



# Effects of new antifouling compounds on the development of sea urchin

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## Abstract

Tributyltin oxide (TBTO) has been used worldwide in marine antifouling paints as a biocide for some time. However, it produced toxic effects, especially in marine water/sediment ecosystems. Consequently, its use in antifouling paints has been prohibited in many countries. In this study, the toxicity of alternative and/or new antifouling biocides compared with TBTO is assessed by a biological method. The effects of these chemicals on marine species have not been well studied. This paper assesses, comparatively, the effects of eight biocides on sea urchin eggs and embryos. The chemicals assessed were TBTO, Irgarol 1051, M1 (the persistent degradation product of Irgarol), Diuron, zinc pyrithione, 'KH101', 'Sea-Nine 211', and copper pyrithione. For these chemicals, toxicity appears to be in the order zinc pyrithione > Sea-Nine 211 > KH101 > copper pyrithione > TBTO > Diuron ~ Irgarol 1051 > M1. Here, we show that zinc pyrithione, Sea-Nine 211, KH101, and copper pyrithione are much more toxic to sea urchins than TBTO or the other chemicals.

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## 1. Materials and methods

Sea urchins of the species *Hemicentrotus pulcherrimus* and *Anthocidaris crassispina* were obtained near the Seto Marine Biological Laboratory, Wakayama Prefecture, Japan. Eggs and sperm were mixed and inseminated in each test seawater. Next, rates of first cleavage, formation of plutei, and of any anomalies in their development were monitored. It is well known that the early developmental stages of sea urchins are very sensitive to many environmental impacts as reviewed by Kobayashi (1995). The environmental effects of some previously used biocides, such as TBTO and copper compounds, on the marine environment are well known. In this study, we investigated eight of the most recently used biocides as follows:

1. TBTO: tributyltin oxide (Tokyo Chemicals, Japan).

2. Irgarol 1051: 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (Ciba Specialty Chemicals, Japan), which is analogue of herbicide.
3. M1: principal degradation product of Irgarol 1051: 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine, which was prepared and purified by us.
4. Diuron: 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Tokyo Kasei Kogyo Ltd, Japan), which is also used as a herbicide.
5. Zinc pyrithione: 2-mercaptopyridine N-oxide zinc salt (Tokyo Kasei Kogyo Ltd, Japan), which is used as an antimicrobial and anti-dandruff agent.
6. KH101: pyridine triphenyl borane (Hokko Chemicals Ltd, Japan).
7. Sea-Nine 211: 4,5-dichloro-2-n-octyl-3(2H) isothiazolone (Rohm and Haas Company, USA).
8. Copper pyrithione: 2-mercaptopyridine N-oxide copper salt (Hayashi Pure Chemical Industries, Ltd, Japan).

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Stock solutions of each test chemicals were prepared at concentrations of 10,000 mg/L in dimethyl sulfoxide (DMSO) except for 5,000 mg/L for KH101 and