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IMPACT OF ANTIFOULING BIOCIDES ON SEA WATER, SEDIMENT AND MARINE ORGANISMS

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Key word : Irgarol 1051, Diuron, Sea-Nine 211, TPBP, Oyster, Sea urchin, Sediment core, Chronology

Abstracts : This research focused on the impact of antifouling biocides on sea water, sediment and marine organisms. In Japan in 1997 and worldwide from September 2008, prohibition of Ot (organotin) compounds was introduced. This meant that the production of paints containing TBT compounds was stopped and alternatives to the available Ot antifoulants had to be developed. It has been claimed that the decomposition characteristics of these alternative Ot antifoulants were better than those of Ot compounds. Since the introduction of the alternative antifoulants, the accumulation of these compounds has been reported in many countries. However, the toxicity of these compounds has still largely gone unreported. Unlike previous research which only investigated Ot compounds, this research also looked at the Ot alternative antifoulants Irgarol 1051,Diuron,Sea-Nine 211 and TPBP.

First there was the investigation of the antifouling biocide's concentration in sea water and sediment, then the monitoring of the effects of toxicity on the fertilized oyster and sea urchin egg's development, followed by the calculation of the risk factor, and finally the evaluation of the environmental risk.

In this r esearch, Sea-Nine 211, Irgarol 1051 and Diuron were detected in seawater samples at not detected (ND) to **0.10 μg /L**, ND to 0.092 μg /L and ND to 0.73 μg /L, respectively. However, TPBP was not detected for this esearch period.

In surface sediment samples, Sea-Nine 211, Irgarol 1051 and Diuron were detected at not detected (ND) to 40ng/g, ND to 28ng/g and ND to 73 μg /g, respectively.

As for the sediment core samples, Sea-Nine 211, Irgarol 1051 and Diuron were detected at not detected (ND) to 140ng/g, 0.4 to 270ng/g and 1.4 to 220 μg /g, respectively.

The toxicity (24h-LC_{50}) of Sea-Nine 211, TPBP, TBT, TPT, Irgarol 1051 and Diuron on oyster embryos was 17μg/L, 6.3μg/L, 3.9 μg/L, 3.7μg/L,<1000μg/L and <1000μg/L, respectively. The toxicity (48h-LC_{50}) of TPBP on sea urchin embryos was 3l μg /L.The NOEC (non effective concentration) levels of Sea-Nine 211, TBT and TPT on oyster embryos were **under 0.10 μg /L**.

In the evaluation of the environmental impact of these chemicals , a risk factor that used the predicted environmental concentration (PEC) divided by predicted no-effect concentration (PNEC) was used. When this value exceeded a risk factor of 1.0, it was decided the chemical had an influence on the environment. The PNEC on the aquatic organism was calculated from the examination result of the acute or chronic effect in the organism species divided by assessment factor. In this research, the chemical resolved in the toxicity experiment were considered, so the assessment factor was set at 10.

In the case of Sea-Nine 211, the toxicity towards the oyster eggs was highest of four chemicals detected in this research. The PEC in Hiroshima Bay was 0.1 μg /L. The deformity rate of oyster embryos exceeded 10% in the solution with a concentration of 0.1 μg /L, so the NOEC was determined to be 0.1 μg /L. PNEC which is the NOEC divided by assessment factor was 0.01 μg /L and the chemical risk factor divided by their PNEC values was 10. In this case, the risk factor was much higher than a value of 1.0, and so it indicates that Sea-Nine 211 has an influence on the marine environment.

It was discovered that Ot alternative antifoulants accumulation characteristics in sediment were similar to Ot compounds, with both having much higher concentrations in sediment core than surface sediment.

Sea-Nine 211 was present in the concentration that affected oyster embryo development, indicating that antifouling biocides have had a negative impact on the northern part of Hiroshima Bay's ecosystem.

Impact of Antifouling Biocides on Sea Water, Sediment and Marine Organisms in Hiroshima Bay

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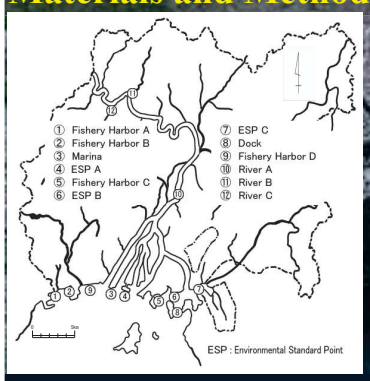
Introduction

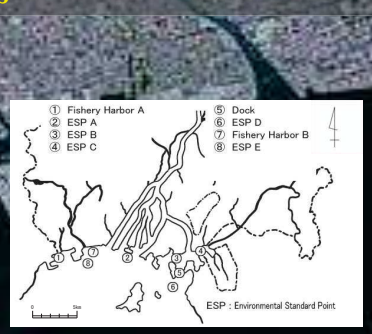
This research focused on the impact of antifouling biocides on sea water, sediment and marine organisms. In Japan in 1997, worldwide from September 2008, prohibition of Ot (organotin) compounds was introduced. This meant that the production of paints containing TBT compounds was stopped and alternatives to the available Ot antifoulants had to be developed. It has been claimed that the decomposition characteristics of these alternative Ot antifoulants were better than those of Ot compounds. Since the introduction of the alternative antifoulants, the accumulation of these compounds has been reported in many countries. However, the toxicity of these compounds has still largely gone unreported. Unlike previous research which only investigated Ot compounds, this research also looked at the Ot alternative antifoulants Irgarol 1051, Diuron, Sea-Nine 211 and TPBP.

First there was the investigation of the antifouling biocide's concentration in sea water and sediment, then the monitoring of the effects of toxicity on the fertilized oyster and sea urchin egg's development, followed by the calculation of the risk factor, and finally the evaluation of the environmental risk.

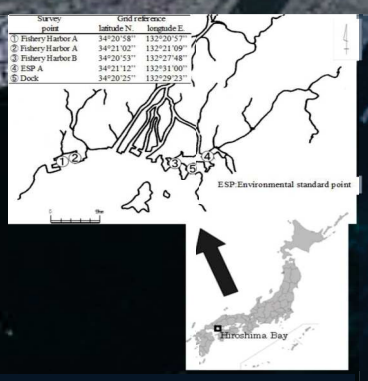
Materials and Methods



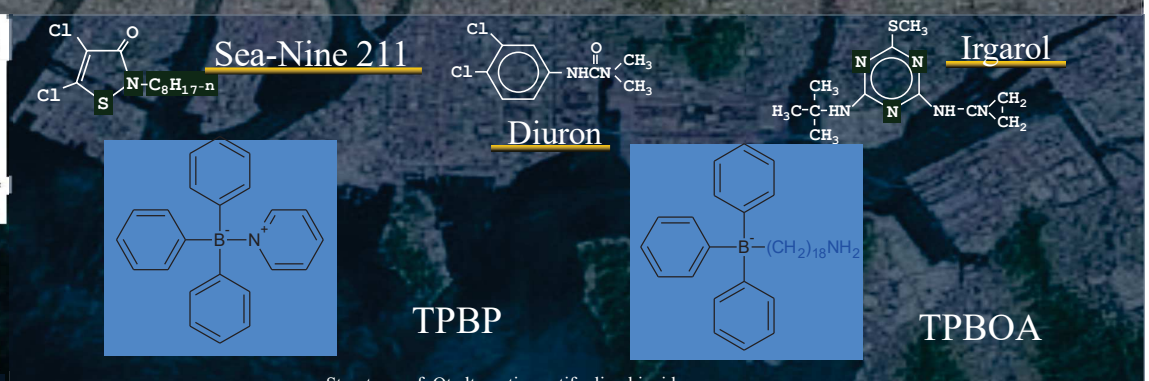
Survey point on seawater samples



Survey point on surface sediment samples



Survey point on sediment core samples



Structures of Ot alternative antifouling biocide

The investigated materials were Diuron, Sea-Nine 211, TPBP, Irgarol 1051 which were all thought to be popularly used in Japan.The oysters came from the breakwater in Itsukaichi Nishi Ward, Hiroshima, Japan. Professor Kenji Torigoe, from the Department of Education at Hiroshima University, identified the oysters used in the experiments as *Crassostrea gigas*. The sea urchins were purchased from Taguchi Educational Laboratory. All the urchins used were *Hemicentrotus pulcherrimus* from Miura Peninsula in Kanagawa Pref., Japan. Seawater samples were collected from 2002 to 2004. Surface sediment samples were collected from 2002 to 2005. Sediment core samples were collected in December 2004 and March 2005.

Results

Table 1. Minimum-maximum concentrations of investigated compounds in sea water samples.

point number	Irgarol 1051	M1	Diuron	Sea-Nine 211
1	ND	ND-1.1	ND-0.43	ND-0.1
2	ND	ND- 1.3	ND-0.73	ND-0.1
3	ND	ND-1.1	ND-0.21	ND-0.097
4	ND	ND-0.051	ND-0.17	ND
5	ND	ND-0.10	ND-0.24	ND-0.067
6	ND	ND-0.10	ND-0.10	ND-0.035
7	ND	ND	ND-0.14	ND-0.085
8	ND-0.092	ND	ND-0.18	ND-0.069
9	ND	ND-0.060	ND-0.17	ND-0.059

ND: not detected (μg/L)

Table 2. Minimum-maximum concentrations of investigated compounds in surface sediment samples.

point number	Irgarol 1051	M1	Diuron
1	ND-4.0	ND-7.0	ND-25
2	ND	1.0-4.0	ND-11
3	ND-3.0	ND-2.0	5.0-8.0
4	3.0	4.0-5.0	8.0-11
5	2.0-28	3.0-7.0	15-73
6	3.0	3.0-4.0	ND
7	ND	2.0-9.0	17-20
8	3.0-4.0	4.0	ND

ND: not detected (μg/kg・wet)

Table 3. Minimum-maximum concentrations of investigated compounds in sediment core samples.

point number	Irgarol 1051	M1	Diuron	Sea-Nine 211
1	2.4-27	ND-0.8	1.4-13	ND
2	7.1-24	0.2-0.5	3.9-10	ND
3	0.4-64	0.1-2.1	2.5-11	ND-3.3
4	2.1-3.5	0.1-0.3	3.0-7.7	ND-0.8
5	9.1-270	0.4-13	11-220	7.6-140

ND: not detected (μg/kg・dry)

Fig.4 Survival and protruding-mantle deformity rates on *Crassostea gigas* embryo after a period of 24h.

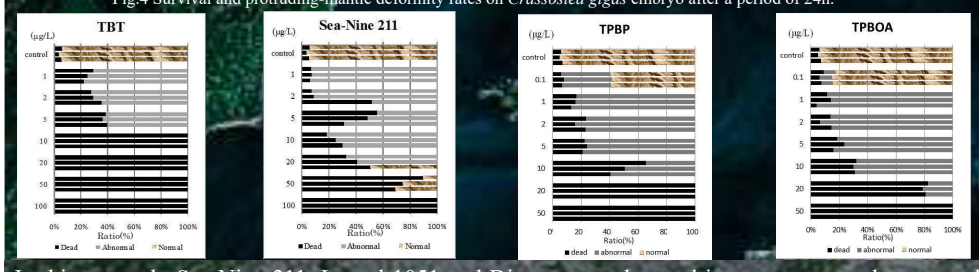


Fig. 1 Concentration of organotin alternative antifoulants in sediment core samples.

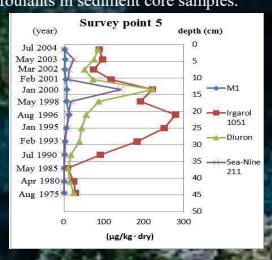


Fig. 2 Concentration of organotin compounds in sediment core samples.

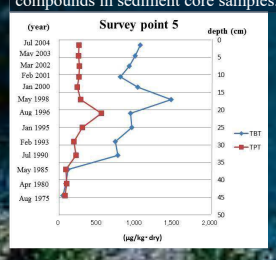


Fig. 3 Concentration of heavy metals in sediment core samples

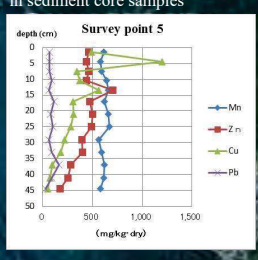


Table 4. Lethal concentrations of antifouling compounds to *Crassostea gigas* embryos.

	2h		24h	
	LC10	LC50	LC10	LC50
TBT	2.6(2.5-2.7)	16(14-18)	0.36(0.31-0.39)	3.9(3.3-4.5)
TPT	2.4(2.3-2.5)	14(12-15)	0.52(0.48-0.54)	3.7(3.2-4.2)
Sea-Nine 211	7.4(6.8-7.7)	28(26-31)	0.90(0.89-0.91)	17(14-21)
Diuron	>1000	>1000	>1000	>1000
Irgarol 1051	>1000	>1000	>1000	>1000

LC50 = 50% lethal concentration(μg/l) ( ) = 95% confidence interval
LC10 = 10% lethal concentration(μg/l)

	2h		24h	
	LC10	LC50	LC10	LC50
TPBP	1.1(1.0-1.1)	7.5(6.7-8.5)	0.58(0.55-0.60)	6.3(5.4-7.4)
TPBOA	2.7(2.6-2.8)	23(20-26)	2.2(2.1-2.8)	10(9.5-12)
DPB	>1000	>1000	>1000	>1000
MPB	>1000	>1000	>1000	>1000
Biphenyl	>1000	>1000	>1000	>1000
Phenol	>1000	>1000	>1000	>1000
Pyridine	>1000	>1000	>1000	>1000
Benzene	>1000	>1000	>1000	>1000
Boric acid	>1000	>1000	>1000	>1000

LC50 : 50% lethal concentration(μg/l) ( ) : 95% confidence interval
LC10 : 10% lethal concentration(μg/l)

Table 5. Lethal concentrations of antifouling compounds to *Hemicentrotus pulcherrimus* embryos.

	2h		48h	
	LC10	LC50	LC10	LC50
TPBP	22(21-23)	73(67-80)	6.4(5.7-6.6)	31(27-36)
TPBOA	130(120-130)	290(270-320)	30(28-32)	73(68-79)
DPB	>1000	>1000	>1000	>1000
MPB	>1000	>1000	>1000	>1000

LC50 : 50% lethal concentration(μg/l) ( ) : 95% confidence interval
LC10 : 10% lethal concentration(μg/l)

In this research, Sea-Nine 211, Irgarol 1051 and Diuron were detected in seawater samples at not detected (ND) to **0.10μg/L**, ND to 0.092μg/L and ND to 0.73μg/L, respectively. However, TPBP was not detected in this research period.In surface sediment samples, Sea-Nine 211, Irgarol 1051 and Diuron were detected at not detected (ND) to 40ng/g, ND to 28ng/g and ND to 73μg/g, respectively.As for the sediment core samples, Sea-Nine 211, Irgarol 1051 and Diuron were detected at not detected (ND) to 140ng/g, 0.4 to 270ng/g and 1.4 to 220μg/g, respectively.The toxicity (24h-LC_{50}) of Sea-Nine 211, TPBP, TBT, TPT, Irgarol 1051 and Diuron on oyster embryos was 17μg/L, 6.3μg/L, 3.9μg/L, 3.7μg/L, <1000μg/L and <1000μg/L, respectively. The toxicity (48h-LC_{50}) of TPBP on sea urchin embryos was 31μg/L.The NOEC (non effective concentration) levels of Sea-Nine 211, TBT and TPT on oyster embryos were **under 0.10μg/L**

Discussion

The concentration of antifouling biocides in sediment core samples from Hiroshima Bay was much higher than the corresponding sea floor sample concentrations. In particular, the survey Point 5 sample had the highest observed concentration of the alternative biocides. As shown in Figures 1 and 2, the concentration of Ot alternative antifoulants and Ot compounds at survey Point 5 began to increase from almost the same point. In the case of Ot alternative antifoulants, it was thought that the rise in the concentration was caused by the increase of the consumption after the regulation of Ot compounds in 1990. On the other hand, in the case of Ot compounds at survey Point 5, the cause was mainly due to the way the dock replaced the Ot compound paints with the Ot alternative antifoulants. When the regulation became effective in Japan, the Ot compounds were stripped from ships before the Ot alternative antifoulants were painted on to the ships. In the case of this dock, the stripped pieces of Ot compound paint were not cleared from the dry dock, so when the ships were relaunched, the stripped paint chips on the ground were washed into the sea water. Obviously, this would have had an impact on the Ot compound concentration levels shown in Figure 2.

In the evaluation of the environmental impact of these chemicals, a risk factor that used the predicted environmental concentration (PEC) divided by predicted no-effect concentration (PNEC) was used. When this value exceeded a risk factor of 1.0, it was decided the chemical had an influence on the environment. The PNEC on the aquatic organism was calculated from the examination result of the acute or chronic effect in the organism species divided by assessment factor. In this research, the chemicals resolved in the toxicity experiment were considered, so the assessment factor was set at 10.

In the case of Sea-Nine 211, the toxicity towards the oyster eggs was highest of the four chemicals detected in this research. The PEC in Hiroshima Bay was 0.1μg/L. The deformity rate of oyster embryos exceeded 10% in the solution with a concentration of 0.1μg/L, so the NOEC was determined to be 0.1μg/L. PNEC which is the NOEC divided by assessment factor was 0.01μg/L and the chemical risk factor divided by their PNEC values was 10. In this case, the risk factor was much higher than a value of 1.0, and so it indicates that Sea-Nine 211 has an influence on the marine environment.

In recent times, the indication of delayed development of oysters in Hiroshima Bay has become more noticeable. If this trend continues, oyster numbers will decrease. If the oyster numbers decrease, there are a number of influences that would be possible. Oysters play an important role as natural filters for the environment so a decline in numbers could see an adverse affect on water quality of Hiroshima Bay. Also, various marine life (e.g. *Acanthopagrus schlegelii, Takifugu poecilonotus*) in Hiroshima Bay use oysters as a food source so any change in numbers could affect not only the organisms which feed off them but also alternative food sources. It is clear that any decline in oyster numbers would have a negative impact on the northern part of Hiroshima Bay's ecosystem.

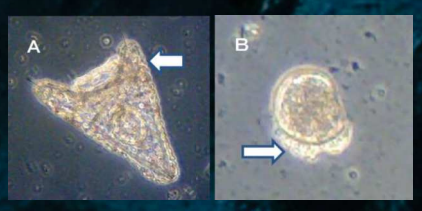
As mentioned previously, Sea-Nine 211, Diuron and Irgarol 1051 were detected while TPBP was not detected in the northern part of Hiroshima Bay. Essentially, the best antifouling biocides should show a high toxicity around the hull, but when they are released into the sea water they should resolve quickly so they do not affect the organisms which inhabit the sea water. Sea-Nine 211 has high toxicity and when it is released into the sea water it remains for a long time so affects organisms. TPBP's toxicity is the same as the toxicity of TBT and TPT, but resolves quickly in the sea water, so it does not affect organisms as much. If the toxicity is almost the same, the material (e.g. TPBP) with the highest resolution speed should be used to lessen the impact on the ecosystem. For this reason, TPBP is the best antifouling biocide from the investigated antifouling biocides.

Conclusions

It was discovered that Ot alternative antifoulants accumulation characteristics in sediment were similar to Ot compounds, with both having much higher concentrations in sediment core than surface sediment.

Sea-Nine 211 was present in the concentration that affected oyster embryo development, indicating that antifouling biocides have had a negative impact on the northern part of Hiroshima Bay's ecosystem.

The antifouling biocides should show a high toxicity around the hull, but quickly resolve in the sea water.



Deformity embryo (**A**) *Hemicentrotus pulcherrimus* (**B**) *Crassostea gigas*