# Biocides in Antifouling Paint Formulations Currently Registered For Use

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# Abstract

Antifouling paints incorporate biocides in their composition seeking to avoid or minimize the settlement and growing of undesirable fouling organisms. Therefore, biocides are released into the aquatic environments also affecting several non-target organisms and, thus, compromising ecosystems. Despite global efforts to investigate the environment occurrence and toxicity of biocides currently used in antifouling paints, the specific active ingredients that have been used in commercial products are poorly known. Thus, the present study assessed the frequencies of occurrence and relative concentrations of biocides in antifouling paint formulations registered for marketing worldwide. The main data were obtained from databases of governmental agencies, business associations and safety data sheets from paint manufacturers around the world. Results pointed out for 25 active ingredients currently used as biocides, where up to six biocides have been simultaneously used in the examined formulations. Cuprous oxide, copper pyrithione, zinc pyrithione, zineb, DCOIT and cuprous thiocyanate were the most frequently ones, with mean relative concentrations of 35.9±12.8 %, 2.9±1.6 %, 4.0±5.3 %, 5.4±2.0 %, 1.9±1.9 % and 18.1±8.0 % (w/w) of respective biocide present in the antifouling paint formulations. Surprisingly, antifouling paints containing TBT as active ingredient are still being registered for commercialization nowadays. These results can be applied as a proxy of biocides that are possibly being used by antifouling systems and, consequently, released into the aquatic environment, which can help to prioritize the active ingredients that should be addressed in future studies.

# Introduction

Antifouling paints have been used to prevent the settlement of fouling in vessel hulls(Omae 2003; Dafforn et al. 2011), aquaculture facilities (Guardiola et al. 2012) and other submerged structures, such as pipes, gates, stationary structures, etc (Bleile and Rodgers 2001; Yebra et al. 2004; Claudi and de Oliveira 2015). The reduction and prevention of fouling in vessel contributes to decrease shipping costs, fuel consumption and greenhouse gas emissions (Schultz et al. 2011). In addition, antifouling paints minimize the risks of non-native species introduction (Minchin and Gollasch 2002; Eldredge and Carlton 2002). Historically, several antifouling paint technologies were used for naval purposes, including insoluble matrix, soluble matrix or ablative/hydration, self-polishing copolymer, and biocide-free (Yebra et al. 2004; Takahashi 2009). Except in biocide-free antifouling paints, all other technologies contain one or more biocides in their composition. In these products, the films covering submerged structures act as a source of biocides to the aquatic environments, which may partition on different environmental matrices and cause deleterious effects to the aquatic organisms (Amara et al. 2018). Therefore, the most susceptible areas to this chemical impact are ship and boat traffic zones, such as harbors, marinas, shipyards, and navigation channels and routes (Dafforn et al. 2011; Harino 2017). In addition, aquaculture zones have also been reported as possible hotspots of biocide contamination due to the presence of facilities using antifouling paints (Guardiola et al. 2012). Identification of deleterious effects related to antifouling biocides has motivated the regulation of some compounds used in paints and coatings. For example, the worldwide banning of tributyltin (TBT) by means of the Antifouling System Convention (AFS Convention) issued by International Maritime Organization in 2008 (IMO 2008). Moreover, Irgarol and chlorothalonil were also banned in the European Commission (ECHA 2019). On the other hand, new chemicals, such as tralopyril (Kempen 2011) and medetomidine (I-Tech AB 2020), have been introduced seeking for more environment friendly and effective antifouling paints (Faÿ et al. 2019).

Although some information on environmental occurrence and ecotoxicological effects of biocides used after TBT world ban is available, most of published papers are 10 to 20 years-old (Omae 2003; van Wezel and van Vlaardingen 2004; Thomas and Brooks 2010; Castro et al. 2011; Dafforn et al. 2011) or refer to data obtained 15 to 20 years ago (Telegdi et al. 2016; Harino 2017; Amara et al. 2018). Based on the literature, there are 23 different antifouling biocides in use after the prohibition of TBT-based antifouling paints. However, except for Japan (Okamura and Mieno 2006), none of these studies estimates the relative usage of each biocide by the paint manufacturers. Some global organizations, associations and/or manufacturers, report the biocides used in antifouling paints to demonstrate compliance with regulations or to serve as a guide for products suitable for the use by professional or amateur users. Therefore, these data were compiled to assess the frequencies of occurrence and concentrations of biocides used in the production of antifouling paints registered for marketing worldwide. Despite only partially reflecting the current general situation, such findings can be applied as a proxy of biocides that are possibly being used by antifouling systems and, consequently, released into the aquatic environment.

# Methodology

# Data sources

Data about active ingredients or biocide compounds used in antifouling paint formulations were obtained from web sources, in several databases of governments and business associations around the world (Table S1, Online Resource 1). Particularly, in the websites of Health and Safety Executive (HSE) of UK (HSE 2018), Japan Paint Manufacturers Association (JPMA) (JPMA 2018), Malta Competition and Consumer Affairs Authority (MCCAA) (MCCAA 2018), United State Environmental Agency (EPA) (EPA 2018), Australian Pesticides and

Veterinary Medicines Authority (APVMA) (APVMA 2018), and websites of marketing and manufacturing companies of paints. The information gathered at HSE, MCCAA and APVMA websites was obtained in a compendium of biocidal registered products classified as antifouling paints. Data at JPMA were obtained in a list of antifouling paint products that comply with AFS Convention. From the EPA database, it was obtained a compilation of products labeled on Pesticide Product and Label System (EPA 2018). However, the list of products labeled was first obtained by searching "products used as antifouling" on the Pesticide Action Network database (Kegly et al. 2018). The Brazilian database and the organotin database were obtained from different data-sheets available for antifouling paints on the website of paint manufacturers.

The dataset used in the present study gathered information from a group of six countries that stands out in world gross tonnage of merchant fleet. Three out of six countries are in the top twelve regarding the deadweight tonnage (DWT) and the six countries together represent approximate 19 % of carrying capacity of DWT (UNCTADstat 2018). Moreover, three of them are in the top 15 and another three are on top 60 of liner shipping connectivity index (LSCI) for 2018 (UNCTADstat 2019), which indicates a country's integration level into global liner shipping networks. Additionally, five out of six countries are in the top twenty countries with the highest gross domestic product (GDP) for 2017 (World Bank Group 2019). This highlight how relevant are these countries for the maritime traffic considering a global coverage and, consequently, the representativeness of the current dataset to identify which biocides are the most likely used by the antifouling paint industry and, thus, released to/found in the environment.

# Data analysis

Raw data were organized to standardize the variables responses. Biocides were harmonized by the IUPAC name, one common name and CAS numbers (Table 1). Manufacturer names were also standardized. The concentration of biocides was reported in percentage by wet weight/weight (% w/w) by most data sources. However, data obtained from Australian dataset (APVMA) were in grams per liter, being transformed into percentage by using the density available in the datasheet provided by the manufacturer. For concentration data provided as minimum and maximum levels, an arithmetic mean was calculated for each biocide.

After standardizing, a single dataset with 1013 antifouling paint products, produced by 64 different manufacturers, was compiled based on available data sources (Data, Online Resource 2). Information about each formulation consisted of 52 variables (Table S2, Online Resource 1). To determine the frequencies of occurrence, it was considered only the unique paint formulations using a particular biocide combination and concentration. The descriptive statistics for biocide concentrations were calculated only for commercial products presenting this information. The concomitant use of more than one biocide was also recorded. The exploratory and data analysis was performed using R language and over RStudio GUI.

## Results And Discussion

# Biocide's occurrence in the antifouling paint formulations registered for use

Different profiles of biocides register and/or use may be associated to different nationwide or international restrictions. Chlorothalonil and Irgarol, for instance, were banned in the EU (ECHA 2019), while TBT and TPT were banned worldwide in 2008 by IMO (IMO 2008). This pattern can be seen in the present study, where cuprous oxide was the only biocide present in all databases, while DCOIT and zinc pyrithione were in all but OTSAF. BRAF and JPMA dataset showed, respectively, 15 and 14 out of 25 different active ingredients registered for use, whilst the remaining presented 8 to 10 biocides (Fig. 1). Although 25 biocides were identified in the current dataset (Fig. 1), the number reached 30 active ingredients registered and/or used in paint or coating formulations already listed in antifouling systems for vessels and other submerged surfaces (Omae 2003; Thomas and Brooks 2010; Castro et al. 2011) (Table 1). Even listed as antifouling biocides in these previous reviews, capsaicin, copper naphthenate, maneb, N-(2,4,6-Trichlorophenyl) maleimide and TCMTB (Busan) were not found in any antifouling paint formulations registered for use in the dataset used in the current study. It does not necessarily mean they are no longer used as biocides and may be a limitation of the current dataset. On contrary, even not previously listed in the reviews, copper, cupric oxide, cupric acetate, N-ethyl-2-methylbenzenesulfonamide and terbutrin have been identified in antifouling paint formulations registered for use.

The biocides most frequently registered for use were the metal-based (e.g., copper or zinc). Cuprous oxide, copper pyrithione, zinc pyrithione, zineb and cuprous thiocyanate were present in 76.1, 28.8, 16.7, 11.5 and 8.8 % of the examined antifouling paint formulations, respectively (Fig. 2). Indeed, cuprous oxide has already been identified as a biocide frequently used in antifouling paints (Omae 2003; van Wezel and van Vlaardingen 2004; Thomas and Brooks 2010; Castro et al. 2011). In addition, zinc oxide and copper were present in 3.7 and 1.6 % of the reviewed formulations. However, the non-metallic biocides DCOIT, Irgarol, PTPB, diuron, tralopyril and dichlofluanid were also listed in 9.3, 4.5, 4.1, 3.9, 2.7 and 1.9 %, respectively, of paint formulations registered for use. Thiram, tolyfluanid, chlorothalonil, tributyltin methacrylate, Ziram, tebutrin, medetomidine, tributyltin oxide, TCMS, cupric oxide, cupric acetate and N-ethyl-2-methylbenzenesulfonamide were listed in less than 1% of examined paints. Thus, there may have been a decrease in the frequency of use of some compounds described in the literature as "commonly used", such as dichlofluanid and chlorothalonil (Omae 2003; van Wezel and van Vlaardingen 2004; Harino 2017), since they were listed in less than 2% of paints formulations currently registered for use. Such decrease is also seen by comparing a previous study in Japan, that reported chlorothalonil and dichlofluanid in 5.2 and 6 %, respectively, of paint formulations (Okamura and Mieno 2006), and the present JPMA dataset, where only chlorothalonil (1.1 %) was reported. Although still among the top 10 most frequently used biocides within the revised paint formulations, the same applies for diuron and Irgarol that have decreased from 16.6 % and 8.4 % (Okamura and Mieno 2006) to 8.2 % and 5.8 % (present JPMA dataset), respectively, their frequency in formulations registered for use. Postulated as antifouling candidates a decade ago (Pérez et al. 2009; Thomas and Brooks 2010), pyridine-triphenylborane (PTPB) (4.1%), tralopyril (2.7%) and medetomidine (0.2%) still presented a relatively low frequency of use in the registered formulations. DCOIT (9.3 %) is the fifth most frequently registered biocide for use, being increased its frequency of use in comparison to what was previously seen in Japan (10.2 % from Okamura and Mieno (2006) to 15.1 % for the present JPMA dataset). Considering the representativeness of the current dataset, these can be considered global trends.

Table 1
Biocides as active ingredients of antifouling paint formulations identified in the databases and literature.

| Common name | IUPAC name | CAS number | Identified in present work | Previously cited reference |
|---|---|---|---|---|
| Capsaicin | (E)-N-[(4-hydroxy-3-methoxyphenyl)methyl]-8-methylnon-6-enamide | 404-86-4 | No | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Chlorothalonil | 2,4,5,6-tetrachloroisophthalonitrile | 1897-45-6 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Copper | Copper | 7440-50-8 | Yes | |
| Copper naphthenate | copper,naphthalene-2-carboxylate | 1338-02-09 | No | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Copper pyrithione | copper, bis(1,hydroxy-2(1H)-pyridinethionato O,S)- | 14915-37-8 | Yes | Thomas and Brooks 2010; Castro et al. 2011 |
| Cupric acetate/copper (II) acetate | copper; diacetate | 142-71-2 | Yes | |
| Cupric oxide/copper (II) oxide | Oxocopper | 1317-38-0 | Yes | |
| Cuprous oxide/copper (I) oxide | copper; hydrate | 1317-39-1 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Cuprous thiocyanate | copper (1+) thiocyanate | 1111-67-7 | Yes | Omae 2003; Castro et al. 2011 |
| DCOIT | 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one | 64359-81-5 | Yes | Omae 2003; Castro et al. 2011 |
| Dichlofluanid | N-[dichloro(fluoro)methyl]sulfanyl-N-(dimethylsulfamoyl)aniline | 1085-98-9 | Yes | Omae 2003; Castro et al. 2011 |
| Diuron | 3-(3,4-dichlorophenyl)-1,1-dimethylurea | 330-54-1 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Irgarol | 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine | 28159-98-0 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Maneb | manganese(2+);N -[2-(sulfidocarbothioylamino)ethyl]carbamodithioate | 12427-38-2 | No | Thomas and Brooks 2010; Castro et al. 2011 |
| Medetomidine | 5-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole | 86347-14-0 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| N-(2,4,6-Trichlorophenyl) maleimide | 1-(2,4,6-trichlorophenyl)pyrrole-2,5-dione | 13167-25-4 | No | Omae 2003; Thomas and Brooks 2010 |
| N-ethyl-2-methylbenzenesulfonamide | N-ethyl-2-methylbenzenesulfonamide | 1077-56-1 | Yes | |
| Pyridine-triphenylborane PTPB | pyridine;triphenylborane | 971-66-4 | Yes | Omae 2003; Castro et al. 2011 |
| TCMS Pyridine / Densil | 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine | 13108-52-6 | Yes | Omae 2003; Castro et al. 2011 |
| TCMTB / Busan | 2-(thiocyanomethylthio)benzothiazole | 21564-17-0 | No | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Terbutrin | 2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine | 886-50-0 | Yes | |

| Common name | IUPAC name | CAS number | Identified in present work | Previously cited reference |
|---|---|---|---|---|
| Thiram | dimethylcarbamothioylsulfanyl N,N-dimethylcarbamodithioate | 137-26-8 | Yes | Thomas and Brooks 2010; Castro et al. 2011 |
| Tolylfluanid | methanesulfenamide, 1,1-dichloro-N-((dimethylamino) sulfonyl)-1-fluoro-N-(4-methylphenyl) | 731-27-1 | Yes | Thomas and Brooks 2010; Castro et al. 2011 |
| Tralopyril | 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile | 122454-29-9 | Yes | Thomas and Brooks 2010; Castro et al. 2011 |
| Tributyltin methacrylate | tributylstannyl 2-methylprop-2-enoate | 2155-70-6 | Yes | Omae 2003 |
| Tributyltin oxide | tributyl(tributylstannyloxy)stannane | 56-35-9 | Yes | Omae 2003 |
| Zinc oxide/zinc (II) oxide | oxozinc | 1314-13-2 | Yes | Castro et al. 2011 |
| Zinc pyrithione | zinc-2-pyridinethiol-1-oxide | 13463-41-7 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |
| Zineb | zinc ethylenebis (dithiocarbamate) | 12122-67-7 | Yes | Thomas and Brooks 2010 |
| Ziram | zinc dimethyl dithiocarbamate | 137-30-4 | Yes | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011 |

### Simultaneous use of biocides in the paint formulations registered for use

The current dataset confirmed that manufactures are still using combinations of different biocides in antifouling paint formulations. Although a simultaneous use of up to four biocides has been previously reported (Okamura and Mieno 2006), the formulations examined in the present study proved that up to six biocides can be used simultaneously. The combination of two (51.6 %), one (33.3 %) and three (10.9 %) biocides were the most frequent, while 4 or more biocides were listed in only 1.8 % of paint formulations registered for use (Fig. 3). Biocide-free products were listed in 2.4 % of antifouling paint formulations. However, this number might be biased since only one database included biocide-free paints. In formulations using only one active ingredient, cuprous oxide, cuprous thiocyanate, zinc pyrithione, copper pyrithione, copper and pyridine-triphenylborane were present in 77.7, 6.2, 5.3, 3.2, 3.0 and 1.5 %, respectively, of examined antifouling paints registrations. DCOIT, Irgarol, cupric oxide, diuron, tralopyril, tributyltin methacrylate and tributyltin oxide were uniquely listed in less than 0.6 % of the assessed paints.

Formulations with more than one active ingredient were assessed and the main pairs of biocide combinations is shown in Fig. 4. Molecules containing copper (half of the circle plot are represented by these compounds), especially cuprous oxide and copper pyrithione, are the most frequent biocides used in the paint formulations registered for use. Although copper pyrithione represents almost 50% of the combinations, other biocides are also commonly associated to cuprous oxide, such as zineb, DCOIT, diuron, Irgarol, zinc oxide and zinc pyrithione. Other associations can also be found at much lower frequency (e.g., thiram and dichlofluanid), while some biocides do not appear in combination with cuprous oxide but with zinc pyrithione, such as cuprous thiocyanate, tralopyril and pyridine-triphenylborane (PTPB), or with DCOIT and with zinc oxide, such as N-ethyl-2-methylbenzenesulfonamide. Tralopyril is used in formulations sold as copper-free antifouling paints (Janssen 2019). In addition to zinc pyrithione, it can be eventually found in combination with zinc oxide or DCOIT. These biocides employed in formulations along with copper- and zinc-based compounds are so-known as booster biocides (Bowman et al. 2003; Takahashi 2009). These so-called co-biocides play an important role by improving the toxicity over the fouling organisms and, thus, the efficiency of antifouling paints (Myers et al. 2006; Silkina et al. 2012; Ohlauson and Blanck 2014).

### Nominal concentration of biocides in the paint formulations registered for use

The biocides reports with the highest nominal concentrations (average ± standard deviation) in the paint formulations registered for use were cuprous oxide (35.9 ± 12.8 % w/w), tributyltin methacrylate (26.9 ± 18.8 % w/w), copper (powder) (19.3 ± 21.0 % w/w) and cuprous thiocyanate (18.1 ± 8.02 % w/w) (Fig. 5). Although the average copper (powder) concentration was 19.3%, this active ingredient was recorded in formulation with concentrations that can reach up to 66% w/w (Fig. 5), which will be mixed to create a product that will ultimately be used as antifouling paint. Those concentrations are probably responsible for the high environmental levels of copper in areas under the influence of maritime activities around the world (Eklund and Eklund 2014; Costa et al. 2016; Bighiu et al. 2016). Formulations using organometallic biocides, such as zineb, zinc pyrithione and copper pyrithione, were listed with average concentrations of 5.4 ± 2.0, 4.0 ± 5.3, 2.9 ± 1.6 % w/w, respectively, while the metal-free biocides, such as tralopyril, diuron, thiram, DCOIT, Irgarol, dichlofluanid and terbutrin, were listed with average levels of 5.2 ± 1.8, 3.9 ± 1.5, 2.4 ± 0.1, 1.9 ± 1.9, 1.7 ± 0.6, 1.6 ± 0.8 and 0.05 ± 0 % w/w, respectively. Concentrations for Ziram (5 % w/w), cupric acetate (3 % w/w) and N-ethyl-2-methylbenzenesulfonamide (3 % w/w) were reported for single paint products (Fig. 5). No information was available regarding concentrations used in the assessed antifouling paint formulations containing chlorothalonil, medetomidine, pyridine-triphenylborane (PTPB), TCMS pyridine/Densil and tolylfluanid.

In general, biocides used at lower concentrations are more toxic (e.g., Irgarol, DCOIT, dichlofluanid) than those used at higher concentration (Brooks and Waldock 2009; Silkina et al. 2012; Harino 2017), which may explain the observed concentration pattern. Some of these biocides have been found in environmental samples nearby areas of intense maritime traffic, which make antifouling paints one of their most likely source, even for formulations using relatively low concentrations (Harino 2017).

## Environmental levels of biocides present in the antifouling paint formulations registered for use

Environmental levels of some biocides used in the antifouling paint formulations reviewed are summarized in Table S3 (Online Resource 1). The high concentrations of copper reported in sediments of Brazil (up to 768 µg $g^{-1}$ dw; (Costa et al. 2016))and biofouling and boat hull in Sweden (4,686 ± 5,506 and 7,122 ± 12,207 µg $g^{-1}$ dw, respectively; (Bighiu et al. 2016))nearby ports and shipyards areas (Table S3, Online Resource 1) could be related, in some cases, to the high frequency of use of highly concentrated copper-based antifouling paints. The present study has pointed out that cuprous oxide and another cooper compounds are the most used active ingredients in paint formulations registered for use. Thus, copper associated to antifouling paints continues to be an important subject of monitoring, especially the most toxic labile fraction for the biota (Brooks and Waldock 2009) and in areas with restrict water circulation and high boat and ship traffic.

Zinc has also been found in high concentrations in the environment (e.g., up to 578 µg $g^{-1}$ dw in sediments of Brazil (Costa et al. 2016); 21,650 ± 41,092 and 29,568 ± 31,024 µg $g^{-1}$ dw, respectively, in biofouling and boat hulls in Sweden (Bighiu et al. 2016)) (Table S3, Online Resource 1), which may be also associate to its wider use as antifouling paint biocide (Soroldoni et al. 2018). Zinc-based biocides made up to 32 % of frequency of use in the assessed antifouling paint formulations (present study), where zinc oxide is used in a high average concentration, while the other zinc-based biocides are used in concentration up to 5 % w/w. Although zinc oxide is considered one of the main contributors to the environment contamination (Costa et al. 2016), less than 4% of the antifouling paint formulations reviewed are using zinc oxide as an active ingredient. However, this frequency of use can be underestimated and should be carefully considered since not all data sources listed this compound as an active biocide in the antifouling paint formulations. In the current dataset, only APVMA and BRAF reported zinc oxide. Although it has antifouling properties and has been used as antifouling biocide since the mid-twentieth century (Castro et al. 2011), in some cases, in legal terms (e.g., European Union, UE), zinc oxide is not considered an active biocide in antifouling paints (DIRECTIVE 98/8/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL 1998).

Despite the relative relevance of copper and zinc pyrithione, and copper thiocyanate as active ingredients in antifouling paint formulations, little information is available about their environmental levels. Although Cu-pyrithione had being detected (22 ng $g^{-1}$ dw) in a study performed in Japan (Harino et al. 2007), most of the few studies carried out in both water and sediments found levels of Cu- and Zn-pyrithiones below detection limits (< LODs) (Harino et al. 2005; Eguchi et al. 2010; Kim et al. 2014, 2015) (Table S3, Online Resource 1). The rapid degradation and transquelation make the detection of these compounds difficult (Soon et al. 2019). Thiocyanate ($SCN^{-}$) had been detected in coastal waters of Japan (Rong et al. 2005) and Portugal (Silva et al. 2011), but the association with its use as antifouling biocide was not assessed. Similar situation can occur with other biocides. Although tralopyril and medetomidine may be present in the environment, since they are offered by the paint industry as a copper-free option (Janssen 2019; I-Tech AB 2020), they have not yet been sufficiently evaluated or reported in monitoring studies. Therefore, the knowledge about the presence and sources of these compounds must be improved to enable a better appraisal towards the risks associated to their use as antifouling paint biocides.

Diuron, Irgarol, DCOIT, dichlofluanid, chlorothalonil, TCMTB and TBT, identified as active ingredients in the present study, have also been detected in the aquatic environment (Table S3, Online Resource 1). Interestingly, the non-metallic biocides detected in environmental samples were present in less than 10% of paint formulations registered for use at average concentrations lower than 5% w/w. In the case of DCOIT, despite its low environmental half-life (Jacobson and Willingham 2000), it has been frequently detected in water and sediments under the influence of maritime activities (e.g., ports and marinas) (Chen and Lam 2017; Abreu et al. 2020), which is a clear indication of the high frequency of use of antifouling paints with this biocide as active ingredient.

Despite pointing out, especially in conjunction with previously reported environmental levels, which biocides may be more relevant to future environment studies, the present study (based on their frequency of occurrence in antifouling paint formulations registered for use in their respective regions) only partially reflects the current general situation. It was not an exhaustive compilation of all paints worldwide registered for use and some relevant information was not available to be considered. To perform a more accurate study, it would have been crucial to consider the relative frequency of use of these antifouling paints (and consequently their active ingredients) by countries or region. As the amount of each antifouling paint used in each region/country is unknown, even a biocide that occurs less frequently in the formulations reviewed can end up having a significant environmental level. In addition, it is also important to consider that some of these biocides, such as diuron, chlorothalonil and dichlofluanid (Jennings and Li 2017; ANVISA 2017; HSE 2021), are also active ingredients of pesticides used in agriculture or as wood preservatives. Thus, these alternative sources can contribute to the contamination levels detected in aquatic environments, mainly when used nearby water bodies. For these reason, marketing studies and databases of antifouling products and frequencies of application in boats and ships must be generated or become publicly available data. This action may potentially improve the understanding of input rates and, consequently, the environment levels, which end up providing a better starting point for environmental and ecotoxicological studies.

# TBT

Despite the harmful and deleterious effects of TBT upon aquatic biota have been widely demonstrated (Dafforn et al. 2011) and its international ban issued by the IMO (IMO 2008), this active ingredient is still registered for use in 5 out of 1013 revised commercial paint formulations. Two types of organotin-based biocides were identified in the dataset. Tributyltin oxide was present in a single paint formulation with a concentration of 5.8 % w/w, while tributyltin methacrylate was present in the remaining 4 with a mean concentration of 26.9 ± 18.8 % w/w. Although the identification of active registrations does not guarantee their production and effective use, these products, except one restricted to military applications (NOFOUL® Rubber), seem to be available to some markets (e.g., Mexico ("Islands 44 Plus" https://www.jrfmarine.com/productos-para-embarcaciones/Islands-44-Plus-Black-GL/75) and Caribbean islands ("Biotin Plus Antifouling TBT Ablative" https://www.islandwaterworld.com/biotin-plus-antifouling-tbt-ablative-black-1-gal-nn13043)) for the maintenance of small and recreational boats. In fact, most of contemporary studies (Table S3, Online Resource 1) have demonstrated recent inputs of TBT associated to traffic and/or maintenance of pleasure and/or fishing boats (Paz-Villarraga et al. 2015; Briant et al. 2016; Cavalheiro et al. 2016; Artifon et al. 2016; Batista et al. 2016; Lam et al. 2017; Mattos et al. 2017; Batista-Andrade et al. 2018; Maciel et al. 2018; Romanelli et al. 2018; Castro et al. 2018; Abreu et al. 2020). Though, a study held in the Swedish coast assessing the coating of vessels in operation pointed out that 10% of ships and 23–29% of leisure boats had organotin compounds related to the old and underlayer coatings in their hulls (Lagerström et al. 2019). However, the commercialization of the organotin-based paints was already mentioned in 2014 (Turner and Glegg 2014) and the situation does not seem to be improved at all (Uc-Peraza et al. Submitted 14June2021).

Despite the Annex III of the Rotterdam Convention (2008), that included 161 participants and 72 signatory countries, restricting the international trade of tributyltin compounds (including tributyltin oxide and tributyltin methacrylate) either for pesticide or industrial use, the commercialization and use of TBT-based paints still seems to be one of the main current sources of fresh inputs to the aquatic environment. By hosting these markets, signatory countries of Rotterdam and AFS Conventions in the Caribbean (e.g., Mexico, Saint Martin, French St Martin, St Lucia and Grenada where these paints are still marketed) are indirectly in disagreement with global initiatives seeking to reduce TBT impacts worldwide (Uc-Peraza et al. Submitted 14June2021). In addition, this TBT-based trading market of antifouling paints are likely to be more alarming in countries with no or poor implementation of national or international restrictions. Therefore, considering the present evidences, TBT is still a matter of concern. Thus, the implementation or maintenance of studies that assess levels and biological effects of TBT are still on high demand. At the same time, effective actions must be taken to ensure the full implementation of Rotterdam and AFS conventions.

## Conclusions

Based on the current dataset, a simultaneous use of up to six biocides was identified in some antifouling paint formulations currently registered for commercial use around the world. Cuprous oxide, copper pyrithione, zinc pyrithione, zineb, DCOIT and cuprous thiocyanate were, respectively, the biocides most frequently found in these formulations. However, due to their relevance and limited information available, copper pyrithione, zinc pyrithione, zineb, DCOIT and tralopyril should be further addressed in future environmental and ecotoxicological studies. Medetomidine should also be appraised since, together with tralopyril, it has been offered as eco-friendly, non-metallic and fast-degrading alternatives by the antifouling paint manufacturers. Surprisingly, antifouling paints containing TBT were still registered for trade and available for current use, indicating this very toxic substance is still a matter of environment concern. Despite only partially reflecting the current general situation, such findings can be applied as a proxy of biocides that are possibly being used by antifouling systems and, consequently, released into the aquatic environment.

## Declarations

### Ethical approval, consent to participate, consent to publish

This manuscript has not been published or presented elsewhere in part or in entirety and is not under consideration by another journal. All study participants provided informed consent, and the study design was approved by the appropriate ethics review board. We have read and understood your ESPR journal's policies, and we believe that neither the manuscript nor the study violates any of these.

### Authors Contributions

César Augusto Paz-Villarraga: Conceptualization, Methodology, Software, Formal analysis, Investigation, Visualization, Writing - Original Draft. Ítalo Braga de Castro: Conceptualization, Writing- Reviewing and Editing. Gilberto Fillmann: Conceptualization, Supervision, Project administration, Writing- Reviewing and Editing. All authors read and approved the final manuscript.

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### Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Availability of data and materials

Database used in the present research is fully provided in a .csv-type file.

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## Figures

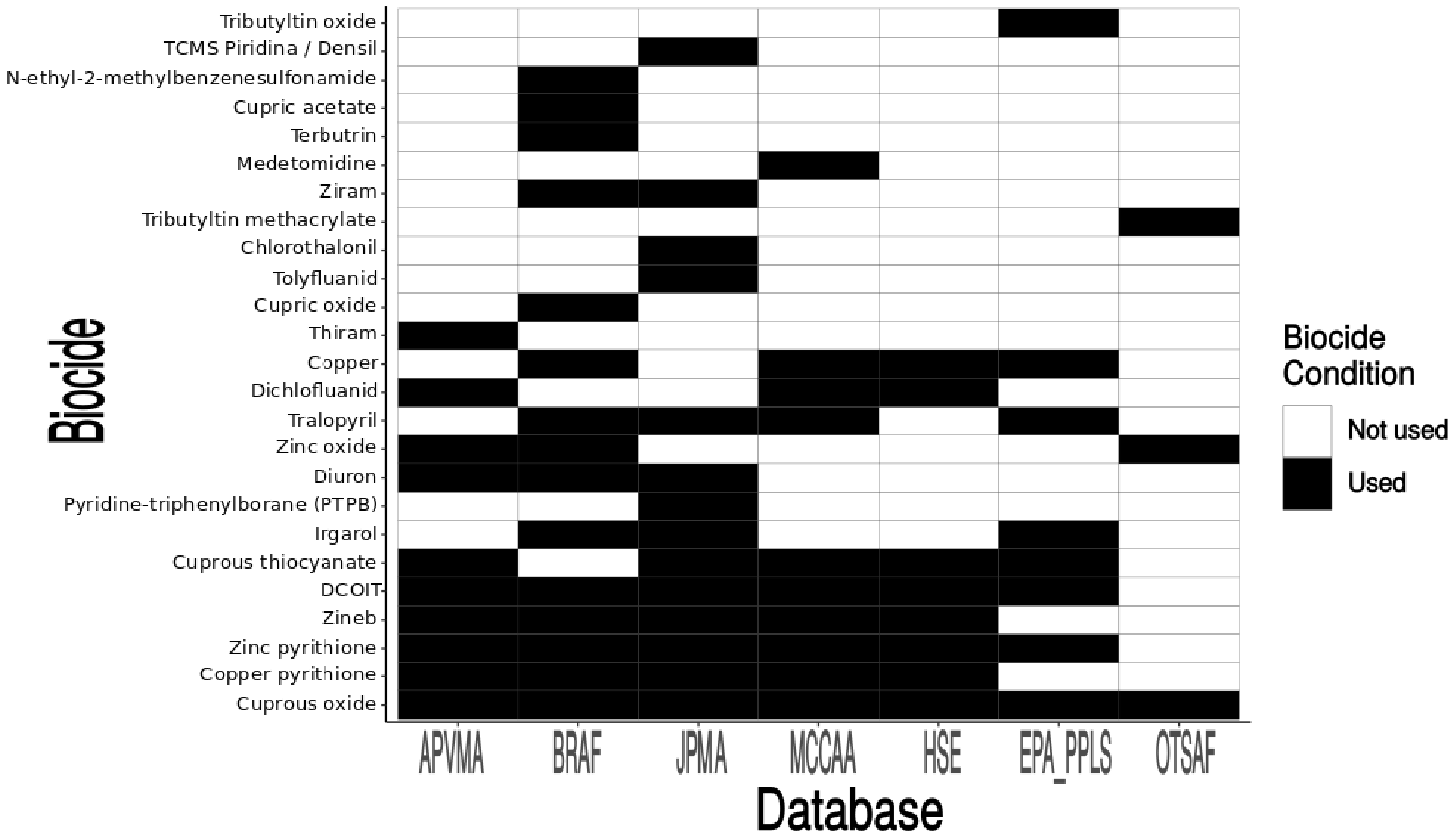

Figure 1

Biocides registered for use as active ingredient in antifouling paints formulations identified in each dataset. APVMA - Australian Pesticides and Veterinary Medicines Authority; BRAF - Brazilian database; JPMA - Japan Paint Manufacturers Association; MCCAA - Malta Competition and Consumer Affairs Authority; HSE - Health and Safety Executive; EPA_PPLA - United State Environmental Protection Agency; OTSAF - Organotin database.

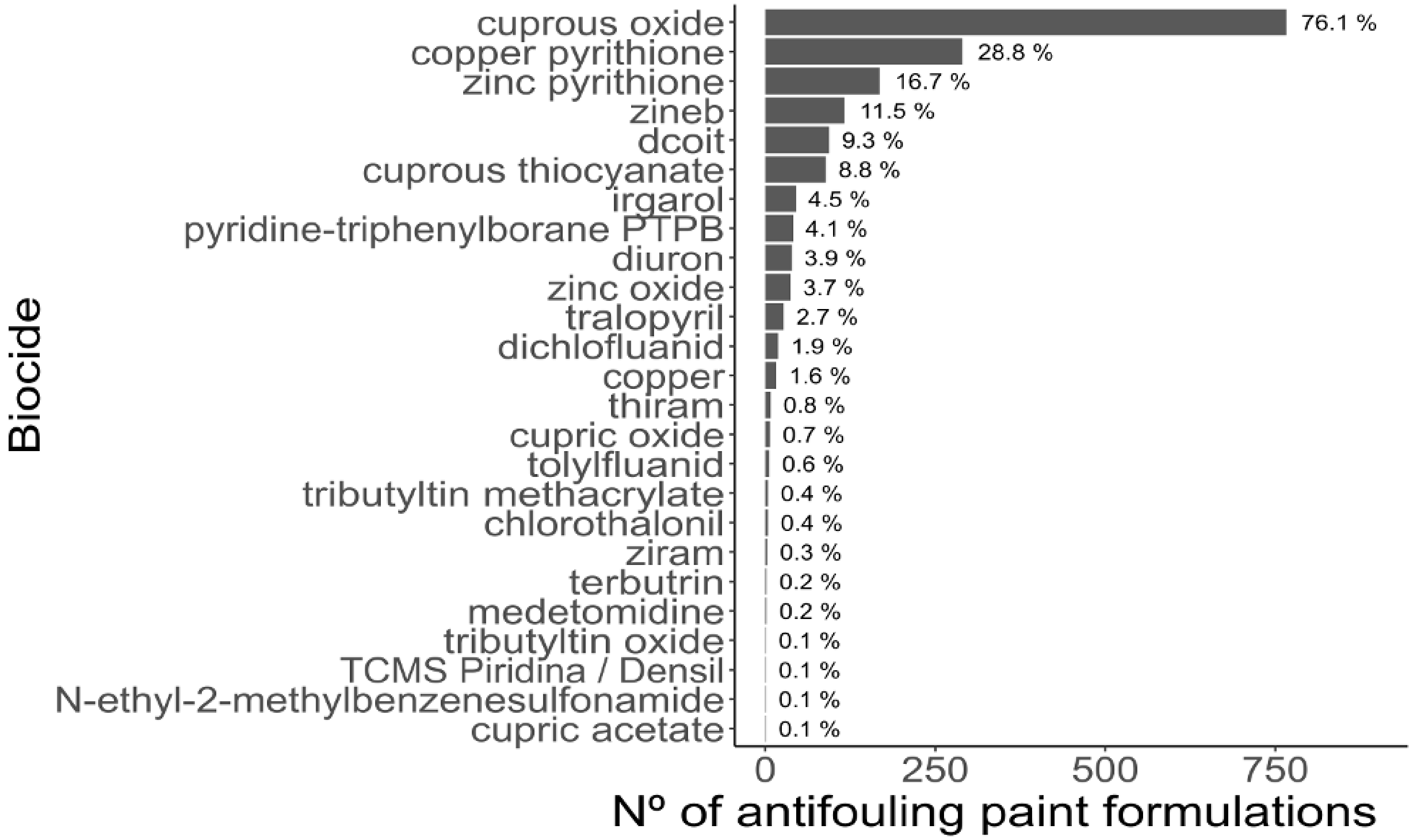

**Figure 2**

Number of formulations (and frequency of occurrence, %) identified in the dataset where each biocide was registered for use as active ingredient in antifouling paints.

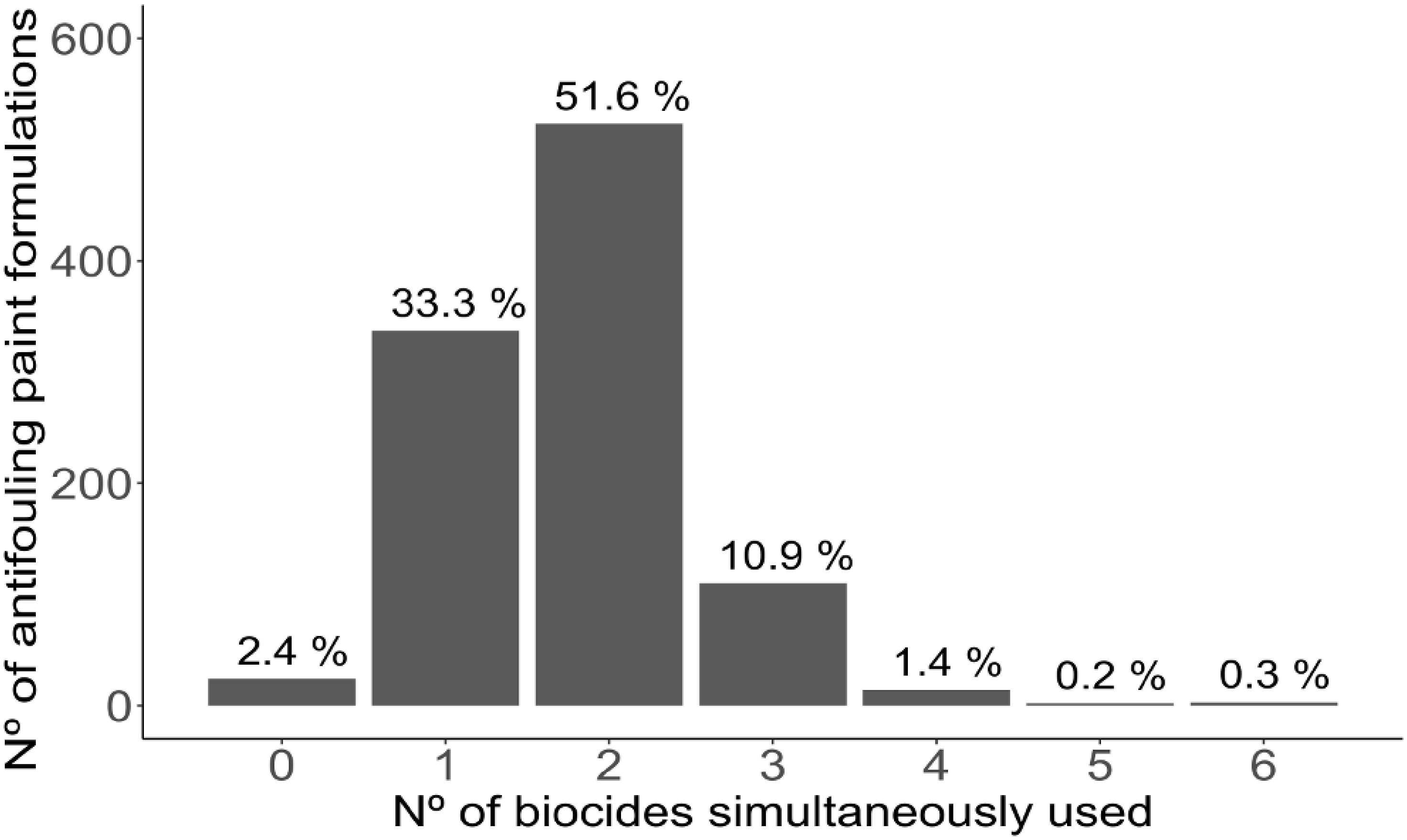

**Figure 3**

Relative frequencies (%) of biocides simultaneously used in antifouling paint formulations identified in the dataset.

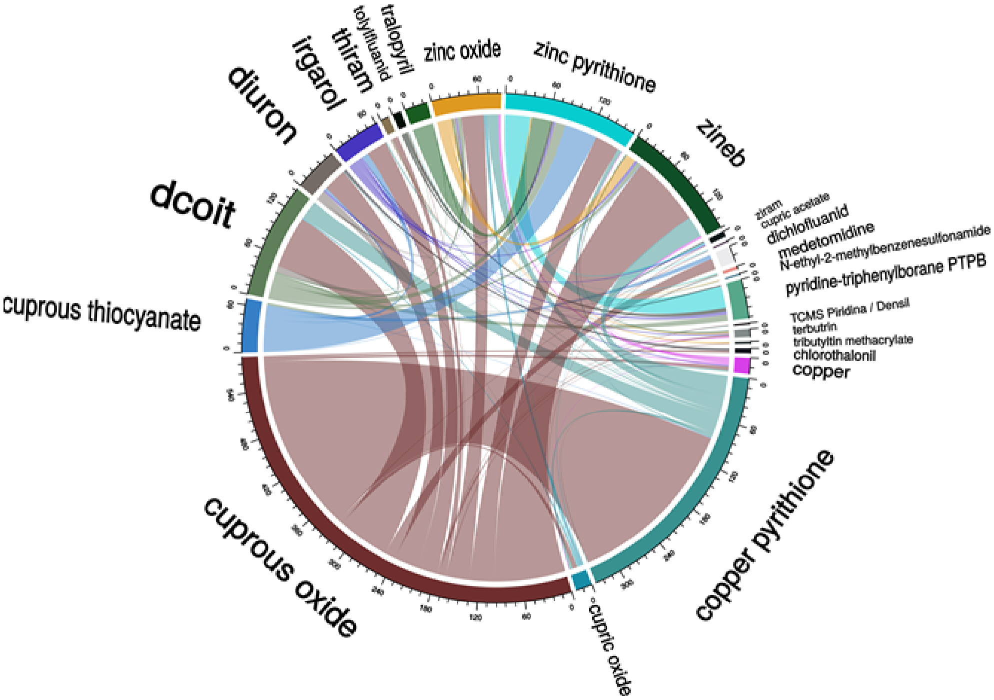

**Figure 4**

Combinations of biocides identified in antifouling paint formulations assessed in the dataset. The scales represent the number of times each biocide has appeared in combination with other biocide(s) and the width of the connections is proportional to the number of paints that have these biocides in their composition.

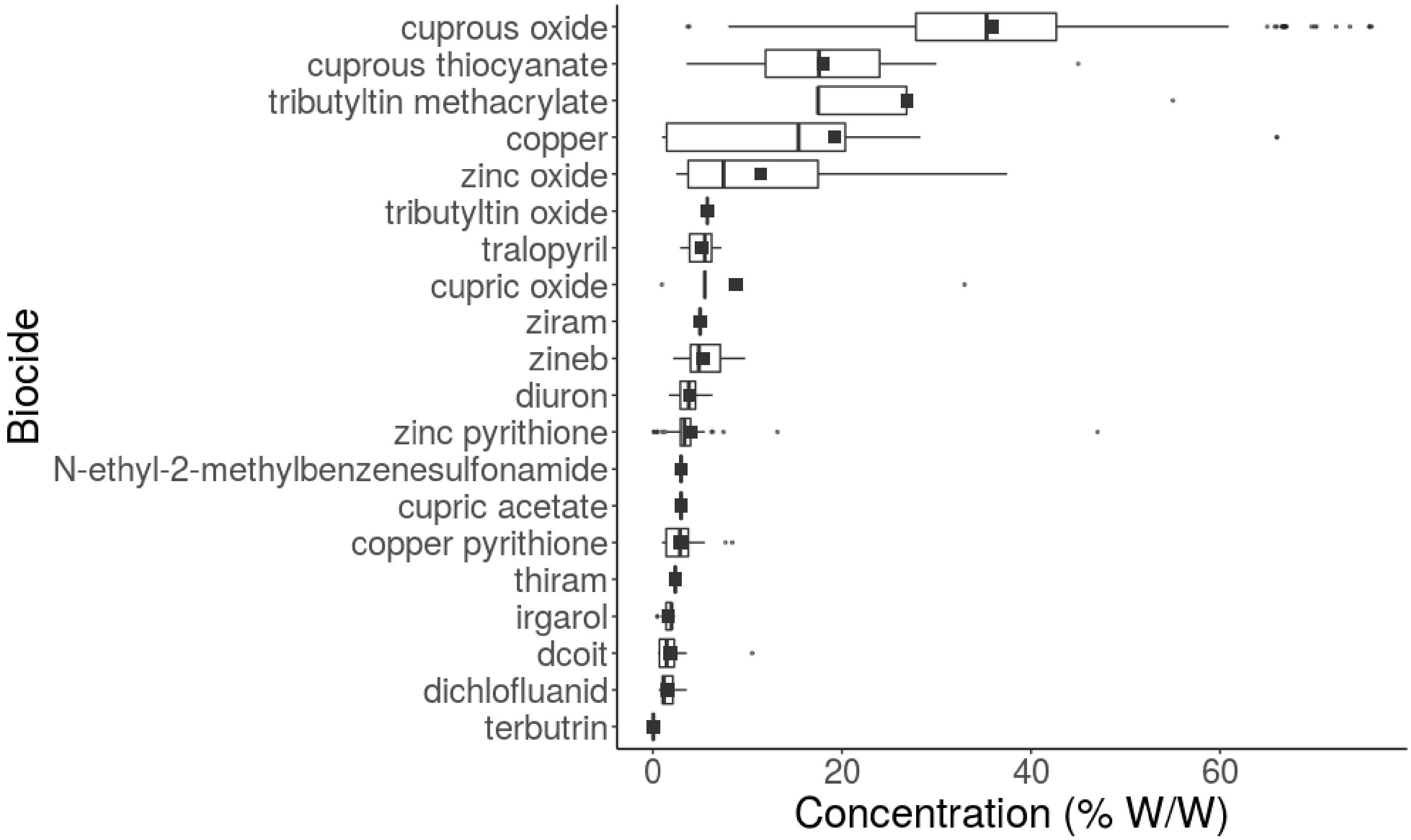

**Figure 5**

Box and whiskers plot of concentrations (% w/w) of biocides present in the antifouling paint formulations. Dark squares represent the average concentration for each biocide. Points and inner box line represent outliers and median, respectively. Percentiles 25 and 75 are indicated by lines on both sides of every box.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- PazVillarragaetal.2021Supplementarymaterial.doc
- datasupplementarymaterial.csv