



Potential ecotoxicity of metals leached from antifouling paint particles under different salinities



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ABSTRACT

Antifouling paint particles (APPs) are residues generated during maintenance of vessels. In boat maintenance areas of South America, waste generation and disposal are not completely regulated. Therefore, APPs can enter into the aquatic environment and act as a source of contamination by metals and other biocides. Thus, the aim of the present study was to evaluate the potential ecotoxicity of the metal mixture present in APPs leached under different salinities. Therefore, the copepod *Acartia tonsa* was exposed to different concentrations of a leachate solution prepared by the addition of APPs (1.25 g/L) in artificial saline water (salinities 5, 15 and 30). Thereafter, complexing agents (EDTA and sodium thiosulfate) were added to the experimental media in order to evaluate metal influence in APPs toxicity. APPs leachate solutions were very toxic to *A. tonsa*, reaching an estimated LC₅₀ of 1% at salinities 5% and 15%, and 2% at salinity 30. The addition of the chelators in leachate solutions showed that metals are the major responsible compounds for the observed toxicity. Moreover, results from the calculated toxic units suggested a slightly synergic effect between Cu and Zn in the paint formulation. A metal speciation modelling showed that Zn was predominant as a free ion at all salinities, therefore, explaining the high leachate toxicity. Furthermore, the release of Zn was observed more at lower salinities, whereas Cu was observed at higher salinities. APPs are frequently released in estuarine systems, under conditions of salinity gradients. Therefore, navigated estuaries might be under the threat of this neglected residue.

1. Introduction

Metals such as copper (Cu) and zinc (Zn) are frequently used in antifouling paints as biocides (e.g., Cu and Zn oxides and Cu thiocyanate) to prevent the attachment of organisms such as microalgae, macroalgae, and invertebrates to boats and other structures submerged in salt water (Almeida et al., 2007). In addition, paint formulations might contain several organic and organo-metallic compounds that are used to boost the biocide effects of Cu and Zn (Singh and Turner, 2009a; Yebra et al., 2004). Antifouling paints are designed to slowly release the biocides from the coatings into the water, and they lose their efficiency against bioincrustation over time (Chambers et al., 2006). Thus, antifouling systems should be replaced periodically. The process of boat maintenance results in generation of antifouling paint particles (APPs) due to the removal of the old coating material (Turner, 2010). These particles often reach aquatic environments and can act as secondary contamination sources. Recent studies have identified APPs as a source of metal contamination (Singh and Turner, 2009b; Soroldoni et al., 2017; Turner, 2013; Turner et al., 2014), leaching large amounts of Cu

and Zn into aquatic environments (Holmes and Turner, 2009; Jessop and Turner, 2011; Singh and Turner, 2009a). Most boatyards and marinas near the coastal areas of Southern Brazil (Costa et al., 2016) and Southwest England (Turner, 2013) do not follow the correct disposal procedures for the APPs generated during boat maintenance, highlighting the importance of better regulations. This is a relevant problem in the boat-maintenance areas, where waste generation and disposal is not completely regulated. In Brazil, the current regulatory procedure only assesses the correct disposal of paint residues that contain TBT-based antifouling paints (NORMAM, 2007). Therefore, the management of booster biocides currently used in paint formulation is not regulated. Around the world, the ship and boat building and repair industry have codes of practice that usually recommend solid waste collection and its correct disposal (British Marine Federation, 2005; Environment Canada, 1995). However, as these documents list general guidelines, correct disposal methods might not be in practice or clearly defined (Srinivasan and Swain, 2007).

As APPs (and also original antifouling paints) are composed of metallic, organometallic and/or organic biocides and other toxic

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substances such as binders, solvents, and preservatives (Karlsson et al., 2010), it is a challenge to identify chemicals associated with toxicity to non-target organisms. The Toxic Identification and Evaluation (TIE) (USEPA, 2007, 1993) method has been developed for this purpose. For the phase I of the TIE method, complexing agents (CA) such as EDTA and sodium thiosulfate have been successfully used to identify harmful substances responsible for the environmental impact of complex mixtures, mainly metals (Camargo et al., 2014; Poleza et al., 2014; USEPA, 2007, 1993). Thus, adding CA to investigate the toxicity of application APP leachates could be very suitable to identify potential toxicity of metals.

Estuarine environments have served as sites for both human settlement and industrial expansion, as well as port development and boat facilities, and thus, act as a sink for trace metals and other hazardous substances, mostly of anthropogenic origin (Xu et al., 2013). In estuarine areas, salinity is one of the main driving factors related to the distribution of metals, with possible effects on their toxicity and speciation (Wright and Welbourn, 2001). Thus, the aim of the present study was to evaluate the potential toxicity of the metal mixture in APPs leached under different salinity conditions.

2. Material and methods

2.1. Antifouling paint particle production

A sample of the commercial antifouling paint Super Marine AF Ionex MB (Renner®), obtained from a boat maintenance facility in Rio Grande, Brazil, was applied on transparent glass sheets (30 cm × 30 cm), with two applications of paint to reach the recommended thickness according to the manufacturer's technical report (www.rennercoatings.com). After drying, the paint layer was scraped off into a glass flask and about 10 g of antifouling paint particles (APPs) were produced, which were dried and sieved. APPs obtained from natural environments are often composed by different layers including old coatings (Karlsson et al., 2010) that may bias the results from toxicity tests. Thus, in the present study, APPs made in the laboratory were chosen to perform the experiments.

2.2. Exposure medium

Leachate solutions were prepared by the addition of 1.25 g APPs in 1 L of artificial saline water, prepared by the addition of artificial salt (Coralife®) in distilled water, yielding three different salinities, i.e., 5, 15, and 30, spanning wide range of salinities observed in estuarine systems around the world. The leachates were prepared in 7 days according to the methodology proposed by Turner et al. (2008), using mechanical shaking (50 rpm) and controlled temperature (20 ± 2 °C), without illumination. After shaking, the leachates were filtered through a Buchner funnel (3 mm pore). The stock solutions (one for each salinity) were used in bioassays and chemical analyses as described below.

2.3. Bioassays

The euryhaline copepod, *Acartia tonsa*, was obtained from a stock culture maintained at the Universidade Federal do Rio Grande, Brazil. Acute toxicity tests were carried out using the methodology described in the standard guidelines ISO 14669 (1999) at three different salinities (5, 15, and 30). The exposure solutions were prepared at the following concentrations: 100%, 45%, 15%, 5%, and 1% of each stock solution in 1 L of artificial saline water at the three above-mentioned salinities. The tests were performed by adding 10 adult organisms, without sex distinction, in 100 mL of the test and control solutions, with four replicates per treatment. At the end of the exposure time (48 h), the lethal concentration (LC₅₀) at each salinity was calculated. Thereafter, complexing agents (CA) were added to the experimental media (USEPA, 2007), in order to evaluate if the APP toxicity was due to toxic effects of

metals in its composition. Copepods were exposed to the previously determined LC₅₀, following the standard guideline ISO 14669 (1999), with and without 100 mg L⁻¹ of both CA compounds (EDTA and sodium thiosulfate), resulting in four treatments for each salinity: control (artificial saline water), control plus CA, LC₅₀, and LC₅₀ plus CA.

All tests were carried out at 20 ± 2 °C, with a 12 h light-dark cycle, for 48 h. The living and dead organisms were counted, and pH, temperature, and dissolved oxygen were measured in the beginning and end of the experiments using a multiparameter probe (Hanna, EDGE). Salinity was measured using a refractometer (Instrutemp, ITREF 10).

2.4. Chemical analyses

Leachate dilutions were filtered (0.45 μm) and three 10 mL aliquots were added to individual plastic tubes and acidified with 250 μL of concentrated HNO₃. Dissolved copper (Cu) and zinc (Zn) concentrations were then quantified by Flame Atomic Absorption Spectroscopy. Cu and Zn standards were prepared using a reference solution. Metal speciation calculations were performed using the geochemical speciation model visual MINTEQ. Input data used for salinities 5 and 15 were based on the composition of seawater (Barnes, 1954), and the composition of artificial salt water Coralife was used for salinity 30.

2.5. Statistics

Nominal LC₅₀ was first calculated by Trimmed Spearman Kabber test (Hamilton et al., 1975). The LC₅₀ based on dissolved metal concentration was also estimated based on the percentage effect observed in the tests. For verifying the relationship between toxicity and metals, a Spearman correlation test was used at a significance level of 95%. For the tests using complexing agents, the differences among exposure treatments were evaluated using one-way ANOVA ($p < 0.05$), followed by Tukey's post hoc test. Differences between the average metal concentrations in each salinity were estimated using two-way ANOVA ($p < 0.05$) followed by Bonferroni post hoc test. Prior to statistical analyses, normality and homogeneity of data were verified using Shapiro-Wilk and Levene tests, respectively. ANOVA and correlation analysis were performed using the software GraphPad Prism (v 5.02 for Windows, San Diego, USA).

Toxic interactions among metals were characterized by calculating toxic units (TUs) based on LC₅₀ estimates from bioassays with mixtures and single metals (Spehar and Fiant, 1986). TUs were calculated by dividing the LC₅₀ estimated from the mixture by the corresponding estimate from the single metal data (from literature). If the sum of TUs equals 1.0 for any single compound, the toxicity is assumed to be simple additive; a more-than-additive toxicity is indicated if the sum of TUs is less than 1.0. If the sum of TUs in a mixture exceeds 1.0, the toxicity of the mixture is indicated as less-than-additive or antagonist (Brown, 1968).

3. Results and discussion

Antifouling paint particles (APPs) leachates were very toxic to the copepod *Acartia tonsa*, showing up to 100% mortality in all the salinities tested. The leachates resulted in 100% mortality until 5% dilution, and the calculated LC₅₀ were 1% for the salinities 5% and 15% and 2% at salinity 30 (Table 1).

Considering the high Cu and Zn contents in Super Marine AF Ionex MB [Cu = 50.4% and Zn = 26.4% (Costa et al., 2016)], the potential toxicity of metals was evaluated by adding complexing agents (CA) to the exposure media. The concentration of CA (100 mg L⁻¹ for each: EDTA and sodium thiosulfate) used in the experiments was not toxic to the organisms, and no significant mortality was observed in the control groups, regardless of the salinity, with or without CA (Fig. 1). Similarly, leachates were not toxic when combined with CA. On the other hand, survival of copepods was severely reduced when the organisms were

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