Copper in Anti-Fouling – Ships and Vessels

Tom Bischoff, American Chemet Corporation

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This article provides an updated overview of the global use of copper in antifouling paints. It gives a brief history of copper in antifouling, describing how copper has been an effective active ingredient for centuries. It follows by addressing misnomers of copper toxicity, while describing the science of speciation of copper in the environment. It discusses the current global regulatory landscape of copper in commercial and pleasure craft antifouling coatings, with recent studies conducted in the EU and United States. Finally, data is presented detailing the sustainability of copper in antifouling.

Brief History of Copper in Antifouling

The use of copper in antifouling dates back to the Phoenicians (1500-300 BC), who used lead and copper sheets to prevent biofouling[1]. The earliest modern use of copper in antifouling was on the HMS Alarm in 1761, with the entire ship bottom covered in copper. At the battle of Trafalgar in 1805, the British fleet used copper cladding giving them more maneuverability than their opponents. Copper plating continued to be the standard method for protecting a ship's hull until the advent of steel ships and antifouling paints in 1915[2,3]. Copper was the predominant inorganic biocide until the development of SPC antifoulants with Tributyltin (TBT). Although TBT was the backbone of the SPC antifoulant systems, copper remained in most formulations to maintain efficacy against numerous biofouling species[3]. Unfortunately, TBT was found to have long term negative impacts on wildlife populations leading to its use being banned. The first ban was introduced in 1989 and use was completely phased out by 2008. Currently, copper based antifouling paints make up >90 % of the antifouling paints used globally[4].

Copper, Heavy Metals, and Toxicity

While copper based antifouling paints are efficacious due to the biocidal properties of copper, it is important to understand the differences in toxicity to target and non-target organisms.

To begin, a common misnomer about copper must be addressed: that Copper is a "heavy metal" and therefore is toxic in any form. First, the term "heavy metal", which has been used for decades to describe metals and metalloids that have been associated with potential toxicity or ecotoxicity, is not a scientific term. There is no authoritative definition in literature that details what or what is not a "heavy metal." Lists of "heavy metals" referred to in various regulations, differ from regulation to regulation, and some regulations do not specify what is meant by "heavy metals." Second, there is no basis in chemical or toxicological data that link the elements referred to as "heavy metals" with the assumption that they and their compounds always have toxic or ecotoxic properties. Dietary supplements of iron, zinc and copper, all of which are considered "heavy metals", are readily available, and often recommended by medical professionals for daily use. Any assertion that "heavy metals" automatically equate to "toxic" is misleading and unsupported by facts. Some elements can be toxic *in certain forms*, but not in *all* forms[5]. This is how copper can be efficacious as an antifoulant but not toxic in the environment.

Before further explanation, the following terms must be defined:

- Total Copper: refers to the total amount of copper present, regardless of form
- Dissolved Copper: refers to the copper ions that are present in a solution, which can include both free and complexed copper ions.
- Bioavailable Copper: refers to the copper ions that are not complexed and can be absorbed into a body.

The cupric ion (Cu^{2+}) is the primary form of copper that is toxic to aquatic species. In antifouling coatings, it is the cupric ion that leaches out of the coating to protect the surface from fouling. The assumption can be made that, since it is leaching out of the coating, particularly when a group of vessels are not moving (such as a marina, harbor, etc.), the excess copper creates a toxic environment beyond the vessel surface and remains toxic in the surrounding environment. This assumption does not accurately account for the natural environmental reactions of the cupric ion. Studies performed to measure the toxicity of copper in water show that copper toxicity decreases with[6]:

- <u>Increased particulate and dissolved organic carbon (POC/DOC) content</u>: Copper has a strong bond to the OC that renders it biounavailable. It is noteworthy that in the immediate vicinity of aquaculture pens, the water is rich with OC as a natural byproduct of the fish-farming process.
- <u>Increased water hardness:</u> Available calcium and magnesium ions will compete for binding sites on organisms, with preferential binding of calcium and magnesium,
- <u>Water chemistry:</u> Inorganic ligands such as carbonate and hydroxide ions can bind with cupric ions to form bio-unavailable copper.

To be toxic to organisms' copper has to be bioavailable. Due to the reasons listed above, the amount of bioavailable copper in the water column is generally significantly less than the dissolved copper. It has been shown that the percentage of bioavailable copper to dissolved copper is between 10-40%[7,8]. If the dissolved copper content is used in environmental risk assessments, it can over-predict the risk by more than 60%. For this reason, even when dissolved copper is at levels above some regulatory water quality criteria, no toxicity is measured due to the copper.

In 2021, the Los Angeles Department of Public Works conducted a Water Effects Ratio (WER) study in Marina Del Rey and found the WER for copper in water in the marina to be 1.32[9]. This WER signals that the original Total Maximum Daily Load (the calculation of the maximum amount of a pollutant allowed to enter a waterbody to meet water quality standards) was underestimated by 32%. This difference is attributed to the difference in the natural chemistry of the marina water and its effect on reducing copper bioavailability. This is consistent with the science discussed above and allows for a higher regulatory concentration limit of copper in the water with no observed toxic effects.

Copper as a Ubiquitous Micronutrient

Copper is a ubiquitous micronutrient. Copper is an abundant naturally occurring trace element found in the earth's crust and surface waters. It is a micronutrient at low concentrations and essential to nearly all plants and animals[10]. Because of its essentiality for multiple biochemical processes in all living organisms, they have evolved complex homeostatic mechanisms which ensure internal concentrations are tightly controlled to enable essential processes while minimizing excess copper which could lead to oxidative stress. If organisms are copper deficient then they will actively sequester it to meet their metabolic requirements. If they are in a copper rich environment, they will either store or excrete it as needed[11].

Bioaccumulation of copper has been extensively reviewed in the EU copper evaluation at the Technical Committee for New and Existing Substances (TCNES) and the Scientific Committee for Health and Environmental Risk (SCHER). The review concluded that because of the essentiality of copper, an increase in body concentration of copper cannot be considered as "bioaccumulation" as commonly understood for non-essential organic molecules. To achieve optimum biological efficiency and growth, organisms actively and deliberately accumulate essential metals in nutrient depleted environments, using bio-regulatory (homeostatic) mechanisms to ensure body concentration does not become harmful. Since the bioconcentration factor (BCF) is a function of body concentration vs. environmental concentration, this can lead to a very high apparent BCF in copper deficient environments. In normal and nutrient rich environments, the internal concentration is balanced by homeostatic mechanisms. However, the relatively higher environmental concentrations lead to a lower observed "bioaccumulation". For this reason, the concepts of BCF, bioaccumulation factor (BAF), and biomagnification factor (BMF) have no meaning for homeostatically regulated essential metals[11].

Copper Regulatory Approvals

To be used as a biocide in antifouling, copper must be approved by regulatory bodies. Every country in the world allows or has formally approved the use of copper antifouling coatings in their waters, and whenever a complete scientific risk assessment has been conducted, the use of copper has been approved. A complete risk assessment is appropriate for a complicated issue such as this because fouling has serious environmental consequences. The environmental benefits of effective antifouling coatings that use safe and approved biocides such as copper are significant.

Due to increasingly stringent risk assessments the number of biocidal active ingredients in use has been reduced to 10, according to the Lloyd's register (as of August 2023). Copper based products are the most prominent on the market (Copper Oxide – 86%; Copper Thiocyanate –

3%). Copper Pyrithione is the most dominant co-biocide (used in 55% of approved coatings)[4]. Copper based antifouling products continue to be the most universally effective and environmentally sound method used worldwide to prevent biofouling across a broad range of use patterns. Some recent positive decisions are highlighted below:

Washington State: Washington in the United States passed legislation in 2011 to phase out the use of copper-based antifouling paints. The Washington Department of Ecology (DOE) conducted surveys in 2017 and 2019 to investigate the availability and environmental impact of alternative products. Both reviews concluded that some non-copper alternatives would be more harmful to the environment than copper. Washington delayed the ban in both 2018 and 2020. In 2020, DOE was directed to continue investigating alternatives. In 2024 DOE issued an updated report with the finding that it could not determine "that safer and effective alternatives to copper-based antifouling paints are feasible, reasonable, and readily available."[12]

California: The Marina Del Rey (Los Angeles) Toxic Pollutants TMDL was established in 2005. In 2014 it was revised to include copper in the water column as impairments. In 2014, there was a provision to conduct a Water Effects Ratio (WER) study. As mentioned previously, this study was conducted and completed in 2021. In 2024, based on the results of the WER study, which reflects the bioavailability of copper in the specific marina, the Los Angeles Regional Water Quality Control Board proposed an increase in the TMDL by a factor of 1.32. This increase in TMDL can be allowed because the concentration at which dissolved copper has been shown to be non-toxic in this marina is higher than previously believed. This conclusion drastically decreased the amount of a reduction in the use of copper-based antifouling systems that would be needed to protect the marina.[9]

The San Diego Port Authority which is responsible for protecting the environmental health of Shelter Island Yacht Basin has shifted to a biological integrity assessment, away from chemical, physical, or laboratory proxies. This assessment uses benthic macroinvertebrates to determine the state of aquatic life and health of water systems. This decision came from the understanding that measured copper levels in the marina do not necessarily correlate with basin health, as this article has discussed. The San Diego Port Authority recognized that measurements and assessments of biological integrity are the best way to protect the biological community.[13]

Copper Sustainability in Antifouling

Alternate non-biocidal antifouling products are often marketed as being "more sustainable" than biocidal coatings, citing less environmental impact. This leads to the belief that copper (and other biocidal) antifouling products are NOT sustainable. This is not an accurate conclusion. Climate change and the actions to prevent it require a very thoughtful analysis of human activity and the consequences of solutions and a brief review of the facts in this case suggests that promoting one solution over another based on limited review of all the associated consequences and biased product promotion is not helpful.

First, the supply of copper for antifouling is a small fraction of the world's resources. The copper used in marine antifouling coatings is obtained from post-industrial recycled copper. On average, 8.5 million tons of copper were recycled annually from 2009-2018. That number has no doubt increased significantly as the world economy has been growing. Recycled copper used in antifouling coatings is presently approximately 50,000 tonnes annually. That is 0.6% of the world's annual recycled copper. Recycled copper is approximately 32% of the copper used annually. That makes the copper used in antifouling coatings just 0.13% of the annual global use. [14]

Second, it is inaccurate to consider only one aspect of sustainability , such as the possibility of a negative impact of the biocide on the local environment; rather, the discussion of sustainability must be holistic, and the effectiveness of coatings should be considered. A 2007 study found that a vessel with 10% barnacle coverage would need a 36 percent shaft power increase to maintain the same speed.[15] This obviously results in additional fuel usage: the worlds shipping industry already emits approximately 3% of the worlds GHG's, and without effective copper antifoulings this would be considerably larger.

The primary feed stock to copper based antifouling paints is cuprous oxide. It is common practice to utilize post-industrial or post-consumer recycled copper in the production of cuprous oxide. Thus, the production of cuprous oxide has been demonstrated to generate low levels of greenhouse gases. The base of many foul release coatings is silicone. It has been documented that the production of silicone can generate up to 180,000 tonnes of carbon dioxide annually[16]. Therefore, the supply chain for copper based biocidal coatings has a lower carbon footprint.

Also, no matter what coating is used on the hull of a vessel, resources are consumed that are not going to be recycled. This includes coatings with alternative biocides, or silicone foul release coatings.

Resources used in any human activity, such as shipping, should be a significant factor in decision making. The 5-year antifouling coating on a 9,200 TEU container vessel could cost $450,000 USD. That yields a cost of $250 per day. The fuel usage of a vessel this size slow steaming to reduce fuel consumption would be approximately 100 tons per day[17]. The current price of bunker fuel is $600/ton. That yields a fuel cost of $60,000/day. While not a direct comparison of CO_2 emission, financial cost is a relative representation of resources used. The financial ratio of fuel cost to antifouling coatings cost is $60,000/$250 or 240:1. Clearly the outstanding issue regarding climate change and sustainability goals with shipping isn't the approved coating type, it is the fuel efficiency of shipping and therefore the effectiveness of the coating.

Climate change and the actions to prevent it require a very thoughtful analysis of human activity and the consequences of solutions. A brief review of the facts in this case proves that promoting one solution over another based on limited review of all the associated consequences and biased product promotion is not helpful.

Summary

Copper has been used in anti-fouling applications for centuries and has shown continued efficacy and safe use. This article demonstrated that, due to natural environmental reactions of the cupric ion, as well as organisms' ability to homeostatically regulate copper, the toxicity of copper in water can be overstated. Copper is formally approved by regulatory bodies wherever it is used as an anti-fouling coating, after undergoing numerous rigorous risk assessments. Copper-based antifouling products are sustainable in that they are naturally occurring, abundant in nature, and are effective in reducing biofouling. The reduction in biofouling plays an important role in meeting long term global sustainability objectives.

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