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RESEARCH ARTICLE

Toxicity of antifouling biocides on planktonic and benthic neotropical species

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Abstract

Organotin-based (OTs: TBT and TPT) antifouling paints have been banned worldwide, but recent inputs have been detected in tropical coastal areas. However, there is a lack of studies evaluating the toxicity of both legacy and their substitute antifouling booster biocides (e.g., Irgarol and diuron) on neotropical species. Therefore, the acute toxicity of four antifouling biocides (TBT, TPT, Irgarol, and diuron) was investigated using the marine planktonic organisms *Acartia tonsa* and *Mysidopsis juniae*, the estuarine tanaid *Monokalliapseudes schubarti* (water exposure), and the burrowing amphipod *Tiburonella viscana* (spiked sediment exposure). Results confirmed the high toxicity of the OTs, especially to planktonic species, being about two orders of magnitude higher than Irgarol and diuron. Toxic effects of antifouling compounds were observed at levels currently found in tropical coastal zones, representing a threat to planktonic and benthic invertebrates. Furthermore, deterministic $PNEC_{marine\ sediment}$ values suggest that environmental hazards in tropical regions may be higher due to the higher sensitivity of tropical organisms. Since regulations on antifouling biocides are still restricted to a few countries, more ecotoxicological studies are needed to derivate environmental quality standards based on realistic scenarios. The present study brings essential contributions regarding the ecological risks of these substances in tropical and subtropical zones.

Keywords Aquatic contaminants · Ecotoxicology · Organotin · Booster biocides · Marine toxicity test · PNEC · Environmental hazard

Introduction

Antifouling paints are required as ship or boat coatings to prevent fouling adhesion and development, which are harmful to naval operations (Amara et al. 2018). However, the release of biocides from these paintings has produced chemical contamination in aquatic systems worldwide (Almeida et al. 2007). Biocides used in antifouling paints have been the target of recent environmental concerns due to their potential impacts on marine biota, reaching the community level (Gallucci et al. 2015). Studies performed in areas under the influence of harbors, marinas, and shipyards have identified and quantified the concentrations of antifouling biocides in different environmental matrices (Thomas and Brooks 2010; Abreu et al. 2020). Similarly, toxicity tests have also shown that many of these biocides may cause deleterious effects on non-target aquatic organisms, in some cases at concentration ranges detected in the environment, as reported in a review organized by Martins et al. (2018).

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Organotin-based antifouling paints such as tributyltin (TBT) and triphenyltin (TPT) were highly efficient and have been used since the 1960s. In 1999, approximately 70% of all commercial vessels in the world used these coatings. However, paints containing TBT or TPT were associated with deleterious effects on marine biota, namely imposex in marine gastropods (Titley-O'Neal et al. 2011), larvae and shell malformations ("balling") in oysters (Alzieu 2000), hormonal disruption in dolphins (Tanabe 1999), and obesogenic metabolic syndrome in fish (Meador et al. 2011). Consequently, in September 2008, the International Convention on the Control of Harmful Anti-Fouling Systems on Ships (AFS Convention) issued by the International Maritime Organization (IMO) banned the use of organotin-based antifouling paints (IMO 2021).

Despite these regulations, some TBT-based products are still being produced and traded (Turner and Glegg 2014; Uc-Peraza et al. 2022a) and recent inputs of triorganotin compounds have been detected (Eklund and Watermann 2018; Jokšas et al. 2019; Uc-Peraza et al. 2022b), mainly in tropical coastal areas of developing countries (Mattos et al. 2017; Castro et al. 2018; Sheikh et al. 2020; Abreu et al. 2020). Organotins (OTs) are persistent and hydrophobic compounds that preferentially partition onto suspended material and then sink to the bottom (Hoch and Schwesig 2004). In the sediment, these compounds remain more stable and might produce adverse effects on benthic organisms (Fang et al. 2017). Besides, the resuspension of contaminated sediments and desorption from the bottom sediments may transfer back the OTs to the water column (Formalewicz et al. 2019), resulting in exposure of pelagic organisms to these chemicals (Oliveira et al. 2020). Therefore, the peer-reviewed literature data demonstrates that OT pollution is still a critical environmental issue (Filipkowska and Kowalewska 2019; Oliveira et al. 2020; Gomes et al. 2021a, b).

Among the substitutes to the OTs, Irgarol, and diuron have been used as co-biocides in antifouling paints (Paz-Villarraga et al 2021). These biocides are used to boost the toxicity of copper and zinc-based antifouling paints (Amara et al 2018). Both Irgarol and diuron are inhibitors of photosynthesis by blocking the electron transport at the photosystem-II; therefore, they are highly toxic to autotrophic organisms (Dafforn et al. 2011). Although Irgarol and diuron are herbicides, studies also reported their adverse effects on invertebrates and fish (Amara et al. 2018). Irgarol is a triazine used as an herbicide, antimicrobial pesticide, and mainly as an antifouling biocide, whereas diuron is a phenylurea herbicide extensively used in agriculture since 1950 (Giacomazzi and Cochet 2004). These compounds have been detected in seawater and surface sediments from ship/boat traffic areas worldwide (Konstantinou and Albanis 2004; Batista-Andrade et al. 2018; Abreu et al. 2020). Consequently, the use of Irgarol and diuron in antifouling paints was regulated in Europe (Price and Readman 2013). Additionally, since January 2016, Irgarol has not been approved as an antifouling product by the EU Commission – Commission Implementing Decision (EU) 2016/107 (EC 2016).

Regarding ecotoxicological data related to OTs, Irgarol, and diuron, most studies are restricted to species from temperate zones (Martins et al. 2018; Campos et al. 2022). Moreover, despite the ecological importance of benthic species, few studies evaluated the toxicity of antifouling biocides, including OTs, in the sedimentary compartment (Abreu et al. 2021a). The present study improved the knowledge related to the toxicity of TBT, TPT, Irgarol, and diuron to estuarine and marine organisms, especially neotropical species. Accordingly, acute toxicity tests in the aqueous phase were carried out using the marine planktonic crustaceans *Acartia tonsa* and *Mysidopsis juniae*, as well as the estuarine tanaid *Monokalliapseudes schubarti*, while the spiked sediment toxicity test was performed using the burrowing marine amphipod *Tiburonella viscana*.

Materials and methods

Stock solutions and analytical procedures

Stock solutions were prepared by dissolving analytical grade OTs (tributyltin chloride and triphenyltin chloride; purity > 98%) and herbicides (Residue Analysis Pestanal standards of Irgarol; purity > 98%; and diuron; purity > 99.5%) in acetone; these stock solutions were chemically analyzed. TBT and TPT were analyzed as described by Castro et al. (2015). In brief, 100 µL of each solution was transferred to a 40-mL vial, derivatized, extracted, and cleaned up. Finally, the extracts were analyzed by gas chromatography using a Perkin Elmer Clarus 500MS. Limit of Detection (LOD) and Limit of Quantification (LOQ) were ≤ 1 and ≤ 3 ng mL^{-1}, respectively, for TBT and TPT. Similarly, Irgarol and diuron concentrations were analyzed according to Biselli et al. (2000). Briefly, 100 µL of each solution was transferred to a 2-mL vial and analyzed in an LC–ESI–MS/MS system (Waters Alliance 2695 liquid chromatography with Micromass Quattro Micro API detector with ESI Waters interface—Milford, MA, USA). LOD and LOQ were ≤ 0.2 and ≤ 0.6 ng mL^{-1}, respectively, for Irgarol and diuron.

Since previous experiments (data not shown) indicated no effects of acetone up to this level of exposure to the planktonic species *A. tonsa* and *M. juniae*, exposure solutions (in

filtered seawater, 1 µm) were prepared so that the acetone levels did not exceed 0.05%.

Acute toxicity tests (water exposure)

The concentration ranges of each antifouling biocide for each species tested were determined after preliminary experiments (unpublished data). Three experiments were performed using *A. tonsa* and two experiments using *M. juniae* and *M. schubarti* for each compound. The exposure concentration ranges, dilution factors, and the number of treatments used in each experiment are shown in the supplementary material (Table S1). The actual exposure concentrations could not be measured since confirmation samples were lost in a lab fire. Thus, they were calculated based on the chemical analysis of stock solutions.

The sensitivities of *A. tonsa*, *M. juniae*, and *M. schubarti* were evaluated using sodium dodecyl sulfate (SDS) as a reference substance to ensure the reliability of toxicity tests. Accordingly, sensitivity tests with SDS were performed during the toxicity assessment of antifouling biocides. Control charts of tested species exposed to SDS are presented in the supplementary material (Figures S1 to S3).

Acartia tonsa

The acute toxicity tests using *A. tonsa* were performed according to the International Standardization Organization (ISO 1999) protocol. Four replicates with ten laboratory-grown adult organisms were prepared for each concentration (glass flasks with 50 mL of exposure solution at salinity 30). Experiments were performed over 48 h at a constant temperature (21 °C) and light/dark cycle of 12:12 h. After the exposure period, the number of dead organisms was counted to evaluate mortality levels.

Mysidopsis juniae

Toxicity tests using *M. juniae* were performed according to the ABNT-15308 protocol (ABNT 2011). Four replicates with ten laboratory-grown juvenile organisms (seven days old) were prepared for each concentration (glass flasks with 200 mL of exposure solutions at salinity 30). Experiments were performed over 96 h at a constant temperature (25 °C) and light/dark cycle of 12:12 h. After this period, the mortality was quantified in each replicate.

Monokalliapseudes schubarti

Tanaids *M. schubarti* were collected from soft subtidal bottoms in the estuarine region of Lagoa dos Patos at the municipality of Rio Grande (Rio Grande do Sul – Brazil) (32° 09′ 23.74'' S/52° 06′ 9.7'' W). A layer of about 20 cm of sediment was collected using a shovel and then gently sieved through a 500-mm mesh. The retained material was taken to the laboratory, where individuals of *M. schubarti* were separated from the debris and acclimated under test conditions for three days.

Toxicity tests using *M. schubarti* were performed according to Zamboni and Costa (2002). Four replicates with ten adult organisms (0.7–1.0 cm) were prepared for each concentration (glass flasks with 100 mL of the test solution at salinity 15). Experiments were performed over 96 h at a constant temperature (25 °C) and light/dark cycle of 12:12 h. After 96 h, the number of dead organisms was counted.

Acute toxicity tests with spiked sediment

Sediment and the amphipods *Tiburonella viscana* used in the acute toxicity tests were collected in the Engenho D'Água beach, Ilhabela (São Paulo – Brazil) (23° 47′ 30.59'' S/45° 21′ 50.76'' W). Sediment was sieved (500 µm mesh) using filtered seawater, allowed to decant for 12 h, and then the supernatant seawater was removed by siphoning. Subsequently, sediment was characterized by determining the percentage of moisture, grain size, and total organic matter and carbonate contents.

Amphipods were collected by using a manual dredge. The organisms were transported to a laboratory and acclimated under the test conditions for 4 days. Sensitivity tests with the reference substance SDS were performed with each batch of amphipods collected. Figure S4 (supplementary material) presents the control chart of *T. viscana* exposed to SDS, carried out during toxicity assessment of antifouling biocides.

Sediment characterization

The sediment moisture content was measured gravimetrically by weighing three sub-samples of approximately 10 g of sediment before and after the material was dried at 60 °C for 48 h (ASTM 2008). Moisture content was determined to calculate the amount of chemical spiked on a dry-weight basis. The sediment grain size was determined according to Gray and Elliott (2009); the classification method was based on the scale established by Wentworth (1922). Calcium carbonate ($CaCO_3$) content was determined by digestion with hydrochloric acid (HCl), followed by gravimetry (Gross 1971). Organic matter content was measured in decarbonated sediment, using the loss of weight on ignition method, described by Luczak et al. (1997).

Sediment spiking procedure

The spiking procedure was based on the slurry spiking method (with adaptations) following the Standard Guide E 1391–03 (ASTM 2008). For each exposure

concentration, biocides aqueous solutions were prepared from the stock solutions in seawater filtered by cellulose acetate membranes (0.45 µm). Aqueous biocides solutions (50 mL) were added to 500 g of sediments to obtain nominal concentrations (dry weight basis), considering the sediment moisture content. The spiked sediments were then homogenized (mixed manually) for 30 min using a glass rod. Test chambers were covered and maintained in a darkroom at a controlled temperature (20 °C) for 24 h to equilibrate. The choice of this equilibration time was based on literature considering the characteristics of compounds (ASTM 2008; Langston and Pope 1995). Accordingly, in spiking procedures using organic compounds with octanol–water partition coefficients (Kow) < 6, the equilibration times can be as short as 24 h (DeWitt et al. 1992). Subsequently, 200 mL of spiked sediments was placed in 1-L beakers (3 replicates for each exposure level) and then carefully covered with 600 mL of seawater (salinity 34) filtered by cellulose acetate membranes (0.45 µm). Sediment exposure chambers were allowed to settle fine particles for 12 h before the introduction of amphipods. During these steps, all chambers were maintained at 20 °C and dark conditions to prevent the photodegradation of biocides. Negative control (biocide-free) sediment received a 50-mL aliquot of biocide-free filtered water, and a solvent control with acetone 0.05% was also prepared. The sediments of both control groups were submitted to the same steps of the biocide treatments. The actual concentrations of spiked sediments could not be measured since confirmation samples were lost in a lab fire. Thus, exposure concentrations were calculated based on the chemical analysis of stock solutions.

Acute toxicity test using Tiburonella viscana

The exposure bioassay was performed according to ABNT-15638 (ABNT 2015), which evaluates the mortality of organisms exposed to the sediment. Tree replicates with ten adult organisms (> 0.5 mm) were used in each treatment group. Experiments were performed at 25 ± 2 °C under constant aeration and light for ten days. Temperature, dissolved oxygen, and pH were measured at the start and end of the test at all treatments, and salinity (34) was adjusted daily during the 10-day test period. Two experiments were performed using *T. viscana* in spiked sediment with each compound. The dilution factors and the number of treatments used in each experiment are shown in Table S2 (supplementary material). After 10 days, sediments were sieved (0.5 mm) to separate the amphipods, which were observed at the stereomicroscope to evaluate mortality levels. Missing organisms were considered dead.

Data analysis

Nominal concentrations of biocides were used to estimate the LC_{50} values (concentration that is expected to be lethal to 50% of organisms under the specified exposure period) and their respective 95% confidence intervals. These values were obtained by Probit parametric method (Abou-Setta et al. 1986) or Trimmed Spearman-Karber nonparametric method (Hamilton et al. 1977). Results were expressed as 48 h-LC_{50} for *A. tonsa*, 96 h-LC_{50} for *M. juniae* and *M. schubarti*, and 10d-LC_{50} for *T. viscana*. The LC_{50} values of different biocides calculated for the same test species were considered statistically different when their 95% confidence intervals did not overlap. However, when confidence intervals presented overlapping, significant differences between LC_{50}s were tested by Litchfield-Wilcoxon method (Environment Canada 2007). The global concentration–response curves of each antifouling biocide and test species were obtained by non-linear regression based on Hill's model using Regtox macro for Microsoft Excel freely available at https://www.normalesup.org/~vindimian/en_index.html. Data for each experiment were adjusted for mortality of the respective controls using Abbott's correction (Abbott 1925).

Results and discussion

Stock solutions

The concentrations of the stock solutions of each biocide were quantified as follows: 1105 ± 21.9 mg L^{-1} (TBT); 1477 ± 28.3 mg L^{-1} (TPT); 5324 ± 19 mg L^{-1} (Irgarol); and 3596 ± 17 mg L^{-1}. Details of these results are presented in the supplementary material (Table S3).

Acute toxicity of waterborne antifouling biocides

Results confirmed the high toxicity of the OTs, especially to planktonic species (Table 1). Although toxicity levels were different considering the evaluated species, TBT and TPT were about two orders of magnitude more toxic than Irgarol and diuron. In general, TBT presented the lowest LC_{50} values for species tested in the aqueous phase. Despite most OTs LC_{50} values presenting overlap in the 95% confidence intervals within the same chemical class, TPT LC_{50} values were considered significantly different from TBT LC_{50} for *A. tonsa* (Table 2).

Regarding the booster biocides, Irgarol seemed to be more toxic than diuron (based on the individual LC_{50} values). However, LC_{50}s were not significantly different since Irgarol and diuron 95% confidence intervals overlapped in all the experiments using *A. tonsa*. For *M. juniae*, diuron

Table 1 LC_{50} values and corresponding 95% confidence intervals (95% CI) estimated for *Acartia tonsa* ($n=3$ experiments), *Misidopsis juniae* ($n=2$), *Monokalliapseudes schubarti* ($n=2$), and *Tiburonella viscana* ($n=2$) exposed to TBT, TPT, Irgarol, and diuron. Geometric means (GeoMean) ± standard deviations (SD) are also presented

	Waterborne antifouling biocides							
Species	TBT (μg L^{-1})		TPT (μg L^{-1})		Irgarol (μg L^{-1})		Diuron (μg L^{-1})	
	LC_{50} (95% CI)	GeoMean ± SD	LC_{50} (95% CI)	GeoMean ± SD	LC_{50} (95% CI)	GeoMean ± SD	LC_{50} (95% CI)	GeoMean ± SD
A. *tonsa*	1.49 (0.83–2.20)		2.52 (2.01–3.17)		651 (377–1124)		1099 (614–1965)	
	1.5 (0.92–2.09)		3.648 (1.97–5.56)		828 (626–1095)		1258 (718–2202)	
	1.56 (1.35–1.81)	1.52 ± 0.04	3.018 (1.87–4.42)	3.03 ± 0.57	868 (508–1484)	776 ± 115	1023 (200–5227)	1122 ± 120
M. *juniae*	1.77 (1.31–2.41)		3.57 (2.86–4.46)		332 (251–439)		609 (481–771)	
	1.89 (1.51–2.19)	1.83 ± 0.08	4.04 (3.09–5.27)	3.80 ± 0.33	350 (267–430)	341 ± 12.7	553 (340–901)	580 ± 39.6
M. *schubarti*	12.7 (8.74–18.44)		15.1 (10.3–22.2)		4129 (3243–5257)		10,707 (8339–12,111)	
	11.9 (10.34–13.79)	12.3 ± 0.53	16.1 (14.2–18.3)	15.6 ± 0.7	5065 (2371–8022)	4573 ± 662	8522 (6210–10,505)	9552 ± 1545
	Spiked sediment antifouling biocides							
	TBT (μg kg^{-1})		TPT (μg kg^{-1})		Irgarol (μg kg^{-1})		Diuron (μg kg^{-1})	
	LC_{50} (95% CI)	GeoMean ± SD	LC_{50} (95% CI)	GeoMean ± SD	LC50 (95% CI)	GeoMean ± SD	LC50 (95% CI)	GeoMean ± SD
T. *viscana*	0.121 (0.012–0.490)		0.101 (0.021–0.274)		54.2 (6.69–152)		464 (173–1239)	
	0.123 (0.017–0.437)	0.122 ± 0.002	0.120 (0.010–0.577)	0.110 ± 0.014	74.2 (18.3–301)	63.4 ± 14.1	522 (218–1252)	492 ± 41

Table 2 Results comparing LC_{50}s within the same chemical class with overlapping 95% confidence intervals (CI) for a given species. LC_{50} values were considered significantly different when the LC_{50} ratio (greater LC_{50}/lesser LC_{50}) exceeded the value for $f_{1.2}$ (Environment Canada 2007)

Species	Organotins						Booster biocides					
	Comparasion		95% CI Overlapping	$f_{1.2}$	LC_{50} ratio	Significant difference	Comparasion		95% CI Overlapping	$f_{1.2}$	LC_{50} ratio	Significant difference
	TBT	TPT					Irgarol	Diuron				
A. tonsa	LC_{50}[1]	LC_{50}[1]	Yes	1.58	1.69	Yes	LC_{50}[1]	LC_{50}[1]	Yes	2.22	1.69	No
	LC_{50}[1]	LC_{50}[2]	Yes	1.78	2.45	Yes	LC_{50}[1]	LC_{50}[2]	Yes	2.19	1.93	No
	LC_{50}[1]	LC_{50}[3]	Yes	1.50	2.03	Yes	LC_{50}[1]	LC_{50}[3]	Yes	5.59	1.57	No
	LC_{50}[2]	LC_{50}[1]	Yes	1.50	1.68	Yes	LC_{50}[2]	LC_{50}[1]	Yes	1.91	1.33	No
	LC_{50}[2]	LC_{50}[2]	Yes	1.71	2.44	Yes	LC_{50}[2]	LC_{50}[2]	Yes	1.87	1.52	No
	LC_{50}[2]	LC_{50}[3]	Yes	1.66	2.02	Yes	LC_{50}[2]	LC_{50}[3]	Yes	5.23	1.24	No
	LC_{50}[3]	LC_{50}[1]	No	-	-	Yes	LC_{50}[3]	LC_{50}[1]	Yes	2.21	1.27	No
	LC_{50}[3]	LC_{50}[2]	No	-	-	Yes	LC_{50}[3]	LC_{50}[2]	Yes	2.17	1.45	No
	LC_{50}[3]	LC_{50}[3]	No	-	-	Yes	LC_{50}[3]	LC_{50}[3]	Yes	5.57	1.18	No
M. juniae	LC_{50}[1]	LC_{50}[1]	No	-	-	Yes	LC_{50}[1]	LC_{50}[1]	No	-	-	Yes
	LC_{50}[1]	LC_{50}[2]	No	-	-	Yes	LC_{50}[1]	LC_{50}[2]	Yes	1.75	1.66	No
	LC_{50}[2]	LC_{50}[1]	No	-	-	Yes	LC_{50}[2]	LC_{50}[1]	No	-	-	Yes
	LC_{50}[2]	LC_{50}[2]	No	-	-	Yes	LC_{50}[2]	LC_{50}[2]	Yes	1.70	1.58	No
M. schubarti	LC_{50}[1]	LC_{50}[1]	Yes	1.71	1.19	No	LC_{50}[1]	LC_{50}[1]	No	-	-	Yes
	LC_{50}[1]	LC_{50}[2]	Yes	1.48	1.27	No	LC_{50}[1]	LC_{50}[2]	Yes	1.38	2.06	Yes
	LC_{50}[2]	LC_{50}[1]	Yes	1.51	1.27	No	LC_{50}[2]	LC_{50}[1]	No	-	-	Yes
	LC_{50}[2]	LC_{50}[2]	No	-	-	Yes	LC_{50}[2]	LC_{50}[2]	Yes	1.66	1.68	Yes
T. viscana	LC_{50}[1]	LC_{50}[1]	Yes	5.56	1.20	No	LC_{50}[1]	LC_{50}[1]	No	-	-	Yes
	LC_{50}[1]	LC_{50}[2]	Yes	5.01	1.22	No	LC_{50}[1]	LC_{50}[2]	No	-	-	Yes
	LC_{50}[2]	LC_{50}[1]	Yes	8.17	1.01	No	LC_{50}[2]	LC_{50}[1]	Yes	5.54	6.25	Yes
	LC_{50}[2]	LC_{50}[2]	Yes	7.52	1.03	No	LC_{50}[2]	LC_{50}[2]	Yes	5.21	7.05	Yes

$f_{1.2} = \text{antilog } \sqrt{[(\log f_1)^2 + (\log f_2)^2]}$

Where: f_1 = upper 95% CI of $LC_{50}[\#_1])/(LC_{50}[\#_1])$. f_2 = upper 95% CI of $LC_{50}[\#_2])/(LC_{50}[\#_2])$. #, experiment number

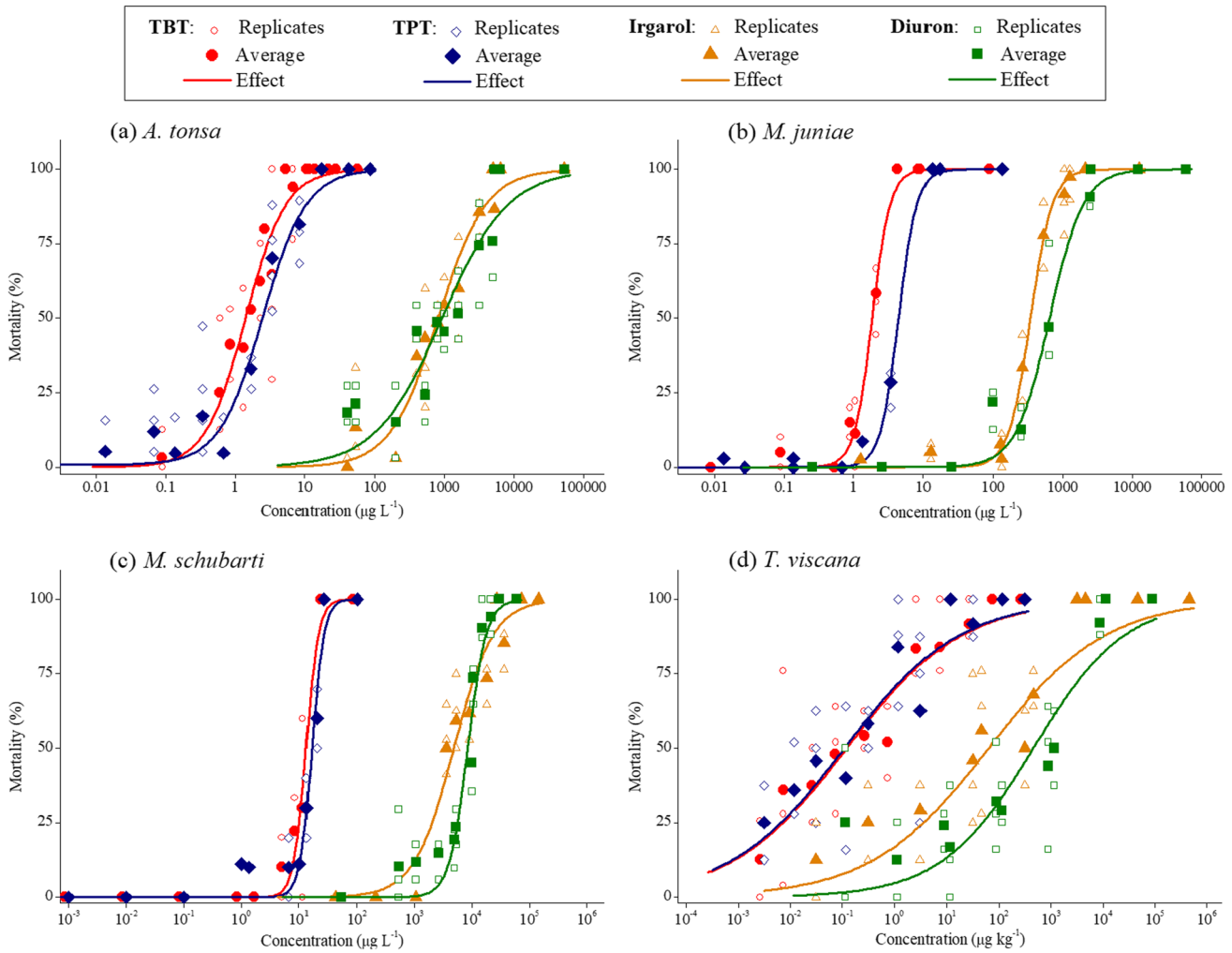

Fig. 1 Concentration–response curves for *A. tonsa* (**a**), *M. juniae* (**b**), *M. schubarti* (**c**), and *T. viscana* (**d**) exposed to TBT, TPT, Irgarol, and Diuron

LC_{50} of experiment #2 overlapped between 95% confidence intervals of Irgarol LC_{50}s, resulting in a non-significant difference. On the contrary, for *M. schubarti*, LC_{50}s of diuron and Irgarol were considered significantly different despite overlapping confidence intervals (Table 2).

For each tested species, concentration–response curves were similar between TBT and TPT, but different patterns were identified between Irgarol and diuron (Fig. 1). At the highest concentrations, the copepod mortality increased at shorter concentration intervals of Irgarol than of diuron (Fig. 1a). Accordingly, diuron effect on *A. tonsa* started at lower concentrations and was less intense between concentrations (lower slope of the line in Fig. 1a). According to Rand et al. (1995), the smaller slope in the concentration–response curve, as observed for diuron, may represent deficient absorption of the substance by the organism. Interestingly, the effects of Irgarol and diuron intersect close to LC_{50} values (slightly before 50% mortality, Fig. 1a), which leads to an assumption that toxicities of both biocides are similar for *A. tonsa* if based only on this endpoint. For *M. juniae*, the effect of Irgarol starts at lower concentrations, and the concentration–response curve presented a higher slope (Fig. 1b), indicating more effective toxicity (Rand et al. 1995). However, no intersections between curves were observed at concentrations with an effect below 100%. For *M. schubarti*, the Irgarol concentration–response curve presented a smaller slope, intersecting the diuron curve close to 75% of tanaid mortality (Fig. 1c).

Differences between concentration–response patterns observed to Irgarol and diuron suggest distinct modes of action, which are well-known only for photosynthetic organisms (Hall et al. 1999; Ranke and Jastorff 2000;

Table 3 LC_{50} values and corresponding 95% confidence intervals (95% CI) reported to copepods and mysids

Taxa	Species	Life stage	Salinity	T(°C)	Test duration	LC_{50} (95% CI); μg L^{-1}			
						TBT	Irgarol	Diuron	Reference
Copepoda	*Acartia tonsa*	Adult	sw	20	72 h	2.1 (1.4–3.0)			U'ren (1983)
		Adult	sw	20	96 h	1.0 (0.8–1.2)			U'ren (1983)
		Adult	10	20	48 h	1.1 (0.7–2.2)			Bushong et al. (1988)
		Adult	18	17.5	48 h	0.47 (0.37–0.61)			Kusk and Petersen (1997)
		Adult	28	17.5	48 h	0.24 (0.19–0.33)			Kusk and Petersen (1997)
		Adult	30	21	48 h	1.52 (±0.11)*$^{n=3}$	776 (±115)*$^{n=3}$	1122 (±120)*$^{n=3}$	Present study
	Eurytemora affins	Adult	10	20	48 h	2.2 (0.20–7.3)			Hall et al. (1988)
		Adult	10	20	48 h	2.5 (1.7–3.9)			Bushong et al. (1988)
	Nitokra spinipes	Adult	7	22	96 h	13 (10–17)	4500 (3400–6900)	4000 (3300–5200)	Karlsson et al. (2006)
	Tigriopus japonicus	Juvenile	35	25	96 h	0.15 (NR)			Kwok and Leung (2005)
		Adult	sw	20	96 h	50 (29–108)			Lee et al. (2007)
		Adult	33	25	96 h	18 (17–20)	2400 (1700–3400)	11,000 (10,500–11,400)	Bao et al. (2011)
		Adult	33	25	96 h		1800 (1600–2100)		Bao et al. (2013)
Mysidacea	*Acanthomysis sculpta*	Juvenile	sw	18	96 h	0.42 (NR)			Davidson et al. (1986)
	Americamysis bahia	Juvenile	19–22	25	96 h	2.0 (1.4–2.6)			Goodman et al. (1988)
		Juvenile	NR	NR	96 h		400 (340–470)	1100 (970–1300)	USEPA (2000)
		Juvenile	sw	NR	96 h		400 (NR)		Hall et al. (1999)
	Metamysidopsis elongata	Juvenile	33–34	13–14	96 h	1.95 (NR)			Salazar and Salazar (1989)
		Adult	33–34	13–14	96 h	2.43 (NR)			Salazar and Salazar (1989)
	Mysidopsis juniae	Juvenile	30	25	96 h	1.83 (±0.09)*$^{n=2}$	341 (±12.6)*$^{n=2}$	581 (±39.3)*$^{n=2}$	Present study

NR, not reported; *sw*, reported as saltwater

*Geometric mean (± standard deviation) of results from *n* tests

Fernández-Alba et al. 2002). However, information about the effects of Irgarol and diuron on more complex cellular systems is scarce. Responses related to the intensity of effects, and consequently, evidence of possible differences in modes of action was reported in a previous study using marine invertebrates. Perina et al. (2011) reported similar NOEC, LOEC, and EC_{50} for embryos of *Lytechinus variegatus* exposed to Irgarol and diuron but observed discrepancies in embryonic development and distinct types of larval anomalies at equivalent concentrations. Such differences were attributed to specific modes of action of each biocide, evidenced in the most sensitive early-life stages of sea urchins. Nevertheless, the mechanism of action was not explained, which requires further studies.

Acute toxicities of TBT, Irgarol, and diuron were also tested on copepods and mysids from all over the world (Table 3). LC_{50} values of TBT estimated in the present study for the cosmopolitan copepod *A. tonsa* were consistent with those reported in the literature, but this species was more sensitive than other copepods. Regarding the booster biocides, *A. tonsa* was also more sensitive

than other copepods species. LC_{50} values of TBT and Irgarol estimated for *M. juniae* were, in general, comparable to those observed for mysids of temperate zones. However, *M. juniae* was more sensitive to diuron than other mysids cited in the literature (Table 3).

Acute toxicity of spiked sediment antifouling biocides

The characterization of the sediment used in the experiments indicated the following: Sediment texture—3.7% medium sand, 29.2% fine sand, 48.5% very fine sand, and 18.4% silt/clay; 7.23% of total $CaCO_3$, and 0.8% of organic matter. Physicochemical parameters did not show significant variations during the experiment, remaining within the acceptable levels for assays with *T. viscana*: pH > 7.7, salinity between 33 and 36, dissolved oxygen > 6 mg L^{-1}, ammonia content < 10 mg L^{-1}, and temperature at 25 ± 2 °C (ABNT 2015).

In the spiked sediment toxicity tests using *T. viscana*, the 10d-LC_{50} values of TBT were slightly higher than TPT (Table 1 and Fig. 1d). However, the estimated values were not considered significantly different between both compounds (Table 2). For the booster biocides, although the result of experiment #2 overlaps the diuron LC_{50}s confidence intervals, 10d-LC_{50} values of Irgarol were about an order of magnitude higher than diuron (Table 1) and were considered significantly different (Table 2). The concentration–response curves presented a similar pattern between the compounds of the same chemical class (Fig. 1d). Therefore, distinct modes of action may not be evidenced only by graphical analysis.

A possible explanation for the different magnitude of LC_{50} values compared with water exposure experiments may be related to the availability of each compound in the interstitial water. In this sense, differences in the toxicity of the tested antifoulants would be explained by their distribution between sediment solid and aqueous phases. These compounds tend to be adsorbed onto the sediment particles and the organic carbon/water partition coefficients (K_{oc}) are helpful to understand their distribution (Artifon et al. 2019). K_{oc} (usually expressed as Log K_{oc}) indicates the sorption of organic compounds on OC associated with sediments. In the present study, organic matter (OM) determined in the sediment was 0.8%, measured by mass loss on ignition (LOI). Since LOI is a semi-quantitative method for OM determination, a conversion factor is necessary to estimate the OC content (Schumacher 2002). Considering that about 50% of the organic matter (determined by LOI) is composed of carbon (Dean 1999), the total OM can be divided roughly by 2, giving 0.4% of OC content in the sediment used in the present study.

These subtle differences between the toxicity of OTs in the sediments (TPT ≥ TBT) compared to aqueous experiments (TBT > TPT) may be due to the lower affinity of TPT to the solid phase. The lower Log K_{oc} of TPT (estimated value = 3.53) compared to TBT (estimated value = 4.5) may lead to a slightly higher bioavailability of TPT even at low concentrations. Indeed, a previous study indicated that TPT

Table 4 Concentrations of organotins and booster biocides in environmental samples of water (μg L^{-1}) reported in the last decade

Localities	TBT*	TPT*	Irgarol	Diuron	Reference
Africa					
Tanzania (Zanzibar harbor)	0.001–0.002				Sheikh et al. (2020)
Algeria (harbor areas)	0.03–1.16				El Hadj et al. (2016)
Nigeria (Lagos harbor)	< 0.04–1.5	< 0.04–0.7			Basheeru et al. (2020)
Americas					
Argentina (Bahía Blanca estuary)	0.052– 0.944				Quintas et al. (2019)
Brazil (Itaqui Harbor)			0.02–4.80	0.05–7.80	Diniz et al. (2014)
USA (Southern California marinas)			0.002–0.254	< 0.002–0.068	Sapozhnikova et al. (2013)
Asia					
Malaysia (harbor areas)			< 0.001–2.021	< 0.0005–0.285	Ali et al. (2021)
Japan (Tanabe bay)	0.004–0.028	0.003—0.0075	< 0.0001–0.002	< 0.0001–0.027	Harino and Yamato (2021)
South Korea (Gwangyang and Busan bays)	< 0.002–0.025	< 0.003–0.009	< 0.0001–0.0021	0.0003–0.0962	Lam et al. (2017)
Europe					
Italy (Gulf of La Spezia)			< 0.001–0.028	< 0.0002–0.0097	Ansanelli et al. (2017)
Italy (Gulf of Napoli)			0.001 –0.135	0.0016–0.0348	Ansanelli et al. (2017)
Finland (dockyard area)	0.023–0.75	0.085–1.4			Haaksi and Gustafsson (2016)

*Concentrations converted from ng Sn L^{-1} to μg L^{-1} using the conversion factor of 2.44 and 2.95 for TBT and TPT, respectively

Table 5 Concentrations of organotins and booster biocides in environmental samples of sediment (μg kg^{-1}, dry weight) reported in the last decade

Localities	TBT*	TPT*	Irgarol	Diuron	Reference
Africa					
Nigeria (Lagos harbor)	0.002–7.11	0.006–2.33			Basheeru et al. (2020)
Tunisia (El Kantaoui marina)	14.9	0.89			Anastasiou et al. (2016)
Americas					
USA (Southern California marinas)			< 0.3–8.9	< 0.3–4.2	Sapozhnikova et al. (2013)
Panama	< 2.4–364				Batista-Andrade et al. (2018)
Peru (Callao harbor)	127–417				Castro et al. (2018)
Chile (Northern Chilean coast)	221–1470				Mattos et al. (2017)
Venezuela (Caribbean coast)	139–4707				Paz-Villarraga et al. (2015)
Argentina (Puerto Madrin)	< 2.4–427				Del Brio et al. (2016)
Argentina (Patagonian coast)	< 2.4–85				Commendatore et al. (2015)
Brazil (northeastern coast)	< 2–827				Maciel et al. (2018)
Brazil (Santos Estuarine System)	< 1.2–1679		< 0.5	< 0.5–9.9	Abreu et al. (2020)
Brazil (Vitoria Estuarine System)	< 2.4–51.5		< 0.4–1.4	< 0.5–2.7	Abreu et al. (2021b)
Asia					
Japan (Tanabe bay)	3.1–24	2.3–37	< 0.1	8.2–9.3	Harino and Yamato (2021)
South Korea (Gwangyang and Busan bays)	< 0.24–5622	< 0.3–202.1	< 0.02–7.79	< 0.06–144	Lam et al. (2017)
South Korea (Gunsan shipyard areas)				< 3.5–236.2	Lee and Lee (2017)
Malaysia (Sungai Pulai estuary)	8.1–10.6	17.1–19.4	< 0.1–22.9	< 0.1–1.4	Mukhtar et al. (2019)
Saudi Arabia (Jubail harbour)	< 0.02	35.4			Hassan et al. (2019)
China (South Hangzhou bay)	< 0.5–42.5	< 0.5–17.4			Chen et al. (2019a)
China (Yangtze estuary)	< 0.5–25.6	< 0.5–30.7			Chen et al. (2019b)
Europe					
Malta (Valletta Grand harbor)	8–5654				Romeo et al. (2015)
Italy (Acciaroli marina)	227–1117				Lofrano et al. (2016)
Italy (Port of Cagliari)	182	2.20			Anastasiou et al. (2016)
Portugal (Ria Formosa lagoon)	4.4–6.3	0.98			Anastasiou et al. (2016)
Portugal (Lima estuary)	< 0.0005–0.859				Laranjeiro et al. (2018)

*Concentrations converted from ng Sn g^{-1} to μg kg^{-1} using the conversion factor of 2.44 and 2.95 for TBT and TPT, respectively

has higher mobility at the solid/liquid interface (Marcic et al. 2006), thus it could be desorbed more easily than TBT. In this sense, the similar toxicity between OTs is possibly due to exposure pathways involving the dissolved phase (dermal contact) and the solid phase (ingestion, dermal contact).

The partitioning of booster biocides between aquatic compartments is influenced by sediment characteristics and environmental factors, which has important implications on bioavailability. In the present study, pH probably did not affect the sorption processes to the inorganic particles since Irgarol and diuron do not present significant variations in the adsorption rates at pH 8 (Voulvoulis et al. 2002). However, calculations using modeled estimations indicated that around 4% of Irgarol in the marine environment would partition into sediments (Rogers et al. 1996). Furthermore, the relatively lower affinity of diuron to sediment (estimated Log $K_{oc} = 2.4$) favors partitioning into the interstitial water compared to Irgarol (estimated Log $K_{oc} = 3.3$). However, the sorption equilibrium of the booster biocides is also strongly influenced by the concentrations (Fernandez-Parez et al. 2000), which could explain the observed dose-dependent responses (Fig. 1d).

Although the actual concentrations of spiked sediments could not be measured, it is essential to highlight that amphipods were exposed to the whole sediment, including both the aqueous (i.e. porewater) and the solid phase. In such conditions, the uptake of the biocides via interstitial water may have been the most critical exposure route for *T. viscana*. Gallucci et al. (2015) pointed out that interstitial water was the primary exposure pathway for meiobenthic organisms to booster biocides, especially Irgarol. In a microcosms study with spiked sediments, these authors reported that nematodes with more permeable cuticles were more affected by Irgarol. In this sense, the experimental procedure appears to have been efficient since the effects observed on the amphipods indicate a concentration–response relationship.

Nevertheless, experiments with spiked sediments using closer intervals between concentrations (e.g., dilution factor of 2) are needed to more clearly determine responses.

Sensitivity of the neotropical species to environmental levels and regulations of antifouling biocides

OTs and booster biocides levels have been reported in seawater and sediment samples of coastal zones worldwide in the last decade (Tables 4 and 5). However, many countries lack regulations addressing the issue of antifouling biocides in natural environments, especially in developing countries of tropical zones. In Latin America, for instance, the AFS Convention was fully implemented only by Brazil, Chile, Panama, Peru, Mexico, and Uruguay (IMO 2021) and there are no legislations for booster biocides. Despite the efforts of the IMO banning the use of TBT-based antifouling paints (September 2008), and the Rotterdam Convention (RC) to forbid the trade of tributyltin (TBT) (www.pops.int), TBT-based paints are still being manufactured and sold (Uc-Peraza et al 2022a). As a consequence, effects have recently been observed around the world, such as in Europe (Laranjeiro et al. 2018; Gomes et al. 2021b), Africa (Van Gessellen et al. 2018), Asia (Mukhtar et al. 2020), and Latin America (Rodríguez-Grimon et al. 2020; Uc-Peraza et al. 2022b), indicating that these compounds still represent a hazard for marine biota. Considering the LC_{50} and corresponding 95% confidence intervals obtained in the present study, current environmental concentrations of OTs may induce lethal effects on marine invertebrates.

Hence, establishing regulatory strategies to reduce environmental contamination by antifouling biocides in tropical coastal areas must be done based on sound science. To achieve that, environmental risk assessment (ERA) is an indispensable tool to estimate the risks of antifoulants, considering both the exposure scenario and the hazard to marine biota. Therefore, ERA should be addressed to support environmental management decisions and regulate these compounds in developing countries of tropical zones, especially the Group of Latin America and the Caribbean (GRULAC) region.

An ERA is a process that evaluates the probability that adverse effects may occur due to exposure to stressors. The EU Technical Guidance Document on Risk Assessment (EC 2003) indicates that the predicted no-effect concentration (PNEC) is a fundamental reference safety value used to protect the biota of an ecosystem and is an essential tool for managing toxic chemicals. Some ERA may provide accurate probabilistic estimates of the adverse effect, and others may be deterministic.

The probabilistic PNEC is based on the species sensitivity distribution (SSD) method and requires a minimum of 8 taxonomic groups, which is calculated through the quotient between the HC_5 value (5% hazardous concentration) and an assessment factor ranging from 1 to 5 (EC 2003). When information on the compound's toxicity is limited (e.g., few species), a deterministic $PNEC_{seawater}$ can be calculated considering assessment factors (AFs), which can range from 10 to 10,000 and are applied on the lowest L/EC_{50}s, L/EC_{10}s or NOECs, depending on the information available (EC 2003). In the case of acute tests with seawater species from a single trophic level, an AF = 1000 is recommended, based on the high uncertainty due to data limitation. For the present data, such "preliminary" $PNEC_{seawater}$ for the tropical environment would be 0.00152 μg L^{-1} for TBT, 0.00303 μg L^{-1} for TPT, 0.341 μg L^{-1} for Irgarol, and 0.580 μg L^{-1} for diuron. For Irgarol and diuron, these PNECs are higher than the probabilistic $PNEC_{seawater}$ proposed in recent review papers, which were 0.0014 μg L^{-1} for Irgarol (Martins et al. 2018) and 0.25 μg L^{-1} for diuron (Campos et al. 2022). Most of the published antifouling biocides environmental monitoring studies have been carried out in the temperate zone using photosynthetic organisms, mainly distributed in the Mediterranean and Northeastern Atlantic (Campos et al. 2022), which may bias the estimation of environmental risks in tropical regions. Hence, further toxicity tests using photosynthetic and other trophic levels of neotropical species would provide information for a hazard assessment and determination of site-specific ERA based on more realistic scenarios.

In the marine environment, the half-life of OTs varies from 7 to 19 days in the water column (Harino et al. 2009; Langston et al. 2009). However, they adsorb onto suspended material and sink into the bottom sediments, where OTs degradation rates are lower, with a half-life ranging from years to decades (Furdek et al. 2016). Thus, such compounds accumulate in sediments and reach concentrations capable of causing toxicity to the biota (Soroldoni et al. 2018). Recent studies have reported OT levels in sediments within the range to cause lethality to *T. viscana*, especially in ports and marinas of Latin America (Table 5).

Irgarol does not degrade quickly in the marine environment, with a half-life between 100 and 350 days in seawater (Thomas et al. 2002) and between 100 and 200 days in sediment (Dafforn et al. 2011). Diuron also persists in seawater (half-life of 180 days) and adsorbs onto suspended material (Okamura et al. 2003) but is less persistent in marine sediments (half-life of 14 days) (Thomas et al. 2002). Furthermore, Irgarol and diuron inputs can also result from their use as an herbicide in crops (Giacomazzi and Cochet 2004). In the last decade, levels of booster biocides in sediments have been found at levels significantly relevant to produce adverse effects on *T. viscana* (Table 5). Although less common, concentrations of Irgarol and diuron were recently reported at values within the range

which produce lethality, considering the 95% confidence interval of LC_{50} values obtained for the studied species.

A deterministic approach to derive the PNEC is often applied to contaminants characterized by a lack of toxicity information (Gredelj et al. 2018), which is the case of sediment data. As previously mentioned, the AFs vary depending on the uncertainty and quality of the databases, ranging from 10 to 10,000 for deriving PNEC for seawater and marine sediments. In this sense, considering the LC_{50}s obtained for *T. viscana* and an AF = 10,000 (one acute toxicity test only; see EC 2003), preliminary $PNEC_{marine\ sediment}$ would be 0.0000122 μg kg^{-1} for TBT, 0.000011 μg kg^{-1} for TPT, 0.00634 μg kg^{-1} for Irgarol, and 0.0492 μg kg^{-1} for diuron. Abreu et al. (2021a) reported a deterministic $PNEC_{sediment}$ of 0.15 μg kg^{-1} for diuron, based mainly on toxicity tests for a single trophic level (producers), and taxonomic group (microalgae), extrapolated from tests with freshwater organisms. These authors estimated a deterministic $PNEC_{sediment}$ of 16 μg kg^{-1} for Irgarol, based on toxicity tests using amphipods of Northeastern Atlantic and freshwater organisms. Our results, despite limited, indicate lower PNECs for neotropical species, suggesting that environmental risks in tropical regions may be higher, due to the elevated sensitivity of tropical organisms. Anyway, further studies should be done to produce information to allow the estimation of more reliable environmental risks of antifouling biocides in neotropical regions.

To estimate reliable PNEC, the EC (2003) recommends a minimum of the toxicity values from three different trophic levels, represented by producers, primary consumers, and secondary consumers. Furthermore, according to Sorgog and Kamo (2019), risk assessments with a higher degree of accuracy can be expected with the SSD method. Thus, whenever possible, probabilistic PNEC is recommended and commonly used in environmental risk assessment frameworks (Gredelj et al. 2018; Figueiredo et al. 2020). Therefore, in addition to the data provided by the present paper, further ecotoxicological studies are necessary to better estimate probabilistic PNEC values. Moreover, chronic toxicity tests using representative neotropical species of different trophic levels are required to increase reliable datasets for such compounds, bringing essential contributions to the refinement of risk assessments.

Conclusion

The acute toxicity tests with neotropical estuarine and marine invertebrates ranked the toxicity of antifouling biocides as TBT > TPT > > Irgarol ≥ diuron for planktonic species, TBT ≥ TPT > > Irgarol > diuron for the benthic tanaid in aqueous exposure, and TPT ≥ TBT > > Irgarol > diuron for the burrowing amphipod in spiked sediments exposure. Lethal effects of OTs were observed at concentrations currently found in coastal waters, implying that these compounds are still a threat to pelagic biota. On the other hand, reported water levels of booster biocides are not enough to cause acute toxicity in the tested organisms. Regarding sediments, current environmental levels of antifouling biocides pose risks to natural populations and may cause biota damage. In addition, deterministic $PNEC_{marine\ sediment}$ values based on acute toxicity data suggest higher environmental hazards of these biocides in tropical regions. Furthermore, ecotoxicological data could integrate datasets to derive site-specific PNECs for the tropical zone, particularly the Southwest Atlantic coast. Hence, the present study brings essential contributions to address environmental hazard and risk assessments from realistic scenarios that may be used to establish strategies to support environmental management decisions.

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Author contribution All authors contributed to the study conception and design. Material preparation was performed by F.C. Perina and I.B. Castro; data collection and analysis were performed by F.C. Perina and D.M.S. Abessa. G. Fillmann and G.L.L. Pinho contributed to the funding acquisition. The first draft of the manuscript was written by F.C. Perina, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author.

Declarations

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