

# Concentration of Antifouling Biocides and Heavy Metals in Sediment Core Samples in the Northern Part of Hiroshima Bay

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## 1. Introduction

Organotin (Ot) compounds that were used for many years as antifouling biocides on ships, marine structures and fishing nets became a problem due to toxicity and accumulation characteristics. From 1997 in Japan, the production of paints that contain TBT compounds was prohibited, and so since then alternative to Ot antifoulants have been used. In September 2008, Ot compounds were prohibited from being used worldwide. In this research, the Ot alternatives to Ot antifoulants Diuron, Sea-Nine 211, Irgarol 1051 and the latter's degradation product M1 were investigated in 5 sediment core samples of the northern part of Hiroshima Bay. The Ot compounds were also investigated to compare the Ot alternative antifoulants. In addition, the heavy metals (Pb, Cu, Zn, Fe, Mn) and the chronology were measured to better understand what happens after they have accumulated on the sea floor.

## 2. Materials and Methods

### 2.1 Sampling Description

At points ① and ② in the fishery harbour there were a lot more leisure boats than commercial fishing boats anchored. In point ③ of the fishery harbour, the ratio of commercial fishing boats to leisure boats is about the same. The environmental standard point ④ was located in a recess of Hiroshima Bay. Point ⑤ was located in the entrance to the dock and it was the point where the concentration of the organotin compounds had been high previously.

### 2.2 Sampling

In the sea area, the sediment from the sea floor was collected with the sediment core sampler, and sliced into 3-5 cm thick sections, and stored at -20 centigrade until analysis.

### 2.3 Chemicals

The investigated materials were Diuron, Sea-Nine 211, Irgarol 1051 and M1, that were all thought to be popularly used in Japan. Structure of antifouling compounds are shown in Fig. 1.

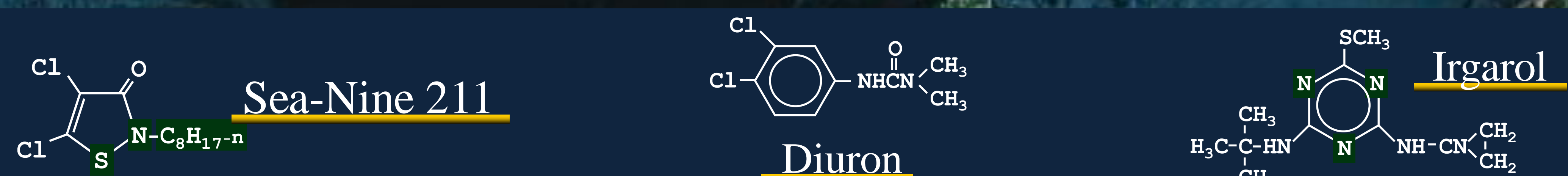


Fig.1 Structures of the alternative Ot compounds

### 2.4 Chronology

The <sup>210</sup>Pb chronology was applied to the cores using the model of Matsumoto (1975), in which core depth is corrected for the sediment compaction (Yasuhara and Yamazaki, 2005). We also employed a geochronology based upon fallout of the fission product <sup>137</sup>Cs from the stratosphere, where it was introduced by nuclear weapons testing. The <sup>137</sup>Cs profile was corrected for decay (half life, 30yr) during the time between the measurement and the sediment deposition, only for the period after ca.1950 because the <sup>137</sup>Cs should theoretically not be detected before then. A <sup>137</sup>Cs maxima (1963 fallout maximum) corroborates <sup>210</sup>Pb ages.

## 3. Results and Discussion

In the present study, Sea-Nine 211, Diuron, Irgarol 1051 and M1 were detected in the sediment core samples from Hiroshima Bay. The concentration of antifouling biocides in sediment core samples was much higher than the sea floor sample's concentration. Especially, the survey point ⑤ sample which had the highest concentration.

Organotin compounds (TBT and TPT) were only investigated at survey point ⑤. TBT and TPT were detected from 48 to 1400 μg/kg and from 78 to 550 μg/kg respectively.

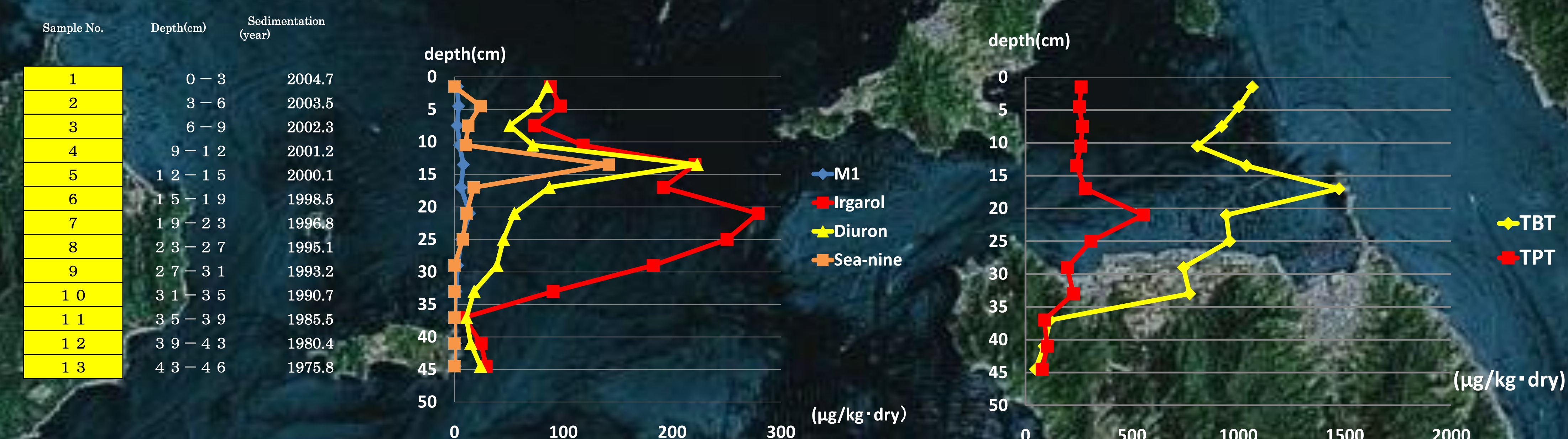


Fig.2 The analytical result of survey point ⑤ on antifouling biocides

In the present study, Pb, Cu, Zn, Fe and Mn were detected in sediment core samples from Hiroshima Bay. The analytical result of survey point ③ and ⑤ was shown in Fig. 3.

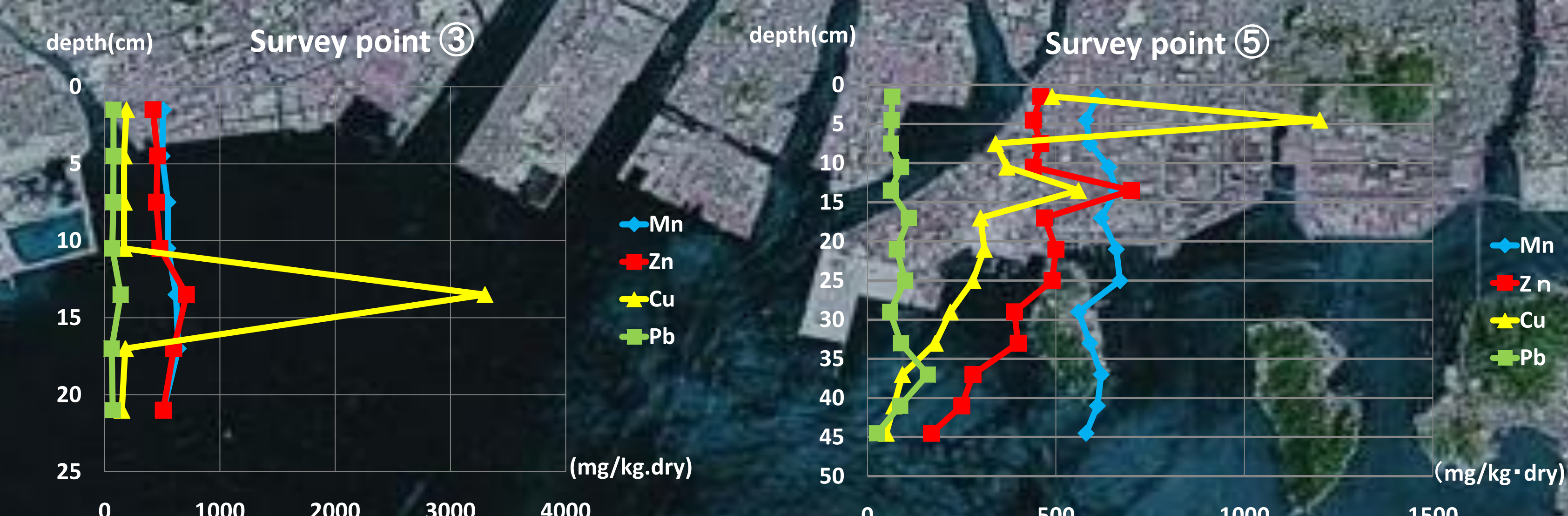


Fig.3 The analytical result of survey point ③ and ⑤ on heavy metals

## 4. Conclusion

In comparison with the sea floor sediment sample, the concentration of antifouling biocides in the sediment core samples was much higher than the sea floor sediment sample. Especially at survey point ⑤ (the entrance to the dock), where high concentration was detected. The beginning of the accumulation of the antifouling biocides coincided with the beginning of the self-control regulation on the organotin compounds. It was clear that the antifouling biocides did not shift in the sediment in the same way that the heavy metals did.

### Acknowledgments

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### Reference

Matsumoto E. <sup>210</sup>Pb geochronology of sediments from Lake Shinji. *Geochemical Journal* 9, 1975, 167-172.

Moriwaki Y and Yamazaki H. The impact of 150 years of anthropogenic pollution on the shallow marine ostracode fauna, Osaka Bay, Japan. *Marine Micropaleontology*, 2005, 55, 63-74.