Marine Pollution Bulletin 62 (2011) 985–991

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

# Probabilistic risk assessment of common booster biocides in surface waters of the harbours of Gran Canaria (Spain)

Álvaro Sánchez-Rodríguez [a], Zoraida Sosa-Ferrera [a], Ángelo Santana-del Pino [b], José Juan Santana-Rodríguez [a,*]

[a] *Departamento de Química, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain*
[b] *Departamento de Matemáticas, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain*

A R T I C L E   I N F O

*Keywords:*
Probabilistic risk assessment
Irgarol 1051
Diuron
Antifouling paint
Canary Islands
Harbour

A B S T R A C T

The presence of booster biocides in the aquatic environment has been associated with a risk to non-target species due to their proven toxicity. The aim of the present study was to determine the spatial and temporal distribution of common booster biocides in different harbours of the island of Gran Canaria (Spain) and evaluate, by means of a probabilistic risk assessment (PRA), the ecological risk posed by these compounds. With these objectives, a monitoring campaign was conducted between January 2008 and May 2009, collecting a total of 182 seawater samples. Four common booster biocides (TCMTB, diuron, Irgarol 1051 and dichlofluanid) were monitored. Diuron levels ranged between 2.3 and 203 ng/L and Irgarol 1051 between 2.4 and 146.5 ng/L. The ecological risk associated with these levels was always low, however, with probabilities of exceeding the 10th percentile of autotroph toxicity below 3.5%.


## 1. Introduction

The undesirable growth of organisms on submerged surfaces is known as biofouling. This phenomena carries with it some negative consequences, including increased fuel consumption and corrosion, as well as the potential for the introduction of foreign species into new ecosystems (Yebra et al., 2004). To prevent its occurrence, antifouling paints containing biocides have traditionally been used. In the past, these antifouling paints were based on lead, arsenic, organic compounds of mercury or pesticides like dichlorodiphenyltrichloroethane (DDT) (Evans et al., 2000). From the beginning of the 1970s, however, antifouling formulations containing organotin compounds like tributyltin (TBT) or triphenyltin (TPT) were introduced, which showed an elevated efficacy as antifouling agents (Konstantinou and Albanis, 2006). Unfortunately, these compounds exhibited a high toxicity over non-target organisms like marine gastropods and bivalves (Alzieu, 2000). For this reason, several restrictions were introduced by European countries in the 1980s. Nowadays, the International Marine Organization (IMO) has encouraged a halt to the use of these compounds on any ship size through the International Convention on the Control of Harmful Antifouling Systems on Ships (AFS Convention) (Sonak et al., 2009).

To replace organotin compounds, paint manufacturers based their new formulations on cooper as the active component, and others biocides which improved their efficacy (Omae, 2003). These biocides are known as booster biocides and in the past were also added to TBT-based paints for large vessels (Konstantinou and Albanis, 2006). Some of these are also frequent compounds in agricultural and industrial products, where they are used as fungicides or herbicides. Several studies have evaluated the toxicity of booster biocides on non-target species and found most of them to be growth inhibitors for freshwater and marine autotrophs (Okamura et al., 2003), influencing key species like sea grasses (Chesworth et al., 2004) and corals (Owen et al., 2002). For this reason, there is increasing interest in the impact of these compounds on aquatic ecosystems, especially evaluating the environmental risk associated with their presence and use.

Recently, the probabilistic risk approach has been gaining acceptance among researchers for ecological risk assessment (ERA). The use of traditional approximations like hazard quotients (HQ) have been branded as extremely conservative estimations (Solomon et al., 2000). Frequently, HQ for pesticides and herbicides exceed values of 1.0 (higher environmental concentration than toxicant reference value) requiring a more complex evaluation. The probabilistic assessment (PRA) is applicable when exposure levels from monitoring campaigns and toxicity levels derived from toxicity assays are available. This approach is based on the studies conducted by several authors (Cardwell et al., 1999; Hall et al., 1999; Solomon et al., 1996), and it has been employed in marine environments to determine the risk associated with the presence of antifouling agents like TBT (Cardwell et al., 1999), Irgarol 1051 (Hall and Gardinali, 2004; Hall et al., 2009) or diuron (Landa et al., 2009).

The aim of the present study is determine the spatial and temporal distribution of booster biocides in the aquatic environment

* Corresponding author. Tel.: +34 928 452915; fax: +34 928 452922.
*E-mail address:* jsantana@dqui.ulpgc.es (J.J. Santana-Rodríguez).

0025-326X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2011.02.038

of several harbours of Gran Canaria Island and evaluate the risk posed by these compounds. In a previous study, the booster biocide levels present in harbours of Gran Canaria Island were reported (Sánchez Rodríguez et al., 2009), but here a more extensive monitoring was conducted from January 2008 to May 2009 (182 samples) for application of a statistical evaluation and a probabilistic risk assessment. To the best of our knowledge, this is the first study of these characteristics carried out for the Canary Islands.

## 2. Materials and methods

### 2.1. Monitoring areas

The Canary Islands, a Spanish archipelago, are situated next to the northwestern African coast, and Gran Canaria is the second most populous island of archipelago. To evaluate booster biocide concentrations in harbours of the island, six different locations were selected. The distribution of the sample points is shown in Fig. 1 and the characteristics of each harbour included in the study are detailed in Table 1.

The commercial port of the island (area A in Fig. 1) is known as Puerto de La Luz y de Las Palmas de Gran Canaria. This harbour centres its activity on frozen fish, container and passenger traffic and the supply of fuel. Inside of its installations five sample points were chosen (A1–A5). The commercial harbour contains two marinas, the Real Club Náutico marina, where four sample points were established (A6–A9), and the Muelle Deportivo marina, where another five sample points were fixed (A10–A14).

The south of the island focuses more on sun and shore tourism. In this area, the Mogán harbour (B, Fig. 1), Puerto Rico marina (C, Fig. 1) and the fishing harbour of Arguineguín (D, Fig. 1) were monitored. Mogán harbour (B1–B4) divides its activity between marina and fishing, with a greater area dedicated to sailboats and yachts.

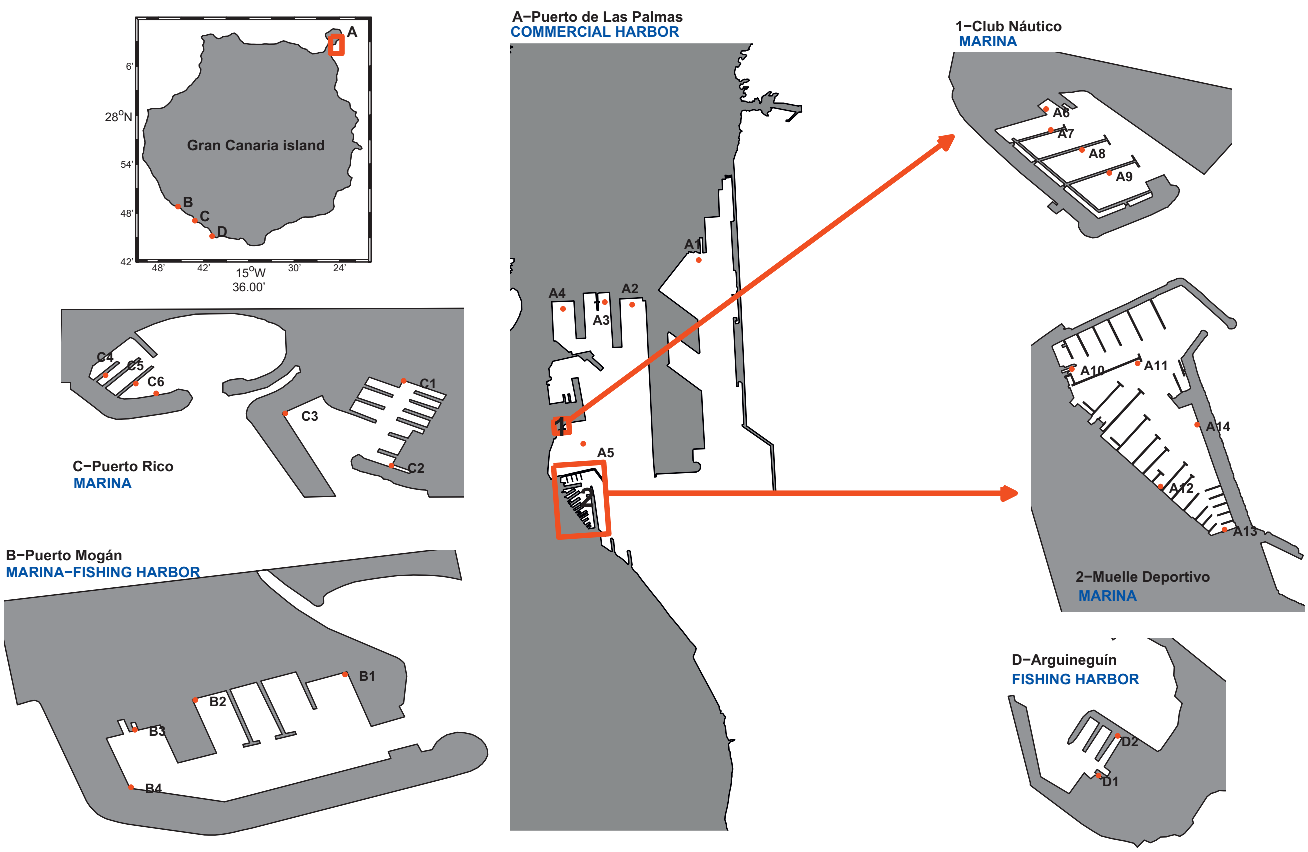


**Fig. 1.** Sample point locations.

**Table 1**
Harbour characteristics.

| Harbour | Designation[a] | Samples | Type | Number of slips | Dry dock |
|---|---|---|---|---|---|
| Puerto de La Luz y Las Palmas de GC | La Luz | A1–A5 | Commercial harbour | – | Yes |
| Real Club Náutico Marina | Club Náutico | A6–A9 | Marina | 135 | Yes |
| Muelle Deportivo Marina | Muelle Deportivo | A10–A14 | Marina | 1134 | Yes |
| Mogán | Mogán | B1–B4 | Marina/fishing harbour | 216 | Yes |
| Puerto Rico Base | Puerto Rico B. | C1–C3 | Marina | 319 | Yes |
| Puerto Rico Escala | Puerto Rico E. | C4–C6 | Marina | 212 | No |
| Arguineguín | Arguineguín | D1–D2 | Fishing harbour | 120 | Yes |

[a] Designation employed in tables and figures.