

## ENVIRONMENTAL OCCURRENCE AND CONCERNS OF ANTIFOULING BIOCIDES

# Biocides in antifouling paints: environmental concentration levels and distribution

Antifouling (AF) paints prevent the settlement, adhesion and growth of organisms on a painted surface by the action of biocides, which are the active ingredients. Many chemicals were and are used as biocides, which have very different physico-chemical properties and therefore differing environmental effects. Copper and organotin compounds have raised concern worldwide: extensive research exists to understand their bioavailability and toxicity. For longstanding biocides, for example Irgarol 1051 and Diuron, there is a large amount of environmental data allowing the assessment of their impact. For other biocides such as dichlofluanid, SeaNine 211 or zinc/copper pyriithione, fate and effects are clear, but only few monitoring studies have been performed

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### Introduction

Colonisation by fouling organisms is a problem for any structure placed in the aquatic environment and can be controlled through both chemical biocides and non-biocidal technologies. In spite of the work on diverse non-biocidal technologies and an increase in the commercial use of fouling-release coatings, the majority of vessels are still protected by antifouling (AF) paints containing biocides.

The key property of a good AF biocide should be its effectiveness in preventing the fouling of the painted surface without persistence at concentrations that can cause detrimental environmental effects. This can

be achieved through rapid transformation following release from the surface or possibly a very specific mode of action.

Physico-chemical data pertinent to the environmental fate of AF compounds are, e.g., octanol-water partition coefficient  $K_{OW}$ , degradation half-life ( $t_{1/2}$ ) and principal degradation mechanisms, as well as their known primary metabolites. Such data are readily available from literature and have been summarized in many excellent reviews [1-4] and therefore will not be discussed or reported here.

Release rates (or leaching rates) are crucial factors to model environmental concentrations. Over the past years, very few studies have been reported on the release of AF biocides from painted surfaces. Standard protocols (ASTM, ISO) can be applied, however published release rate data are scarce and there is concern that standard laboratory methods do not replicate what occurs in the environment and, therefore, are not representative [5].

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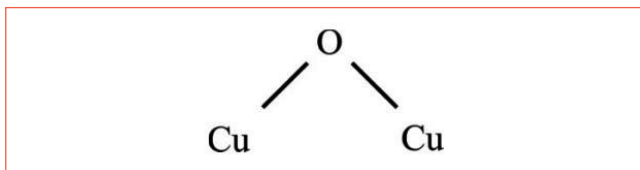
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## Environmental fate and occurrence

Processes controlling persistence and sinks are very important because biocides are deliberately released into the water column. Key processes important in understanding the fate of AF biocides are degradation, partition onto sediments and uptake into organisms. Compounds with a half-life >50 days are considered to be persistent, whereas those with a  $\log K_{OW} > 3$  are considered as bioaccumulating. The sediment-specific equilibrium sorption constant,  $K_d$ , describes the distribution of a compound between sediment and water. The values range from  $10^5$ , for compounds such as DDT and PCBs that bind strongly to sediments, to <1 for compounds that are weakly sorbed and soluble in water.

## Copper oxide

Copper oxide leaches from the boat surface and enters the water as a free copper ion ( $\text{Cu}^+$ ) and is immediately oxidized to  $\text{Cu}^{2+}$ , forming complexes with inorganic and organic ligands. The process is thought to occur within the first few micrometers of the painted surface. The presence of a biofilm on the vessel surface can act as a source of DOC, which can bind the free copper. In the dissolved phase, the speciation varies greatly with respect to water properties, such as DOC, pH, hardness and salinity. Copper easily adsorbs to suspended particulate matter (SPM), settling and accumulating in the sediment. As a result, copper concentrations are often two to three orders of magnitude higher in the sediment than in the water column [6]. In aerobic sediments, copper is mainly bound to metal oxides and high molecular weight organic matter while in anaerobic sediments, copper is bound strongly to sulphides reducing bioavailability. However, for both aerobic and anaerobic conditions, sediment



Copper oxide

disturbance events, such as dredging and storms can significantly increase the copper input into the water column from the underlying sediment.

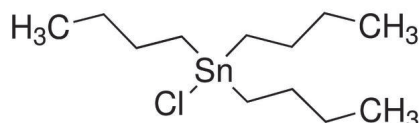
Copper obviously occurs naturally in the environment. Natural background concentrations of copper within estuarine and coastal seawater typically range between 0.5 and  $3 \mu\text{g L}^{-1}$ . Copper concentrations can potentially rise in the marine environment in enclosed harbours and marinas with little water exchange and high boat densities, but despite the projected problem in these high risk areas, very little monitoring work has been carried out [1].

Most monitoring studies reporting on copper concentrations in the marine environment measure total dissolved copper concentration, which fails to provide information on the bioavailability of the metal. The speciation of copper is fundamental to its bioavailability and toxicity, with the free ion considered as the most toxic form. In a recent survey of UK coastal waters [6], total dissolved copper ranged from 0.30 to  $6.68 \mu\text{g L}^{-1}$ , with only one concentration above the EQS of  $5 \mu\text{g L}^{-1}$ . Also in this case, elevated concentrations were found in an enclosed marina with little to no water exchange. The labile copper concentrations for the same water samples ranged from 0.02 to  $2.69 \mu\text{g L}^{-1}$ , with labile copper contributing 10–30% of the total dissolved copper concentration. Despite the elevated concentrations of total dissolved copper at some marinas, the labile copper concentration remained stable.

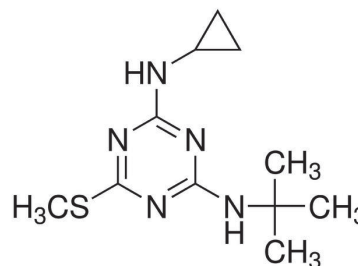
Being a strongly regulated metal in biota, bioconcentration is not an issue for copper as BCF (bioconcentration factor) is a meaningless parameter in this case.

## Tributyltin (TBT)

TBT compounds are organic derivatives of tin ( $\text{Sn}^{4+}$ ), having the general formula  $(n\text{-C}_4\text{H}_9)_3\text{Sn-X}$ , where X is an anion or a group linked covalently through a heteroatom. X influences the physicochemical properties (water solubility, vapour pressure, etc.). Generally, the toxicity of the organotin is more influenced by the alkyl substitutes than by the anionic substitutes. Tributyltin oxide (TBTO) and tributyltin chloride



Tributyltin (TBT)



Irgarol

have been normally used in laboratory experiments to investigate organotin toxicity. In the aquatic environment, TBT is quickly removed from the water column to bed sediments: TBT has a high specific gravity (about 1.2 kg L<sup>-1</sup> at 20 °C), low solubility (<10 mg L<sup>-1</sup> at 20 °C and pH 7.0), and log K<sub>ow</sub> values near 4.4 at pH 8.

Additionally, TBT is ionisable having pK<sub>a</sub>=6.25. Therefore, TBT sorption/desorption from natural sediment can be strongly influenced by changes in pH and salinity, similarly to what has been reported for other ionisable hydrophobic organic contaminants in sandy sediments or soils. The reversible adsorption of TBT makes contaminated sediments a long-term source of dissolved-phase contamination to water column. Adsorption to sediments is positively correlated to the extent of substitution on the Sn atom (monobutyltin (MBT)<dibutyltin (DBT)<TBT).

Many studies have involved surveys of TBT distribution in the water column, sediments, and biota [4]. Given its strong affinity, benthic sediments are the major sink for TBT in the environment. Measurements taken prior to restrictions on TBT use in antifouling paints have shown levels higher than 500 ng L<sup>-1</sup> in North American and European marinas. In recent investigations, it has been reported that TBT concentrations in water, sediment and biota have generally declined, rarely exceeding 100 ng L<sup>-1</sup>. This testifies that past measures against pollution caused by organotin compounds have been at least partly successful [2]. Nevertheless, this decline might be called into question, as several monitoring campaigns did not reach conclusive results. Exceptions to this general decline of TBT in

bottom sediments have been reported as hot spots associated with ship channels, ports, harbours, and marinas [7,8]. Other exceptions to this general decline of TBT pollution have been observed in newly industrialising countries [9].

### Irgarol

Irgarol 1051 does not easily degrade in water, which may explain its persistence once released from painted surfaces. In natural seawater, Irgarol 1051 has a half-life of between 100 and 350 days whilst being very persistent in anaerobic sediments. 2-methylthio-4-tert-butylamino-6-amino-s-triazine (M1) is the main transformation product of Irgarol 1051, produced through n-dealkylation following biodegradation, photodegradation or chemical hydrolysis. Other metabolites (M2, M3) have been shown to occur in the environment. The persistence of the metabolites is largely unknown, but M1 is relatively stable in water (t<sub>1/2</sub> >200 days) and sediment (t<sub>1/2</sub> >260 days).

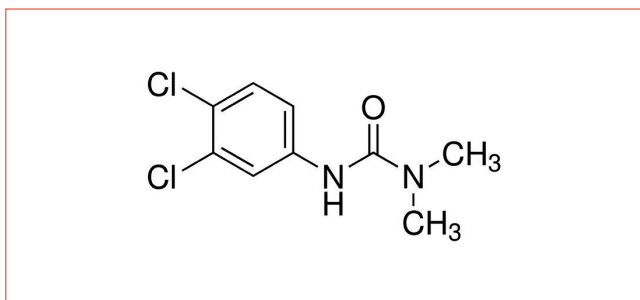
Water-sediment partitioning coefficients suggest that Irgarol 1051 will be mainly associated with the dissolved phase and estimations suggest that around 4% of Irgarol 1051 in marina waters will partition to sediments. Indeed, Irgarol 1051 occurs in sediments with numerous reported campaigns [1,10]. A few studies have also reported the occurrence of M1 in sediments, at lower concentrations than Irgarol 1051. Irgarol 1051 is persistent in sediments whether adsorbed to sediment particles or associated with paint particles. Little is known about the bioavailability of Irgarol 1051 present in sediments. It has been shown

that the resuspension of sediments contaminated with Irgarol 1051 can result in release of bioavailable Irgarol 1051 into the water column.

Irgarol 1051 is the most studied of the non-organotin AF biocides with a large number of reports on its environmental occurrence. Irgarol 1051 was first reported as an aquatic contaminant in 1993 in the Mediterranean, with its occurrence subsequently reported in Europe, the US, Caribbean, Asia and Australia in areas where there are boats coated with AF paints containing Irgarol 1051. Freshwater environments where intensive boating activity, combined with limited water exchange, are present can have very high aqueous concentrations of Irgarol 1051.

### Diuron

Diuron also persists in seawater, but is less persistent in marine sediments with a half-life of 14 days. The aerobic degradation of Diuron results in the transformation of Diuron to 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichlorophenyl)urea (DCPU). Anaerobic degradation in sediments results in the formation of 1-(3-chlorophenyl)-3,1-dimethylurea (CPDU). Diuron is relatively soluble in water (35 mg L<sup>-1</sup>) and has a reported log K<sub>OW</sub>=2.8, suggesting that it will predominantly be found in the dissolved phase and only weakly sorbed to sediments, which is in line with reported environmental concentrations. In fact, although Diuron can be present at high concentrations in marina surface waters, it has only been detected at low concentrations in sediments



Diuron

[11,12]. Concentrations as high as 1.4 µg g<sup>-1</sup> have been reported in sediments collected from an enclosed marinas in the UK. However, these high concentrations are likely to be due to the contamination of marina sediments with AF paint particles that are washed into the water, following shore-side scrubbing of boat hulls on hard standings [5]. Albeit relatively persistent in seawater, Diuron is thought to undergo degradation under anaerobic conditions to form CPDU (t<sub>1/2</sub> >14 days). When associated with AF paint particles, this transformation is significantly reduced, with very little degradation seen over 42 days.

### Conclusions

Extensive monitoring of biocides concentration in water, sediment, and biota is needed to support concerted actions to ban or regulate the use of booster biocides. Enough data are available for the biocides most commonly used in Europe, North America and Japan (Irgarol 1051, Diuron, SeaNine 211), whilst few or no data are available for other biocides, or developing countries. Few data are also available on the occurrence of degradation products that are mainly referred to Irgarol 1051 and Diuron metabolites. For new or candidate biocides (triphenylborane pyridine, capsaicin, etc.) very scarce information seems to be available at the moment.

Monitoring, behaviour and toxicity of degradation products should be emphasized. The need for further research in several vitally important areas, such as occurrence, fate and effects of booster biocides, is well established by the scientific community, in order to underpin risk assessments and protect the environments close to moored vessels. Although the concentration levels of some biocides were not high enough to have acute toxic effects directly on higher species, their chronic effects at low concentrations are unknown and difficult to determine. Gaps in the available data make the evaluation of their impact on the aquatic environment difficult. The precautionary principle provides a good basis on which to formulate policies to the marine environment, and should be invoked when it comes to the use of booster biocides. ●

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