrolysis in acid and alkaline conditions (Shade et al., 1993). Jacobsen et al. (1993) was reported that biological degradation was rapid and Sea-Nine 211 degrades rapidly in natural water sea water (Table 4). Figure 3 shows the degradation pathway of isothiazolone ring (Thomas, 2001a). The cleaved isothiazolone ring was oxidized and produced the alkyl metabolites. The primary degradation products were *N*-octyl oxamic acid, 4,5 dichloro-thiazole and *N*-octyl carbamic acid.

There was no available half-life data of Diuron. Ellis and camper (1982) reported that photochemical degradation of Diuron was minor importance and most of the degradation was due to biological activities and over 80% of Diuron was degraded in seawater within 27 days. In aerobic condition, Diuron produced 3-(3,4-dichlorophenyl)-1-methyl urea, 3,4-dichlorophenyl urea and 3,4-dichloroaniline. In the case of anaerobic condition, Diuron was formed 3-(4-chlorophenyl)-1,1′-dimethylurea (Fig. 4).

There are many studies on degradation of Irgarol 1051. The half-life of Irgarol 1051 was over 36 days in aquatic environment. Liu et al. (1997) reported the major route of Irgarol 1051 metabolism in the white rot fungus *P. chrysosporium*. The pathway includes N-dealkylation of a cyclopropyl group from the cyclopropylamino side-chain at the 6-position of the s-triazine ring to yield the stable metabolite M1 (2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine) (Fig. 5). M1 could not be metabolized further by the *P. Chrysosporium* culture and appeared to accumulate as a terminal metabolite. Irgarol 1051 also degraded M1 by Hg—catalyzed hydrolysis (Liu et al., 1999b).

Chlorothalonil was degraded rapidly by sunlight (Table 4). Chlorotalonil was also hydrolyzed in soft water (Ernst et al., 1991). In fresh water with pH less than 8.0, hydrolysis was insignificant. At pH values greater than 8.0, hydrolysis occurred at 1.8% per day. Chlorothalonil was hydrolyzed to 4-hydroxy-2,5,6-trichloroisophtalonitrile and 3-cyano-2,4,5,6-tetrachlorobenzamide in water of pH 9.0. Sakkas et al.(2002b) reported the photodegradation of chlorothalonil in different natural water (sea, river and lake). Half-life of chlorothalonil ranged form 1 to 48 h. Further, the dissolved organic matter such as humic and fulvic substances enhanced the photodegradation of chlorothalonil. Chlorothalonil produced chloro-1,3-dicyanobenzen, dichloro-1,3-dicyanobenzene, trichloro-1,3-dicyanobenzene and benzamide. The biotic and abiotic degradation in estuarine water in vitro was reported by Walker et al. (1988). The fate in simulated marine environments was similar to that in freshwater systems. The half-life of Chlorothalonil was 10 and 8–9 day in sterile water and non-sterile water, respectively. Biotic and abiotic degradation of Chlorothalonil was slower in comparison with photodegradation and hydolysis.

A study on the degradation of Dichloflunanid by Thomas et al. (2002) showed that the degradation of Dichlofluanid was

Table 4. Summary of common booster biocides half-lives in various environmental matrices.

	Study type	Condition	Half-lives (day)	Reference
Sea-Nine 211	Hydolysis	Sterile water (pH 5)	9	Shade et al., 1993
		Sterile water (pH 7)	>30	Shade et al., 1993
		Sterile water (pH 9)	12	Shade et al., 1993
	Photodegradation	Sunlight	13.4	Shade et al., 1993
	Aquatic metabolism	Aerobic seawater (25°C)	<1	Shade et al., 1993
		Aerobic seawater (15°C)	1.9	Thomas et al., 2004
		Anaerobic seawater (25°C)	<1	Shade et al., 1993
		Anaerobic	<0.5	Thomas et al., 2004
Diuron	Biodegradation	Anaerobic	<27 (Over 80% of Diuron was degraded)	Ellis and Camper, 1982
	Aquatic metabolism	Anaerobic	14	Thomas et al., 2004
Irgarol 1051	Hydrolysis		>200	Hall et al., 1999
	Photodegradation	Fresh water (no solvent)	36	Hall et al., 1999
		Fresh water (with solvent)	85 (0.5% methanol)	Hall et al., 1999
			148 (1% acetonitrile)	Hall et al., 1999
		Seawater (with solvent)	273 (1% acetonitrile)	Hall et al., 1999
	Aquqtic metabolism	Aerobic freshwater	96	Hall et al., 1999
		Aerobic seawater	201	Hall et al., 1999
		Aerobic seawater (15°C)	82	Thomas et al., 2004
		Anaerobic	No degradation	Hall et al., 1999
		Anaerobic	>226	Thomas et al., 2004
Chlorothalonil	Hydrolysis	Soft water (pH 6.5–7.4)	1.25	Ernst et al., 1991
	Photodegradation	Outdoor (Distilled water)	2	Sakkas et al., 2002b
		Outdoor (Lake water)	0.3	Sakkas et al., 2002b
		Outdoor (River water)	0.4	Sakkas et al., 2002b
		Outdoor (Sea water)	1.9	Sakkas et al., 2002b
	Aquatic metabolism	Aerobic seawater (15°C)	2.8	Thomas et al., 2004
		Marine and fresh water	10	Walker et al., 1988
		Anaerobic	<0.5	Thomas et al., 2004
Dichlofluanid	Aquatic metabolism	Aerobic seawater (15°C)	0.8	Thomas et al., 2002
	Aquatic metabolism	Anaerobic	<0.5	Thomas et al., 2004
Zinc pyrithione	Hydrolysis	Abiotic artificial seawater	>90	Turley et al., 2000
		Biotic natural seawater	4	Turley et al., 2000
		Biotic river/pond seawater	0.3	Turley et al., 2000
	Photodegradation	Abiotic (Xe lamp) artificial seawater	0.01	Turley et al., 2000
		Abiotic (sunlight) artificial seawater	0.001	Turley et al., 2000
	Aquatic metabolism	Aerobic seawater/sediment	0.08–0.92	Turley et al., 2000
		Anaerobic seawater/sediment	0.02	Turley et al., 2000
Copper pyrithione	Hydrolysis	Abiotic artificial seawater	12.9	Turley et al., 2000
		Biotic natural seawater	4	Turley et al., 2000
	Photodegradation	Abiotic (Xe lamp) artificial seawater	0.02	Turley et al., 2000
	Aquatic metabolism	Aerobic seawater/sediment	0.08–0.92	Turley et al., 2000
		Anaerobic seawater/sediment	0.02	Turley et al., 2000
Pyridine triphenylboron	Photodegradation	Abiotic (254nm) Seawater	<0.04	Amey and Waldon, 2004
		Abiotic (sunlight) artificial seawater	<0.125	Amey and Waldon, 2004
	Biodegradation	Aerobic natural seawater	<5	Amey and Waldon, 2004

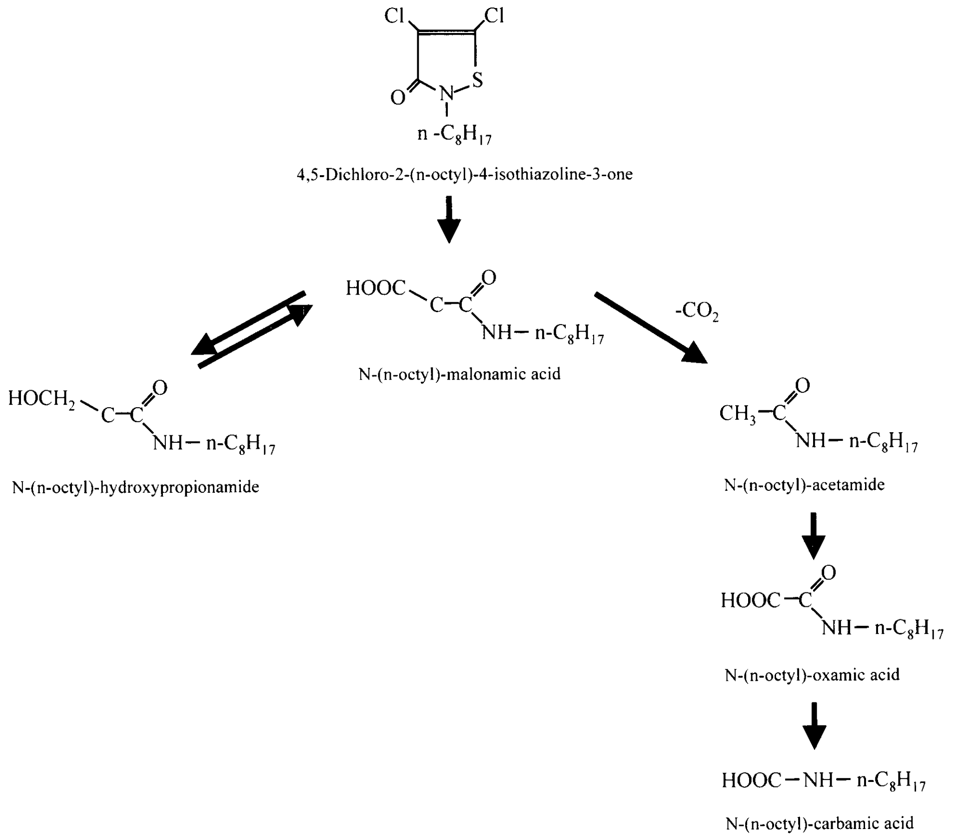


Fig. 3. The degradation pathway of Isothiazolene ring (Thomas et al., 2001).

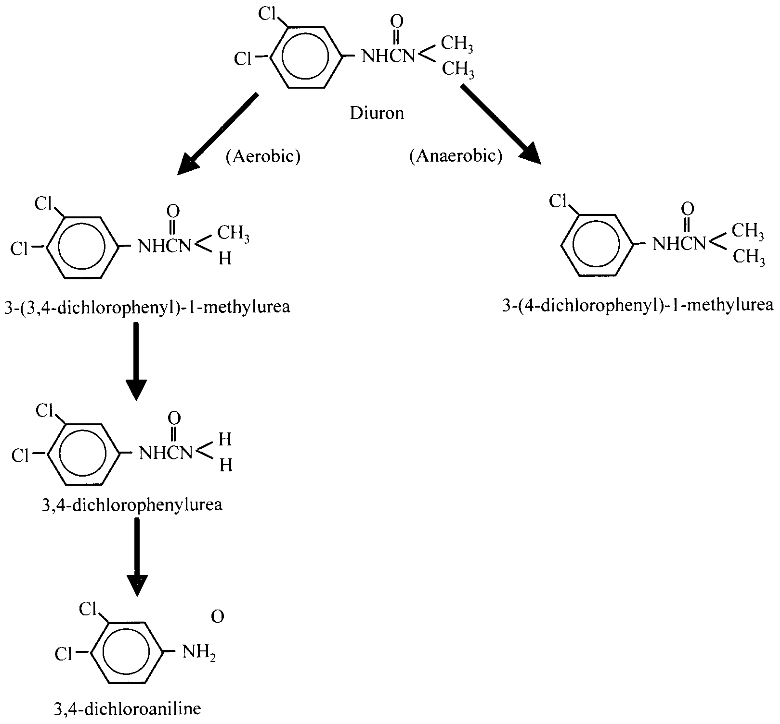


Fig. 4. The degradation pathway of Diuron (Ellis and Camber, 1982).

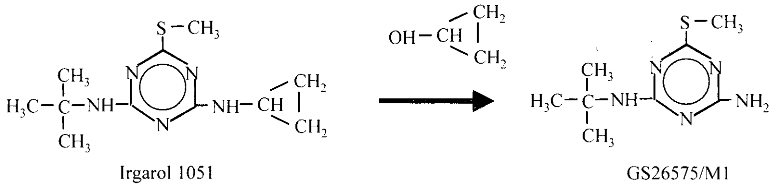


Fig. 5. The degradation pathway of Irgarol 1051 (Liu et al., 1997).

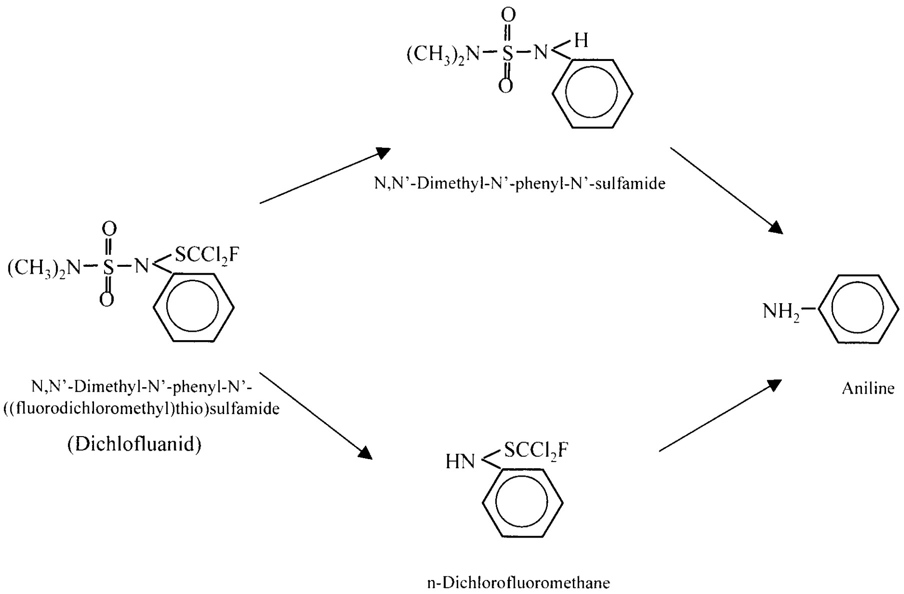


Fig. 6. The degradation pathway of Dichlofluanid in anaerobic condition (Thomas et al., 2004).

complete in natural seawater at 25°C. The degradation pathway in anaerobic condition is displayed in Fig. 6. Dichlofluanid yielded *N,N'*-dimethyl-*N'*-phenylsulfamide, *n*-dichlorofluoromethylthion-aniline, aniline and dichlorofluoromethane in anaerobic condition (Thomas et al., 2004).

Pyrithione containing Zinc and Copper pyrithiones was flexible group. Figure 7 shows some of the chemistry of pyrithione (Seymour and Bailey, 1981). H-pyrithione, the free form of pyrithione, was an acid with pKa of 4.4. Its salts, Na pyrithione and NH_4 pyrithione, were soluble in water, methanol. Pyrithione$^-$ combined with metal ions to form complexes and many of them had no net charge and were insoluble in water. Some of these complexes could be extracted into chloroform and were brightly coloured such as Copper pyrithione. The stability constants of pyrithione complexes were pH-dependent and varied among different metal ions. Pyrithione$^-$ released one type of metal ion and combined with another depending on the type and amount of ions present. Pyrithione$^-$, its salts and its metal complexes were also light sensitive. When H-pyrithione was irradiated with ultra-violet (UV) light in any one of several organic solvents, it dimerizes. This compound was oxidized to 1-oxpyridine-2-sulfonic acid

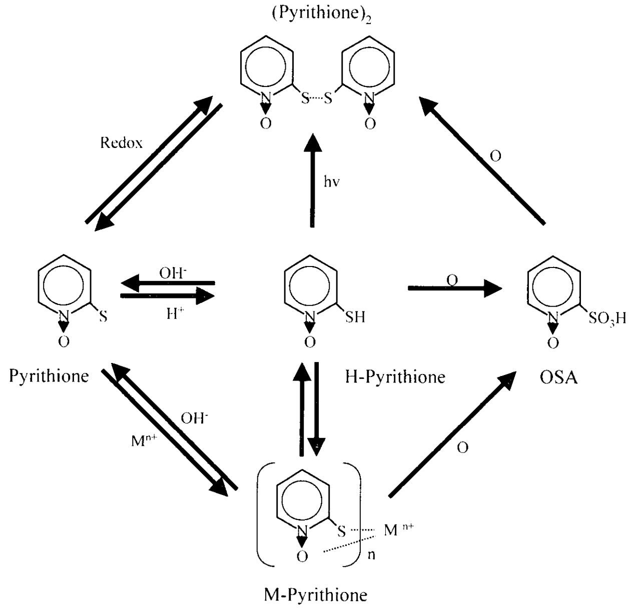


Fig. 7. Solution chemistry of Pyrithione (Seymour and Bailey, 1981).

(OSA) by reaction with molecular oxygen after further irradiation.

Turkey et al. (2000) studied on degradation of Copper pyrithione and Zinc pyrithione using radiolabeled compounds. The half-life of Copper pyrithione by hydrolysis in sterilized artificial seawater (pH 8) was 12.9 days at the initial concentration of 50 $\mu g\,l^{-1}$. Further, biological degradation of Copper pyrithione was researched. Concentration of radiolabeled Copper pyrithione was 52 $\mu g\,l^{-1}$. In the seawater die-away study, the observed half-life was approximately 4 day at the initial concentration of 52 $\mu g\,l^{-1}$. In a die-away method using freshwater from the Connecticut River, the half-life of Copper pyrithione was 7 hours at ambient temperature. Copper pyrithione was more sensitive for light. The half-lives of Copper pyrithione (50 $\mu g\,l^{-1}$) was 29.1 min under a filtered xenon arc lamp (154 watts m^{-2}).

In artificial water, the hydrolytic half-life of Zinc pyrithione was >90 days. Zinc pyrithione was compound which has high sensitivity for light as well as Copper pyrithione. The half-life of Zinc pyrithione in artificial seawater (borosilicate glass vials under a filtered xenon arclamp) was 17.5 min and photolytic degradation in natural sunlight had a half-life of <2 min. The observed half-life of Zinc pyrithione (33 $\mu g\,l^{-1}$) by bacteria was approximately 4 days in seawater.

There were no available information on the hydrolysis and biodegradation for Pyridine triphenyl boron. The photolysis of Pyridine triphenyl boron was done in aerated artificial seawater by Amey and Waldron (2004). The light source was a low-pressure mercury lamp providing 5.5 watts of UV radiation output at 254 nm. Under these conditions, Pyridine triphenyl boron was degraded rapidly and finally, H_3BO_3 was produced by elimination of pyridine and phenol at less than one hour (Fig. 8).

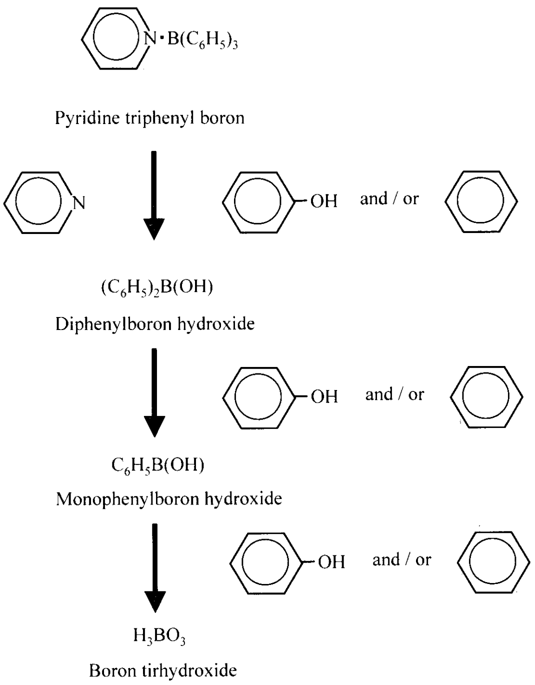


Fig. 8. The degradation pathway of Pyridine triphenylboron by photolysis (Amey and Waldron, 2004).

Crossmedia Partitioning

Water/sediment partitioning (Kd) of booster biocides are important factor on discussion of behaviour in aquatic environment. Shade et al. (1993) investigated about the absorption and desorption of Sea-Nine 211 to aquatic sediment. Log Koc (adsorption coefficients which were corrected for organic carbon content) ranged from 5.662 for silt loam to 15.441 for aquatic sediment, while desorption coefficients ranged from 7.575 for silt loam to 21.541 for aquatic sediment.

Comber et al. (2002) calculated Kd of Diuron between the sediments and seawater over a period of 20 days. Log Kd of Diuron ranged from 2.28 to 5.20, indicating that Diuron is predominantly in the dissolved form. Callow and Willingham (1995) reported that log Koc of Diuron was 2.6.

Log Koc of Irgarol 1051 ranged from 2.41 to 4.89, suggesting that Irgarol 1051 is predominantly in the dissolved form in aquatic environment as well as Diuron (Comber et al., 2002). Tolosa et al.(1996) analyzed concentration of Irgarol 1051 in the dissolved and suspended phases of the water column and estimated log Kd of 3.4 and a log Koc of 3.0. Bowman et al. (2003) reported that values of log Kd ranged from 2.2 to 4.2, and no correlation was found between Kd and sediment organic matter content. A mean value log Koc of Irgarol 1051 which was estimated based on the water and sediment samples of the Baltic Sea marina was 3.3 (Biselli et al., 2000).

Thomas et al. (2002) reported that Kd and log Koc of Chlorothalonil were 37 and 3.3, respectively.

To our knowledge, no information for Kd of Dichlofluanid, Copper pyrithione, Zinc pyrithione and Pyridine triphenylboron could be found. Kd of rapid degradation compounds in seawater may not be an important parameter when considering their fate.

Conclusion

The ideal antifouling paint for aquatic environment was to degrade rapidly in the environment, to be lower Kd, to be lower bioaccumulation and to show the minimal toxicity for aquatic organisms at concentrations present in the environment. Rapid degradation and lower Kd of booster biocides were found by this review. However, it is not clear about bioconcentration and toxicity for aquatic organisms of booster biocides. Most of booster biocides produce degradation product in water, however little informations were available for behaviour and toxicity of degradation products in aquatic environment. Further studies is to be clear the fate and effect of biocides containing the degradation product.

Acknowledgment

The author would like to express sincere thanks to Dr. Kazunobu Takahashi of Kanae Paint Co. Ltd. for providing many articles, reviews and books.

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