



# The influence of seawater properties on toxicity of copper pyrithione and its degradation product to brine shrimp *Artemia salina*



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## ARTICLE INFO

### Keywords:

Antifouling biocide  
Copper pyrithione  
Mixture toxicity  
Brine shrimp  
Organic matter  
Salinity

## ABSTRACT

Copper pyrithione (CuPT) is a biocide, used worldwide to prevent biofouling on submerged surfaces. In aquatic environments it rapidly degrades, however, one of the degradation products (HPT) is known to react with cupric ion back to its parent compound. Not much is known about the behavior and toxicity of CuPT and its degradation product HPT in different water systems. Hence, our aim was to investigate the ecotoxicity of CuPT, HPT as well as  $\text{Cu}^{2+}$  to the brine shrimp *Artemia salina* in natural seawater and organic matter-free artificial seawater. Moreover, in order to elucidate the influence of ionic strength of water on CuPT toxicity, tests were performed in water media with modified salinity. The results showed that CuPT was the most toxic to the exposed crustaceans in a seawater media with the highest salinity and with no organic matter content. HPT in a presence of cupric ion converted to CuPT, but the measured CuPT concentrations and the mortality of *A. salina* in natural water were lower than in artificial water. The toxicity of CuPT to *A. salina* was significantly influenced by the organic matter content, salinity, and proportions of constituent salts in water. In a combination with cupric ion, non-hazardous degradation product HPT exhibits increased toxicity due to its rapid transformation to its parent compound.

## 1. Introduction

Biofouling, i.e. the adhesion of organisms on submerged surfaces represents a great economic burden for shipping industry. It significantly increases the fuel consumption (even up to 40%) and elevates the costs for hull maintenance (Champ, 2000). Moreover, it can represent a serious environmental threat due to the transfer of invasive species during the ship voyages. In order to prevent the accumulation of organisms, the protection of the immersed surfaces is crucial. The principal and effective strategy to restrain the fouling is by application of antifouling paints. These in most cases consist of copper compounds and one or more booster biocides (Takahashi, 2009). For the effective prevention of accumulation of fouling organisms, such as algae, barnacles, mussels and tubeworms, antifouling coatings are designed to achieve a constant leaching of a sufficient concentration of copper and biocides to the outer surface layer. Concerns occur when antifouling biocides are not selective only to target organisms, therefore the ecotoxicity studies are vital to perform.

After the ban of tributyltin, the most notorious antifoulant for its high toxicity, new antifouling biocides were developed and applied in paints (Konstantinou, 2006). Among them is copper pyrithione (CuPT) which is acknowledged for its exceptional and broad antimicrobial

activity (Mochida et al., 2006). In Japan, CuPT remains one of the most commonly used antifouling booster biocide, with 240 t of manufactured or imported quantities per year (data for year 2014, J-Check, 2017). In antifouling coatings it is most frequently combined with cuprous oxide (Okamura and Mieno, 2006). CuPT is not stable in the aquatic environment, however its presence has been reported in sediments collected from the bay in Japan in concentrations up to 22  $\mu\text{g}/\text{kg}$  dry sediment weight (Harino et al., 2007). A research study of Onduka et al. (2010) has shown high CuPT toxicity to non-target species of different trophic levels, such as algae *Skeletonema costatum* (72-h  $\text{EC}_{50} = 1.5 \mu\text{g}/\text{L}$ ), crustacean *Tigriopus japonicus* (24-h  $\text{EC}_{50} = 23 \mu\text{g}/\text{L}$ ), and a fish *Pagrus major* (96-h  $\text{LC}_{50} = 9.3 \mu\text{g}/\text{L}$ ).

The advantage of CuPT among several other antifoulants is its rapid degradation under the light, which impedes the biocide to excessively accumulate in the aquatic compartments and in aquatic organisms. The estimated half life in a sterile seawater is 7.1 min (Maraldo and Dahllöf, 2004). Yet, one of the photodegradation products reported, 2-mercaptopyridine-N-oxide (HPT), was shown to transform back to its parent compound in the presence of  $\text{Cu}^{2+}$  (Onduka et al., 2010). The toxicity of the degradation product HPT was found to be much lower than of the CuPT when tested on a crustacean *T. japonicus*, with a 24-h  $\text{EC}_{50} > 12,500 \mu\text{g}/\text{L}$  ( $\text{EC}_{50} = 23 \mu\text{g}/\text{L}$  for

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CuPT), and a fish *P. major* (96-h LC<sub>50</sub> = 4500 µg/L for HPT and 9.3 µg/L for CuPT). In contrast to crustaceans and fish, the toxicity of HPT was similar to the toxicity of CuPT when tested on alga *S. costatum* (72-h EC<sub>50</sub> = 1.1 µg/L for HPT and 1.5 µg/L for CuPT), however researchers suggest the toxicities were similar due to the conversion of HPT to CuPT upon the reaction with Cu<sup>2+</sup> (Onduka et al., 2010).

The degradation pathway is in case of CuPT not straightforward due to the reverse reaction of HPT to CuPT that may occur in the presence of free Cu<sup>2+</sup>. Not only for HPT, the conversion to CuPT in the presence of free Cu<sup>2+</sup> was revealed for an additional CuPT's degradation product – 2,20-dithio-bis-pyridine-N-oxide (Onduka et al., 2010). The interaction of degradation products with Cu<sup>2+</sup> is likely since booster biocides are commonly incorporated to copper-containing paints (Okamura and Mieno, 2006). Besides that, free Cu<sup>2+</sup> is as a micronutrient naturally present in aquatic ecosystems (Grunnet and Dahllöf, 2005).

From the studies conducted up to now, only the principle basics are known regarding the behavior of CuPT and its degradation products in the presence of free Cu<sup>2+</sup> in aqueous media. The behavior of organic compounds, bioavailability and toxicity may differ considerably depending on the properties of the water media. Not much is known about the influence of water properties on a toxicity of CuPT to aquatic organisms, as well as the behavior of HPT and Cu<sup>2+</sup> binary mixture in different water media. During voyages it is expected that CuPT will leach out and enter different aquatic environments, with different water chemical and physical properties (DOC content, salinity, electrical conductivity and salt constitution, for instance). However, in laboratory ecotoxicity and stability experiments the organic matter free artificial water is commonly used. Since immense quantities of CuPT are still used to protect the submerged surfaces from fouling, it is mandatory to know the fate and possible adverse impacts of CuPT when it is released to the natural water ecosystems. For that reason, our study aimed to investigate the behavior and ecotoxicity of CuPT, HPT and Cu<sup>2+</sup> as well as Cu<sup>2+</sup>/HPT binary mixture to the brine shrimp *A. salina* in natural seawater and organic matter-free artificial seawater. Moreover, in order to elucidate the influence of ionic strength of water on CuPT toxicity, several artificial and natural seawater media were used differing in ionic strength and ion constitution.

## 2. Materials and methods

### 2.1. Test organism

A marine water crustacean *Artemia salina* was selected as a test organism to examine the effects of cupric ion (Cu<sup>2+</sup>), copper pyrithione (CuPT) and its degradation product 2-mercaptopyridine-N-oxide (HPT) in different seawater media. *Artemia* is a favorable test organism in marine ecotoxicity studies due to its worldwide distribution, short generation time and ease of culture. As our tests investigated also the influence of salinity to CuPT toxicity, *artemia* was chosen as a suitable organism due to its tolerance to different water salinities (Naceur et al., 2012). For the toxicity test, commercially available dormant eggs (cysts) were used, from which the hatched nauplii are of similar age,

genotype and physiological condition (Persoone et al., 1989). In natural environments, *artemia* plays a significant ecological role as a food source to higher trophic level aquatic invertebrates and fishes (Sorgeloos, 1980).

Dried eggs of *A. salina* were harvested in Vietnam and furtherly prepared by A & A Marine LLC, USA. To our laboratory they were provided by Fujimoto Kaiyodo Co. Ltd, Japan. Before starting the test, eggs were placed in a sterile petri dish (φ 90 mm, H16 mm, 101VR20, Sterilin) containing artificial seawater (ASW). Then, to initiate the hatching of the eggs, the petri dish was incubated in a weather simulator (LH-55-RD/RDS, Nihon Ikakikai) with the light intensity of 8.6 klux and the temperature of 25 °C. Approximately after 15 h the nauplii started hatching, however, only the nauplii which hatched from the cysts during the 20–22 h of incubation were used to start the toxicity tests.

### 2.2. Chemicals

Analytical standards of copper pyrithione (CuPT, Hayashi Pure Chemicals), 2-mercaptopyridine-N-oxide (HPT, Tokyo Kasei Industry) and CuSO<sub>4</sub>·5H<sub>2</sub>O (Wako Pure Chemical Industries) were of > 98.7%, > 95% and > 99.5% purity, respectively. The structural formulae of copper pyrithione and its degradation product 2-mercaptopyridine-N-oxide are presented in Table 2.

DMSO (> 99.5% purity, spectroscopy grade), used as a carrier solvent in toxicity tests, was purchased from Wako Pure Chemical Industries.

All other chemicals used in chemical analysis and test media preparation were of analytical grade, with a purity of 95% or higher.

### 2.3. Test media

Several different types of seawater were used for toxicity testing: artificial seawater (ASW), natural seawater (NSW), three natural seawater media, each amended with different salt (NSW-Na, NSW-Ca, NSW-Mg,) and additional seven artificial seawater media differing in electrical conductivity (ASW-EC). All seawater types were freshly prepared before they were spiked with chemicals and used in toxicity tests. The results of their characterization – pH value, electrical conductivity (EC), total hardness, the concentration of dissolved organic carbon (DOC), and concentrations of selected ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>) are presented in Table 1. The procedure of their preparation is described below.

*Artificial seawater (ASW)* was prepared in accordance with the Standard practice for the preparation of substitute ocean water (ASTM, 2003). Ultra-pure water (production system Aquarios RFU554CA, Advantec) was used as a basis into which inorganic salts were added in proportions as instructed by the Standard. ASW is free of dissolved organic carbon (DOC) and is often used in stability studies and ecotoxicity tests with marine organisms as it standardized and therefore allows to attain the reproducible experiments.

To prepare the *natural seawater* medium (NSW), sea surface water

**Table 1**

Properties (dissolved organic carbon, pH, electrical conductivity, total hardness, and concentrations of selected ions (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>)) of seawater media used in toxicity tests.

Seawater media	DOC (mg/L)	pH	EC (S/m)	Total hardness (mg/L)	Na <sup>+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	K <sup>+</sup> (mg/L)
ASW	< 0.5	8.23	5.06	7500	17,000	480	1 500	450
NSW	2.6	8.02	3.25	4400	7700	290	900	280
NSW-Na	2.6	8.07	5.03	4100	15,000	300	810	280
NSW-Ca	2.6	8.01	5.06	20,000	7400	6 500	890	290
NSW-Mg	2.6	8.07	5.02	21,000	7300	290	4 900	280
ASW-EC	< 0.5	8.20	5.58–1.98 <sup>a</sup>					

Abbreviations: ASW – artificial seawater, ASW-EC – artificial seawater with modified electrical conductivity, NSW – natural seawater, DOC – dissolved organic carbon, EC – electrical conductivity.

<sup>a</sup> The electrical conductivity of each subsequent dilution of ASW-EC media is lower for ca. 0.5 S/m from the preceded solution.

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