Biocides in antifouling paint formulations currently registered for use

César Augusto Paz-Villarraga1,2 · Ítalo Braga Castro2,3 · Gilberto Fillmann1,2

Received: 19 July 2021 / Accepted: 16 November 2021 / Published online: 8 January 2022 © The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

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 nontarget organisms and, thus, compromising ecosystems. Despite global efforts to investigate the environmental 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. The 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 thiosulfate were the most frequent 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 an 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.

Keywords Antifouling paints · Antifouling biocides · Formulations registered · Currently used biocides

Introduction
Antifouling paints have been used to prevent the settlement of fouling on vessel hulls (Omae 2003; Daﬀorn et al. 2011), aquaculture facilities (Guardiola et al. 2012), and other submerged structures, such as pipes, gates, and stationary structures (Bleile and Rodgers 2001; Yebra et al. 2004; Claudi and de Oliveira 2015). The reduction and prevention of fouling on vessels contribute 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/hydraulic, 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 general, there is a main copper- or zinc-based biocide along with one or more organic biocides that are also known as booster biocides (Bowman et al. 2003; Takahashi 2009). Combinations of biocides in these paints increase their efficacy because the range of action against fouling biota is broadened, since there are organisms with low sensitivity to the main biocide (Voulvoulis 2006). 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.
Environmental Science and Pollution Research (2022) 29:30090–30101

pen 2011) and medetomidine (I-Tech AB 2020), have been banned by the European Commission (ECHA 2019). Moreover, Irgarol and chlorothalonil were also banned by the International Maritime Organization in 2008 (IMO 2008). Moreover, Irgarol and chlorothalonil were also banned by the European Commission (ECHA 2019). On the other hand, new chemicals, such as tralopyril (Kempen 2011) and medetomidine (I-Tech AB 2020), have been prospected as more environmentally friendly and effective antifouling paints. However, even having half-lives of less than 10 h for tralopyril (Oliveira et al. 2016) and less than 36 h with a low bioaccumulation factor for medetomidine (Hilvarsson et al. 2009; Cai et al. 2021), the actual “green label” might rely also on other factors such as their intensity of use and consequent environmental levels (Oliveira et al. 2017; de Campos et al. 2021).

Although some information on the environmental occurrence and ecotoxicological effects of biocides used after TBT world ban is available, most of the 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) and/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 to products suitable for use by professional or amateur users. On the other hand, due to the high cost and complex logistics required by studies to assess the effective use at a worldwide scale, the present review offers an alternative way to understand which biocides are the most likely used by the antifouling paint industry and, thus, released to/found in the 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 the Health and Safety Executive (HSE) of the 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 2018a), 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 the 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 (Kegey et al. 2018). The Brazilian dataset (BRAF) and the organotin dataset (OTSAF) 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 the world gross tonnage of merchant fleet. Three out of six countries (Japan, USA, and UK) are in the top twelve regarding the deadweight tonnage (DWT), and the six countries together represent approximately 19% of the carrying capacity of DWT (UNCTADstat 2018). Moreover, three of them (UK, USA, and Japan) are in the top 15, and another three (Malta, Brazil, Australia) are on top 60 of liner shipping connectivity index (LSCI) of 2018 (UNCTADstat 2019), which indicates a country’s integration level into global liner shipping networks. As an indirect measure of the presence of large shipyards, in 2018 the ranking of countries by gross tonnage of ships built included Japan (3rd), Brazil (10th), USA (12th), UK (34th), and Australia (35th) (UNCTADstat 2021). 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 highlights the relevance of 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

The raw data were organized to standardize and unify the information in the response variables to confirm that each paint formulation is unique. Biocides were harmonized by the IUPAC name, one common name and CAS numbers (Table 1). Manufacturer names were also standardized into unique names among the different data sources. The concentration of biocides was reported in percentage by wet weight/weight (% w/w) by most data sources. However, data obtained from the Australian dataset (APVMA) were in grams per liter, being transformed into a percentage by using the density available in the datasheet provided by the manufacturer. For concentration data provided as the 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, only unique paint formulations using particular name, biocide combination, and concentration were taken into consideration. Only commercial products providing the concentrations of biocides used, as well as figures production, were performed using the R language (R version 4.0.5) on RStudio (version 1.4.1106–5).

Results and discussion

Biocide’s occurrence in the antifouling paint formulations registered for use

Different profiles of registration and/or use of biocides 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). In fact, different profiles of biocides registered for use in the antifouling paints were seen by the present study, where cuprous oxide was the only biocide present in all data sources, while DCOIT and zinc pyrithione were in all but OTSAF dataset. BRAF dataset and JPMA database showed, respectively, 15 and 14 out of 25 different active ingredients registered for use, while the remaining presented 8 to 10 biocides (Fig. 1). Although 25 biocides were identified in the current dataset (Fig. 1), up to 30 active ingredients have been mentioned as registered and/or used in paint formulations or coatings in antifouling systems for boats 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, capsacin, copper napthenate, manebe, 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 database/dataset. On contrary, even not previously listed in the reviews, cupric oxide, cupric acetate, N-ethyl-2-methylbenzenesulfonamide, and terbutryn 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 nonmetallic 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, terbutryn, 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 the 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. The decrease in the use of these biocides in paint formulations is probably due to the regulations and bans which have been gradually implemented around the world. For example, the use of diuron and chlorothalonil and of Irgarol in antifouling products
| Common name                          | IUPAC name                                                                 | CAS number       | Identified in present work | Previously cited reference                                      |
|-------------------------------------|-----------------------------------------------------------------------------|-----------------|----------------------------|-----------------------------------------------------------------|
| Capsaicin                           | (E)-N-[(4-hydroxy-3-methoxy-phenyl)methyl]-8-methyl-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 (in powder)                  | Copper                                                                      | 7440–50-8       | Yes                        | Castro et al. 2011                                              |
| 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)-                          | 14,915–37-8     | Yes                        | Thomas and Brooks 2010; Castro et al. 2011                      |
| Cupric acetate/copper (II) acetate | Copper; diacete                                                             | 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                                  | 64,359–81-5     | Yes                        | Omae 2003; Castro et al. 2011                                  |
| Dichlofluanid                       | N-[dichloro(fluro)methyl]sulfanyl-N-([dimethylsulfonyl]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                | 28,159–98-0     | Yes                        | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011           |
| Maneb                               | Manganese(2+);N-[2-(sulfdocarbathiobylamino)ethyl] [carbamothioate             | 12,427–38-2     | No                         | Thomas and Brooks 2010; Castro et al. 2011                      |
| Medetomidine                        | 5-[1-(2,3-Dimethylphenyl)ethyl]-1H-imidazole                                 | 86,347–14-0     | 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                                  | 13,167–25-4     | 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                             | 13,108–52-6     | Yes                        | Omae 2003; Castro et al. 2011                                  |
| TCMTB / Busan                       | 2-(Thiocyanomethylthio) benzothiazole                                      | 21,564–17-0     | No                         | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011           |
| Terbutryn                           | 2-N-tert-butyl-4-N-ethyl-6-methylsulfonyl-1,3,5-triazine-2,4-diamine        | 886–50-0        | Yes                        |                                                                  |
| Thiram                              | Dimethylcarbamothioylsulfanyl N,N-dimethylcarbamothioate                    | 137–26-8        | Yes                        | Thomas and Brooks 2010; Castro et al. 2011                      |
| Tolyfluanid                         | Methanesulfoamide, 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     | 122,454–29-9    | 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(tributylstannoyl)stannane                                         | 56–35-9         | Yes                        | Omae 2003                                                       |
| Zinc oxide/zinc (II) oxide          | Oxo-zinc                                                                    | 1314–13-2       | Yes                        | Castro et al. 2011                                              |
| Zinc pyrithione                     | Zinc-2-pyridinethiol-1-oxide                                                | 13,463–41-7     | Yes                        | Omae 2003; Thomas and Brooks 2010; Castro et al. 2011           |
| Zineb                               | Zinc ethylenebis (dithiocarbamate)                                          | 12,122–67-7     | Yes                        | Thomas and Brooks 2010                                          |
is no longer allowed in the EU and UK since 2008 and 2017, respectively (HSE 2021). 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. However, this is probably also due to the short time these compounds have been approved for use. In the EU, for instance, tralopyril and medetomidine were approved in 2015 and 2016, respectively (ECHA 2021a, b). 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.

![Fig. 1](image1.png)

**Fig. 1** Biocides registered for use as an active ingredient in antifouling paints formulations identified in each dataset. APVMA, Australian Pesticides and Veterinary Medicines Authority; BRAF, Brazilian dataset; JPMA, Japan Paint Manufacturers Association; MCCAA, Malta Competition and Consumer Affairs Authority; HSE, Health and Safety Executive; EPA_PPLA, United States Environmental Protection Agency; OTSAF, Organotin dataset

![Fig. 2](image2.png)

**Fig. 2** Number of formulations (and frequency of occurrence, %) identified in the dataset where each biocide was registered for use as an active ingredient in antifouling paints

---

### Table 1 (continued)

| Common name | IUPAC name | CAS number | Identified in present work | Previously cited reference |
|-------------|------------|------------|---------------------------|---------------------------|
| 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 manufacturers 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 presence of two (51.6%), one (33.3%), and three (10.9%) biocides was 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 are 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. Copper oxide is normally used as the main biocide due to its balance among cost, solubility, and toxicity (Brook and Waldock 2009). 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 with cuprous oxide can also be found at a much lower frequency (e.g., thiram and dichlofluanid). However, in general, these combinations seek to improve the effectiveness of the product as antifouling, since there are organisms that are not very sensitive to copper. So, other (booster) biocides can improve the product’s toxicity against fouling organisms by an additive or synergistic effect (Mochida and Fujii 2009a, b). 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. In some cases, cuprous oxide is replaced by cuprous thiocyanate to obtain light-colored paints (Brook and Waldock 2009). Tralopyril is used in formulations sold as copper-free antifouling paints (Janssen 2019). In addition, zinc pyrithione can be eventually found in combination with tralopyril or DCOIT, a combination that could increase the spectrum of antifouling activity against microbes, algae, and invertebrates (Arrhenius et al. 2014; Janssen 2019).

Nominal concentration of biocides in the paint formulations registered for use

The biocides reported 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 (in powder) (19.3 ± 21.0% w/w), and cuprous thiocyanate (18.1 ± 8.02% w/w) (Fig. 5). Although the average concentration of copper (in powder) was 19.3%, this active ingredient was recorded in formulations with concentrations reaching up to 66% w/w (Fig. 5). Those concentrations are

![Fig. 3 Relative frequencies (%) of biocides simultaneously used in antifouling paint formulations identified in the dataset](image-url)
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 tralopyrill, diuron, thiram, DCOIT, Irgarol, dichlofluanid, and terbutryn, 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 tolyfluanid. However, it is worth noting that other formulations available worldwide may differ from those obtained in the current data source. The antifouling paint Islands 99 Plus™ (https://www.seahawkpaints.com/product/islands-99-plus/), for instance, uses between 4 and 10% of chlorothalonil in their composition. Although manufactured in the USA, it has not been included in the EPA_PPLS database because it is offered for export only. Its use is not permitted in the USA.

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 sources, 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...
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) and 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 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. Interestingly, in APVMA zinc oxide is considered an active compound in the registered antifouling formulations, but agricultural or veterinary products containing zinc oxide are exempt from approval for its use (APVMA 2018b). The BRAF dataset includes zinc oxide because this data was gathered from the safety data sheet for each product, where it is reported as an ingredient hazardous for health and the environment. 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, EU), zinc oxide is not considered an active biocide in antifouling paints (Directive 98/8/EC of The European Parliament and of the Council 1998). This allows manufacturers not to report zinc oxide as an active substance, since it was not added with the intention of acting on or against organisms (European Parliament and of the Council 2012). However, the EU itself considered zinc oxide as very toxic to aquatic life (ECHA 2021c), and, when used in any product, it must be labeled as such in the safety data sheets.
would have been crucial to consider the relative frequency of use of these antifouling paints (and consequently their active ingredients) by countries or region to perform a more accurate study. 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 reasons, 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-GL75) and Caribbean islands (“Biotin Plus Antifouling TBT Ablative” https://www.islandwaterworld.com/biotin-plus-antifouling-tbt-ablative-black-1-gal-n13043)) 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 probably 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. 2022).

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 seem to be one of the main current sources of fresh inputs to the aquatic environment (Uc-Peraza et al. 2022). 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. 2022). In addition, this TBT-based trading market of antifouling paints is 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 is 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, nonmetallic, 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 environmental 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.
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-17662-5.

Author contribution César Augusto Paz-Villarraga, conceptualization, methodology, software, formal analysis, investigation, visualization, writing—original draft. Italo 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.

Funding The present work was sponsored by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior — CAPES (CIMAR No 1988/2014) and FINEP — Financiadora de Estudos e Projetos (Proc. No 1111/13—01.14.0141.00). Italo Braga de Castro (PQ 302713/2018–2) and Gilberto Fillmann (PQ 312341/2013–0 and 314202/2018–8) were research fellows of CNPq, and Cesar Augusto Paz-Villarraga (88882.158665/2014–01) was a PhD fellow of CAPES.

Availability of data and materials Database used in the present research is fully provided in a .csv-type file.

Declarations

Ethical approval and consent to participate 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.

Consent for publication This manuscript has not been published or presented elsewhere in part or in entirety and is not under consideration by another journal.

Competing interests The authors declare no known competing interests.

References

Abreu FEL, Lima Da Silva JN, Castro IB, Fillmann G (2020) Are antifouling residues a matter of concern in the largest South American port? J Hazard Mater 398:122937. https://doi.org/10.1016/j.ijhazm.2020.122937

Amara I, Miled W, Slama RB, Ladhari N (2018) Antifouling processes and toxicity of antifouling paints on marine environment. A Review Environ Toxicol Pharmacol 57:115–130. https://doi.org/10.1016/j.etap.2017.12.001

ANVISA (2017) Listas de ingredientes ativos com uso autorizado e banidos no Brasil. In: Agência Nacional de Vigilância Sanitária - Anvisa. https://www.gov.br/anvisa/pt-br/assuntos/noticias-anvisa/2017/listas-de-ingrediente-ativos-com-uso-autorizado-e-banidos-no-brasil. Accessed 26 May 2021

APVMA (2018a) Public chemical registration information system-PubCRIS database. In: Public Chemical Registration Information System Search. https://portal.apvma.gov.au/pubcris/p_auth=mNNID9Yv&p_p_id=pubcrisportlet WAR_pubcrisportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=3&p_p_col_count=5&pubcrisportlet WAR_pubcrisportlet_java.portlet.action=search. Accessed 25 Oct 2018

APVMA (2018b) Active constituents exempt from the requirements of APVMA approval for use in agricultural or veterinary chemical products. In: Australian Pesticides and Veterinary Medicines Authority. https://apvma.gov.au/node/4176. Accessed 1 Oct 2021

Artifon V, Castro IB, Fillmann G (2016) Spatio-temporal appraisal of TBT contamination and imposex along a tropical bay (Todos os Santos Bay, Brazil). Environ Sci Pollut Res 23:16047–16055. https://doi.org/10.1007/s11356-016-6745-7

Batista RM, Castro IB, Fillmann G (2016) Imposex and butyltin contamination still evident in Chile after TBT global ban. Sci Total Environ 566–567:446–453. https://doi.org/10.1016/j.scitotenv.2016.05.039

Batista-Andrade JA, Caldas SS, Batista RM et al (2018) From TBT to booster biocides: Levels and impacts of antifouling along coastal areas of Panama. Environ Pollut 234:243–252. https://doi.org/10.1016/j.envpol.2017.11.063

Bighiu MA, Eriksson-Wiklund A-K, Eklund B (2016) Biofouling of leisure boats as a source of metal pollution. Environ Sci Pollut Res 24:997–1006. https://doi.org/10.1007/s11356-016-7883-7

Bleile H, Rodgers SD (2001) Marine coatings. In: Buschow KHJ, Cahn RW, Flemings MC et al (eds) Encyclopaedia of Materials: Science and Technology. Elsevier, Oxford, pp 5174–5185

Bowman JC, Readman JW, Zhou JL (2003) Seasonal variability in the concentrations of Irgarol 1051 in Brighton Marina, UK; including the impact of dredging. Mar Pollut Bull 46:444–451. https://doi.org/10.1016/S0025-326X(02)00464-2

Briant N, Bancon-Montigny C, Freyder R et al (2016) Behaviour of butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue, South of France). Chemosphere 150:123–129. https://doi.org/10.1016/j.chemosphere.2016.02.022

Brooks S, Waldock M (2009) The use of copper as a biocide in marine antifouling paints. In: Heliyo C, Yebra D (eds) Advances in marine antifouling coatings and technologies. Woodhead Publishing, pp 492–521

Cai Y, Apell JN, PFlug NC et al (2021) Photochemical fate of medetomidine in coastal and marine environments. Water Res 191:116791. https://doi.org/10.1016/j.watres.2020.116791

Castro IB, Iannacone J, Santos S, Fillmann G (2018) TBT is still a matter of concern in Peru. Chemosphere 205:253–259. https://doi.org/10.1016/j.chemosphere.2018.04.097

Castro JB, Westphal E, Fillmann G (2011) Third generation antifouling paints: new biocides in the aquatic environment. Quim Nova 34:1021–1031. https://doi.org/10.1590/S0100-40422011000600020

Cavalleiro J, Sola C, Baldanza J et al (2016) Assessment of background concentrations of organometallic compounds (mercury, ethyllead and butyl- and phenyltin) in French aquatic environments. Water Res 94:32–41. https://doi.org/10.1016/j.watres.2016.02.010

Chen L, Lam JCW (2017) SeaNine 211 as antifouling biocide: a coastal pollutant of emerging concern. J Environ Sci (china) 61:68–79. https://doi.org/10.1016/j.jes.2017.03.040

Claudi R, de Oliveira MD (2015) Chemical strategies for the control of the golden mussel (Lymnoperna fortunei) in industrial facilities. In: Boltovskoy D (ed) Lymnoperna Fortunei: the ecology, distribution and control of a swiftly spreading invasive fouling mussel. Springer International Publishing, Cham, pp 417–441

Costa LDF, Mirlean N, Wasserman JC, Wallner-Kersanach M (2016) Variability of labile metals in estuarine sediments in areas under dredging. Mar Pollut Bull 46:444–451. https://doi.org/10.1016/j.marpolbul.2014.07.011

De Souza ARHENHIUS A, Backhaus T, Hilvarsson A et al (2014) A novel bioassay for evaluating the efficacy of biocides to inhibit settling and early establishment of marine biofilms. Mar Pollut Bull 87:292–299. https://doi.org/10.1016/j.marpolbul.2014.07.011

Dafforn KA, Lewis JA, Johnston EL (2011) Antifouling strategies: history and regulation, ecological impacts and mitigation. Mar
Mochida K, Fuji K (2009a) Toxicity in plankton and fish. In: Arai T, Harino H, Ohji M, Langston WJ (eds) Ecotoxicology of Antifouling Biocides. Springer Japan, Tokyo, pp 364–382
Mochida K, Fuji K (2009b) Further effects of alternative biocides on aquatic organisms. In: Arai T, Harino H, Ohji M, Langston WJ (eds) Ecotoxicology of Antifouling Biocides. Springer Japan, Tokyo, pp 383–393
Okamura H, Mieno H (2006) Present status of antifouling systems in Japan: tributyltin substitutes in Japan. In: Konstantinou IK (ed) Antifouling Paint Biocides. Springer, Berlin, Heidelberg, pp 201–212
Oliveira IB, Schönenenberger R, Barroso CM, Suter MJ-F (2016) LC-MS/MS determination of tralopyril in water samples. Chemosphere 145:445–449. https://doi.org/10.1016/j.chemosphere.2015.11.098
Oliveira IB, Groh KJ, Schönenenberger R et al (2017) Toxicity of emerging antifouling biocides to non-target freshwater organisms from three trophic levels. Aquat Toxicol 191:164–174. https://doi.org/10.1016/j.aquatox.2017.07.019
Omae I (2003) Organotin antifouling paints and their alternatives. Appl Organometal Chem 17:81–105. https://doi.org/10.1002/aoc.396
Paz-Villarraga CA, Castro IB, Miloslavich P, Fillmann G (2015) Venezuelan Caribbean Sea under the threat of TBT. Chemosphere 119:704–710. https://doi.org/10.1016/j.chemosphere.2014.07.068
Pérez MC, Stupak ME, Blustein G et al (2009) 21 - Organic alternatives to copper in the control of marine biofouling. In: Hellio C, Yebra DM, Kiil S, Dam-Johansen K (2004) Antifouling technology—past, present and future steps towards efficient and environmentally friendly antifouling coatings. Prog Org Coat 50:75–104. https://doi.org/10.1016/j.porgcoat.2003.06.001
Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.