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Impact of Antifouling Biocide on Marine Environment

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Introduction

Organotin (Ot) compounds had been used for many years on ships, marine structures and fishery nets until detection of toxicity and accumulation characteristics. Ot compounds were subsequently prohibited on the 17th of September, 2008. Alternative compounds began to be used for ships with the thought that Ot alternative antifoulants would not accumulate in seawater and sediment as much as Ot compounds, due to the faster resolution speed. However, Ot alternative antifoulants have been detected at higher levels than initially expected which has caused concern about the possible affects on marine organisms.

In this research, sea water samples from the northern part of Hiroshima Bay were used to evaluate the toxicity of Diuron, Sea-Nine 211, TPBP, TPBOA and Irgarol 1051 on oysters. These chemicals were chosen due to their popular use in Japan following the prohibition in 1997 of paints that used TBT. For comparative reasons, TBT and TPT were also investigated. Oysters were chosen because of their high sensitivity to chemical compounds and the fact that they can be found worldwide.

The research sought to not only analyze the chemical compounds in survey points but also to measure the effect of antifouling biocides on fertilized oyster egg's development. Finally, the environmental risk was evaluated.

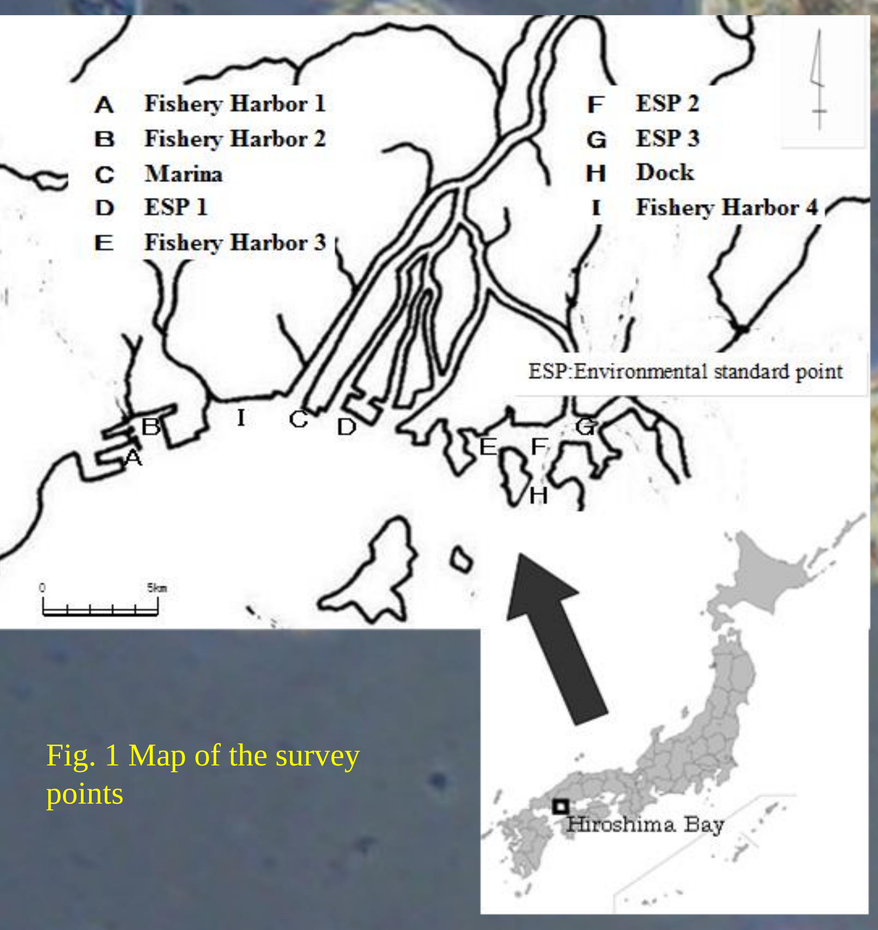

Fig. 1 Map of the survey points

Results

Residual antifouling biocides in environmental samples

In this study, Sea-Nine 211, Diuron, Irgarol 1051 and the latter's degradation product M1 were detected in seawater from Hiroshima Bay whereas TPBP was not detected. Analysis results over the research period are shown in Table 1.

Effects of antifouling biocide on oyster embryo development

In this report, the survival rate of the eggs and the occurrence of deformity in D-shaped embryos were investigated. In the report by His et al., four types of deformity were shown: convex hinge, indented shell margin, incomplete shell, and protruding mantle. In our experiments, only protruding-mantle deformities were observed.

The LC_{10} and LC_{50} values of each compound were calculated from the survival rate of the fertilized oyster eggs after an exposure time of 2 and 24 h using the Ecotox-Statics software package. The results are shown in Table 2.

Discussion

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 that were resolved in the toxicity experiment had their PNEC evaluated, so the assessment factor was set at 10.

In this research period, Sea-Nine 211 was detected at values that exceeded Sea-Nine 211's PNEC in almost all survey points. This means that Sea-nine 211 is present in the concentration that effect oyster embryo's development in the northern part of Hiroshima Bay. If the effects that were observed in the laboratory took place in nature, at least 10% of oyster embryos would exhibit a deformity. It is reasonable to say that oyster embryos which show signs of deformity are unlikely to develop into adult oysters.

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's numbers decrease, there are a number of influences that could be possible. Oysters play an important role as natural filters for the marine environment so a decline in numbers could see an adverse affect on the 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 oyster numbers could affect not only the organisms which feed off them but also the alternative food sources. It is clear from the aforementioned examples that any decline in oyster numbers would have a negative impact on the northern part of Hiroshima Bay's ecosystem.

Table 1: Minimum-Maximum concentration of antifouling biocides in seawater from Hiroshima Bay

Survey point	Irgarol 1051	M1	Diuron	Sea-Nine 211
A	ND	ND - 1.1	ND - 0.43	ND - 0.10
B	ND	ND - 1.3	ND - 0.73	ND - 0.10
C	ND	ND - 1.1	ND - 0.21	ND - 0.097
D	ND	ND - 0.17	ND - 0.17	ND
E	ND	ND - 0.10	ND - 0.24	ND - 0.067
F	ND	ND - 0.10	ND - 0.10	ND - 0.035
G	ND	ND	ND - 0.14	ND - 0.085
H	ND - 0.092	ND - 0.12	ND - 0.18	ND - 0.069
I	ND	ND - 0.060	ND - 0.17	ND - 0.052

ND: not detected (μg/L)

Table 2: Lethal effects of antifouling compounds to oyster embryo

	2h		24h	
	LC_{10}	LC_{50}	LC_{10}	LC_{50}
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)
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)
Diuron	>1000	>1000	>1000	>1000
Irgarol 1051	>1000	>1000	>1000	>1000
Degradation product				
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

LC_{50} : 50% lethal concentration (μg/l) ( ) : 95% confidence interval
LC_{10} : 10% lethal concentration (μg/l)

Conclusions

- Although Sea-Nine 211 is present in lower concentration than the other chemical substances, it is the most harmful on oyster embryos in investigated compounds because Sea-Nine 211 should be changed another compound.
- Chemical substances bring negative impacts to the northern part of Hiroshima Bay's ecosystem.
- Antifouling biocides should show a high toxicity around the hull, but quickly resolve in the sea water.