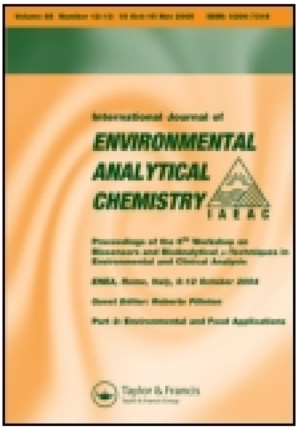

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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To cite this article: Álvaro Sánchez Rodríguez, Zoraida Sosa Ferrera & José Juan Santana Rodríguez (2011): An evaluation of antifouling booster biocides in Gran Canaria coastal waters using SPE-LC MS/MS, International Journal of Environmental Analytical Chemistry, 91:12, 1166-1177

To link to this article: http://dx.doi.org/10.1080/03067310903524848

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 12, October 2011, 1166–1177

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An evaluation of antifouling booster biocides in Gran Canaria coastal waters using SPE-LC MS/MS

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(*Received 22 May 2009; final version received 18 November 2009*)

A solid phase extraction (SPE) technique for seawater samples coupled to quantification using liquid chromatography tandem-mass spectrometry (LC-MS/MS) is described to quantify relevant antifouling booster biocides of ecotoxicological concern (Diuron, TCMTB, Irgarol 1051 and Dichlofluanid). The optimised methodology provides a sensitive, easy to use and efficient analytical procedure with detection limits in the range of between 0.1 and 0.2 $\mathrm{ng\,L^{-1}}$ and appropriate reproducibility (with analytical standard deviations of less than 10%). Spiked recoveries for all compounds exceeded 72%. The method was tested through a thorough monitoring regime of commercial port and marinas on the island of Gran Canaria (off the north-west coast of Africa) over a period of several months in 2008. Results provide the first data for antifouling booster biocides in the Canary Islands. Concentrations of Diuron and Irgarol 1051 in samples ranged between 2 and 195 $\mathrm{ng\,L^{-1}}$ and 2 and 146 $\mathrm{ng\,L^{-1}}$, respectively. TCMTB and Dichlofluanid were not detected.

Keywords: booster biocides; Diuron; TCMTB; Irgarol 1051; Dichlofluanid; SPE; LC-MS/MS; the Canary Islands

1. Introduction

The term ‘biofouling’ is used to refer to the undesirable accumulation of microorganisms, plants and animals on artificial surfaces immersed in water. This accumulation causes various problems, such as greater frictional resistance and deterioration of the coating, among others, with resulting economic losses [1].

In the late 1950s and early 1960s, tributyltin (TBT) was introduced into marine paints as an antifouling agent, proving to be highly efficient. Although due to its toxicity, several restrictions have been applied to its use. At present, the European Union (EU) has forbidden all boats painted with orgatonin-based paints to sail in its waters [2].

As a result, the manufacturers introduced other compounds, such as biocides, into their antifouling paint formulations. These compounds are commonly referred to as ‘booster’ biocides. They are added to copper oxide-based paints [3] nowadays but, in the

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ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067310903524848
http://www.tandfonline.com

past, were also added to TBT-based paints to improve antifouling efficiency for large vessels [4]. Some of these booster biocides are frequent compounds in agricultural and industrial products since they are used as fungicides or herbicides. However, at the time they were introduced as antifouling agents, no reliable data existed with respect to their potential toxicity, characteristics nor distribution in seawater. This lack of knowledge motivated abundant studies in this field. For example, the project running under the title of 'Assessment of Antifouling Agents in Coastal Environments (ACE)', supported by the EU [5], has contributed to know-how in the field through its numerous publications. In Spain, studies on booster biocides have largely focused on the Mediterranean coastline [6–10].

Recent studies have evaluated the toxicity of booster biocides on non-target species [11, 12]. Most booster biocides are growth inhibitors for freshwater and seawater algae [13]. For example, Diuron and Irgarol 1051, to cite two of the most frequently used booster biocides, have toxic effects on macrophytes and phytoplankton communities, at levels of $\mu g\,L^{-1}$ or $ng\,L^{-1}$ [14]. Both of these compounds reveal equal patterns of toxicity in the case of plants, inhibiting photosynthesis through the blockage of electron transport. Diuron and Irgarol 1051 have been measured at levels of 2190 and $1000\,ng\,L^{-1}$, respectively, in Spanish coastal waters [7,10]. Similar concentrations have also been found in other countries [15]. Such levels may affect the photosynthetic efficiency of species of great ecological importance such as *Zostera marina* [16].The environmental consequences have led to the introduction of legal restrictions on the use of booster biocides. For example in the UK, neither Diuron nor Irgarol 1051 can be used as antifouling agents as of November 2002 [17]. Diuron, moreover, was included in the list of priority substances in the field of water policy and amending Directive 2000/60/EC of European Community [18].

The determination of these compounds is possible either by gas chromatography (GC) or high performance liquid chromatography (HPLC). Phenylureas such as Diuron degrade under gas chromatography conditions but may be determined by previous derivatisation [19], and this procedure can, thus, be used for their determination in seawater samples [20]. The most frequently used detection technique is mass spectrometry (MS) coupled with GC [8,10] or LC [7,21,22]. This technique is an excellent confirmation tool, offering high sensitivity and, when coupled with liquid chromatography, provides even greater applicability. Over the last few years, the most widely deployed technique in the case of booster biocide detection has been liquid chromatography tandem mass spectrometry (LC-MS/MS), in particular when Diuron is one of the targeted analytes [23,24].

The most common extraction methods used in seawater monitoring studies are solid phase extraction (SPE) [6,25–27] and liquid-liquid extraction (LLE) [28–30]. High preconcentration is achieved with both extraction methods and, hence, low levels of booster biocides may be detected in aqueous samples. SPE, in particular, requires only a low volume of solvents and is easy to apply, giving excellent results in most cases.

The aim of the present study is to investigate the occurrence of four common booster biocides (Diuron, TCMTB, Irgarol 1051 and Dichlofluanid) in the coastal waters of the island of Gran Canaria. To our knowledge, this is the first study of its kind, researching antifouling booster biocide concentrations in seawater samples taken from the commercial port and various different marinas in the Canary Islands. The campaign from which these data are derived took place between May and November 2008 in the marinas, the commercial port and the fishing harbours on the island of Gran Canaria. An optimised SPE-LC MS/MS methodology is employed in the determination process.

2. Experimental

2.1 *Reagents and chemicals*

Diuron, 2-(thiocyanomethylthio)benzothiazole (TCMTB), Irgarol 1051 and Dichlofluanid were purchased from Dr. Ehrenstorfer (Germany) at levels of purity over 98%. Stock standard solutions of each analyte were prepared at 1000 mg L^{-1} in methanol, and stored at 4°C. The methanol LC-MS-grade, formic acid and ammonium formate were supplied by Panreac Química S.A. (Barcelona, Spain). The ultra-high-quality water was obtained from the Milli-Q purification system (Millipore, USA). The SPE cartridges (Envirelut Pesticide 500 mg) were supplied by Varian (Madrid, Spain).

2.2 *Sampling*

The blank seawater samples used in method optimisation were collected from the beach at Melenara, located in the East of the island of Gran Canaria. To ensure the absence of booster biocides in the matrix, both the extraction and determination procedures were carried out.

A total of 104 seawater samples were collected from the commercial port and various different marinas around the island of Gran Canaria between May and November, 2008. All the samples were taken at 1 metre depth and stored in amber 2.5 L glass bottles at 4°C in the dark until extraction.

2.3 *Solid phase extraction*

All samples were filtered through a 0.65 µm Durapore membrane filter (Millipore, USA).The solid phase extraction procedure had been previously optimised [31]. The Envirelut Pesticide cartridge was conditioned with 3×5 mL of methanol and 3×5 mL of ultra-pure water. Thereafter, a volume of 1L was passed through a cartridge at a flow-rate of 10 mL min^{-1}. To remove the salts retained in the cartridge, a wash step was introduced, using 2×5 mL of ultra-pure water. Subsequently, the cartridge was dried under vacuum for 5 minutes, and the retained analytes were eluted with 1 mL methanol at a low flow rate (~1 mL min^{-1}). Duplicate analyses were carried out for all the samples.

2.4 *LC-ESI-MS-MS analysis*

The LC-MS analyses were carried out in a Varian 320-MS LC/MS/MS system (triple quadrupole) equipped with an electrospray ionisation (ESI) interface. The stationary phase used was a Varian Pursuit UPS 2.4 C_{18} 50×2.0 mm (2.4 µm particle size) column set at 40°C. The chromatographic separation was performed under isocratic conditions with 40% of 5 mM ammonium formate, acidified with 0.2% (v/v) formic acid and 60% methanol. A flow rate of 0.2 mL min^{-1} was held for 8 minutes and the injection volume employed was 10 µl.

The mass spectrometer parameters are detailed in Table 1. The housing temperature was set at 60°C, the nebulising gas pressure at 50 psi, the drying gas pressure at 30 psi, and the shield and needle voltages at 0.6 kV and 5 kV respectively. Nitrogen was used as the nebulising and drying gas, and argon as the collision gas at a pressure of 3.87×10^{-5} psi.

Table 1. Optimised MS/MS conditions and transitions selected under the MRM mode for the quantification and confirmation of booster biocides in seawater samples.

Compound	Mass	Precursor ion	Capillary (V)	Quantification ion (Coll. eV)	Confirmation ion (Coll. eV)
Diuron	232	233	52	72 (16)	160 (28)
TCMTB	238	239	30	180 (10)	136 (22)
Irgarol 1051	253	254	40	198 (11.5)	91 (22)
Dichlofluanid	332	333	52	123 (12.5)	224 (9.5)

To optimise the mass spectrometer parameters (Table 1) a standard solution of each analyte ($1\,\mathrm{mg\,L^{-1}}$) was infused directly into the detector at a flow rate of $10\,\mu\mathrm{L\,min^{-1}}$. The determination of analytes was carried out under the multiple reaction monitoring (MRM) mode. The detector voltage was fixed at the maximum extended dynamic range (EDR) to optimise the signal, and the mass width was set at 2 and 1.5 amu for the first and third quadrupole respectively. The dwell time for all the transitions was 0.1 s.

Simultaneous presence of the quantification and confirmation ions and retention time based on authentic standards was used to positively identify the presence of booster biocides in real samples.

2.5 *Calibration*

To determine the analytical parameters, reproducibility and recovery experiments were carried out over six blank seawater samples spiked with the analytes, at three different levels (500, 50 and $5\,\mathrm{ng\,L^{-1}}$).

Calibration curves were performed on blank seawater samples fortified at six different levels between 2.5 and $700\,\mathrm{ng\,L^{-1}}$. Subsequently, the optimised solid phase extraction procedure was applied. Correlation coefficients of over 0.995 were obtained by applying the least square method. Limits of detection (LODs) and quantification (LOQs) were calculated using a signal-to-noise ratio equal to three and ten, respectively.

3. Results and discussion

3.1 *LC-MS/MS optimisation*

The optimisation of the mass spectrometer parameters for the studied compounds was carried out by direct infusion into the detector. Positive (PI) and negative (NI) ionisation modes were tested. Although the TCMTB and Dichlofluanid are frequently measured in NI [32], in this case, the PI offered better signals for all the compounds.

Mass spectrometry acquisition was achieved under the MRM mode. The fragment ions in the MRM mode were produced as a result of the collision of selected precursor ions into the collision cell of the triple quadrupole. Two transitions were acquired for the confirmation of each analyte, but only one was used for quantification. The precursor ions and their product ions, used for quantification and confirmation purposes, together with the capillary voltage and collision energy are summarised in Table 1.

In the case of Diuron, the main product ion obtained was *m/z* 72 corresponding to $[\mathrm{MH\text{-}C_6H_5Cl_2N}]^+$ [21]. The confirmation ion selected was *m/z* 160. This ion has been

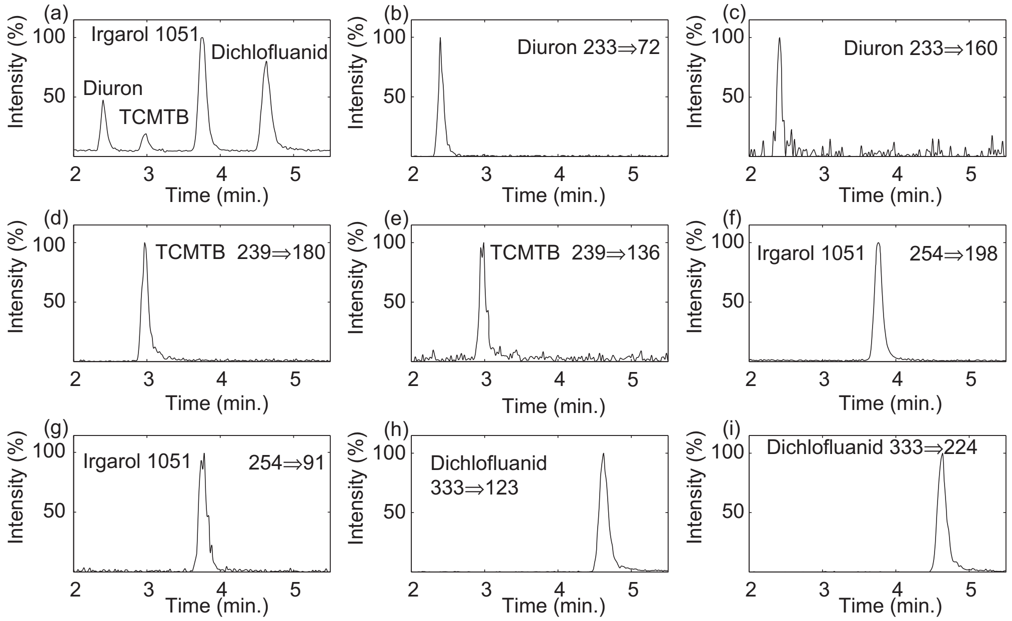

Figure 1. Total ion current (a) and selected ions (b–i) chromatogram obtained with a spiked seawater sample (10 ng L^{-1}) by LC-MS under MRM mode.

used on other occasions to monitor for the presence of Diuron in real samples taken from the port of Osaka [33]. For Irgarol 1051, the product ion selected for quantification was *m*/*z* 198 $[MH\text{-}C_4H_8]^+$ [34], with the second ion used for confirmation criterion, *m*/*z* 91. In the case of the TCMTB, the quantification and confirmation ions were *m*/*z* 180 $[M\text{-}SCN]^+$ and *m*/*z* 136 respectively. For Dichlofluanid, at 52 V, the main ion obtained was *m*/*z* 333 $[M+H]^+$. The product ion used for quantification was *m*/*z* 123 $[PhNS]^+$ and the confirmation ion was *m*/*z* 224 $[M\text{-}SO_2N(CH_3)_2]^+$. Both the TCMTB and Dichlofluanid fragment ions were identified using gas chromatography mass spectrometry and electron impact ionisation [8].

Figure 1 shows a total ion current (TIC) and selected ion chromatogram obtained from the analysis of a seawater sample spiked with 10 ng L^{-1} of all the compounds.

The response of the precursor ions to the drying gas temperature was also examined. In most cases, an increased signal and rise in temperature were observed; only *m*/*z* 333 (the Dichlofluanid precursor ion) decreased, probably due to its fragmentation. To avoid this, the drying gas temperature was set at 250°C.

3.2 *Method performance*

The method was evaluated with respect to recovery and precision, together with detection and quantification limits. Table 2 summarises the results obtained. The analyte recoveries throughout the whole process (SPE extraction and LC-MS/MS determination) were evaluated at three different concentrations (500, 50 and 5 ng L^{-1}).The recoveries tended to decline at low levels, but adequate values (>72%) were obtained for all the analytes.

Table 2. Analytical parameters of the SPE-LC-MS/MS method.

Compound	500 ng L^{-1} ($n=6$) Recovery (%)	RSD[a] (%)	50 ng L^{-1} ($n=6$) Recovery (%)	RSD[a] (%)	5 ng L^{-1} ($n=6$) Recovery (%)	RSD[a] (%)	LODs[b] (ng L^{-1})	LOQs[c] (ng L^{-1})
Diuron	100.6	3.3	88.0	4.6	83.7	4.2	0.1	0.4
TCMTB	91.0	3.4	93.4	6.8	79.3	6.8	0.2	0.5
Irgarol 1051	86.1	4.0	84.9	5.2	78.9	2.5	0.1	0.3
Dichlofluanid	84.0	5.7	72.8	8.3	81.8	6.0	0.1	0.3

[a] Relative standard deviation.
[b] Limit of detection.
[c] Limit of quantification.

These values are comparable to those given in other studies where different polymeric sorbents were used [7,35]. With respect to the Dichlofluanid, greater values were obtained than with the other SPE procedures where the relatively poor recovery rates were associated with the evaporation step [22,36]. In our case, the evaporation step was avoided by using a low volume of eluate. The relative standard deviations (RSDs) for the recovery experiments were, in all the cases analysed, under 10%, with the Dichlofluanid offering high values. This behaviour may be attributable to its fast degradation into *N*′-dimethyl-*N*-phenyl-sulphonamide (DMSA) under basic conditions [37].

Linearity ranges (2.5–700 ng L^{-1}) were obtained with satisfactory correlation coefficients of over 0.995 for all the analytes. The LODs obtained ranged from 0.1 to 0.2 ng L^{-1}. Low LOQs were also achieved, with values ranging from 0.3 to 0.5 ng L^{-1}.

3.3 *Determination of booster biocides in seawater samples from Gran Canaria island*

The SPE-LC-MS/MS method was applied to samples taken from several locations in the north-east and south-southwest of the island of Gran Canaria. The samples were collected in marinas, fishing harbours and a commercial port every two months between May and November 2008.

Figure 2 shows the 26 sites under study. A total of 104 samples were collected. Five points (A1–A5) were sampled in the commercial harbour of Las Palmas de Gran Canaria, known as Puerto de La Luz. This harbour is one of the most important in Spain due to its location between America-Africa-Europe, on the main shipping routes. In Las Palmas de Gran Canaria, two marinas with heavy yachting activity: the Club Náutico (A6–A9) and the Muelle Deportivo (A10–A14), were also sampled. In the south of the island, three locations were selected: the Puerto de Mogán (B1–B4), used both as a marina and a fishing harbour, Puerto Rico (C1–C6) with two marinas, and the fishing harbour of Arguineguín (D1 and D2).

All samples with the exception of site D2 for Diuron were above the LOQs for both Diuron and Irgarol 1051. The range levels of Diuron and Irgarol 1051 found in the samples are summarised in Table 3. These booster biocides are frequently found in real seawater samples from harbours due to their widespread use. They also show low degradation in the media. By means of laboratory experiments, a half-life of 350 days has

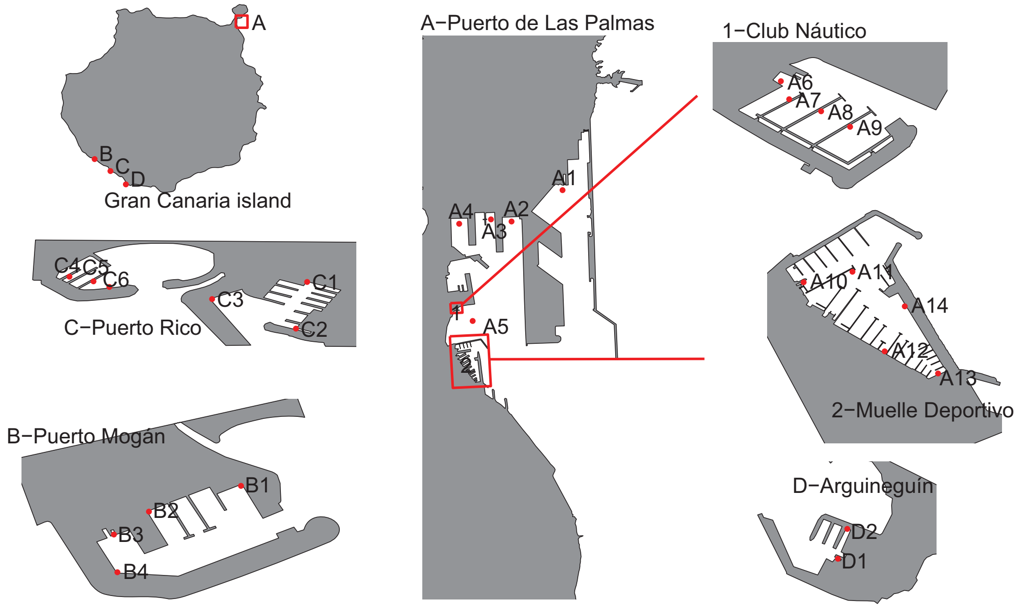

Figure 2. Sample points monitored on the island of Gran Canaria.

been established for Irgarol 1051 in seawater, whereas Diuron did not show any degradation [38]. Moreover, Harino *et al.* [39] measured no biodegradation over 13 days using bacteria culture, besides no remarkable changes as the result of sunlight irradiation over 17 days for both compounds.

The concentration levels of Diuron ranged from 2 to 195 ng L^{-1}. The highest concentration was found at the Muelle Deportivo in the A11 sample in September. This marina is situated inside the commercial port of Las Palmas de Gran Canaria and presents intense yachting and sailing activity. Higher levels of Diuron have been found previously in various different world locations: Port Osaka (Japan) with up to 1540 ng L^{-1} [33]; Pozzuoli Marina di Maglietta (Italy) with 475 ng L^{-1} [22]; Veerse Meer (Netherlands) at 1130 ng L^{-1} [35]; Southampton (UK) at 6700 ng L^{-1} [15]; and Blanes (Spain) at 2,190 ng L^{-1} [6]. The levels found in the present study are comparable to the values reported in some of the articles studying the Spanish Mediterranean region (10–180 ng L^{-1}) [40] or the west coast of Sweden (10–100 ng L^{-1}) [41]. Lower levels of Diuron were recently measured along the California coast, with values ranging from <2 to 12 ng L^{-1} [32] and from 5 to 27 ng L^{-1} [24]. Diuron is used in other applications such as agriculture, and the marine coast levels may be the accumulated result of various different inputs [42].

With respect to Irgarol 1051, the concentration levels ranged from 2 to 146 ng L^{-1}. The highest concentrations were measured at the Marina of Puerto Rico in May and July, although a high concentration was also measured in Mogán (July, 135 ng L^{-1}). These two marinas are in the south of the island and show significant tourist activity. In real samples, levels of up to 4200 ng L^{-1} have been found in the coastal waters of Singapore [43], up to 1421 ng L^{-1} along the southern coast of the UK [15] and up to 1000 ng L^{-1}

Table 3. Range levels, mean and standard deviation of Diuron and Irgarol 1051 for each harbour and month expressed as ng L^{-1}. Sample values are the mean of two determinations.

Simple area	Date	Diuron	Mean	Standard deviation	Irgarol 1051	Mean	Standard deviation
Puerto de La Luz (A1–A5)	May (2008)	3.6–22.2	9.2	7.4	2.4–5.9	3.2	1.5
Club Náutico (A6–A9)		17.6–41	30.7	11.4	7.9–12.4	10.1	1.8
Muelle Deportivo (A10–A14)		52.6–113	70.3	24.9	24.9–50.7	33.7	11.5
Mogán (B1–B4)		4.5–9.2	6.5	2.3	8.2–40.9	24.1	14.7
Puerto Rico (C1–C6)		5.1–37.1	21.0	12.6	14.8–145.8	66.2	54.7
Arguineguín (D1–D2)		<LOQ[a]–23	23.0	–[b]	6.3–11.8	9.1	3.9
Puerto de La Luz (A1–A5)	July (2008)	18.1–55.2	36.9	15.6	3.2–6.4	5.2	1.2
Club Náutico (A6–A9)		14.7–46.6	25.9	14.1	4.4–9.9	6.8	2.7
Muelle Deportivo (A10–A14)		27.5–111.2	53.7	15.0	7.3–29.3	20.0	9.4
Mogán (B1–B4)		12–93.1	39.3	37.2	25.9–134.6	67.2	47.3
Puerto Rico (C1–C6)		2.3–24.4	13.3	8.7	15.2–146.5	61.6	48.6
Arguineguín (D1–D2)		9.6–34.5	22.1	17.6	3.3–11.5	7.4	5.9
Puerto de La Luz (A1–A5)	September (2008)	8.4–19.1	13.7	4.8	3.8–9.5	6.1	2.1
Club Náutico (A6–A9)		26.7–155.2	72.3	56.7	14.6–46.7	25.1	14.6
Muelle Deportivo (A10–A14)		52–195	126.3	47.1	12.5–37.5	28.0	7.4
Mogán (B1–B4)		11.7–34.4	23.4	12.4	11.7–52.5	28.8	17.3
Puerto Rico (C1–C6)		13.7–34.7	24.0	8.4	24–89.3	48.8	27.5
Arguineguín (D1–D2)		11.7–59.4	35.5	33.7	7.1–16.9	12.0	6.9
Puerto de La Luz (A1–A5)	November (2008)	19.6–28.4	23.2	3.5	10.1–51.6	29.3	17.5
Club Náutico (A6–A9)		40–47.5	43.7	3.1	46.9–72.1	57.7	11.3
Muelle Deportivo (A10–A14)		20.6–80.8	44.8	23.9	12.4–50.5	23.9	15.5
Mogán (B1–B4)		10.1–25	16.9	6.9	8.2–17.8	14.0	4.6
Puerto Rico (C1–C6)		2.4–15.2	7.7	5.0	10–54.2	27.4	15.6
Arguineguín (D1–D2)		22.1–31.2	26.6	6.5	18.8–19.7	19.2	0.6

[a] below the limit of quantification.
[b] not calculated.

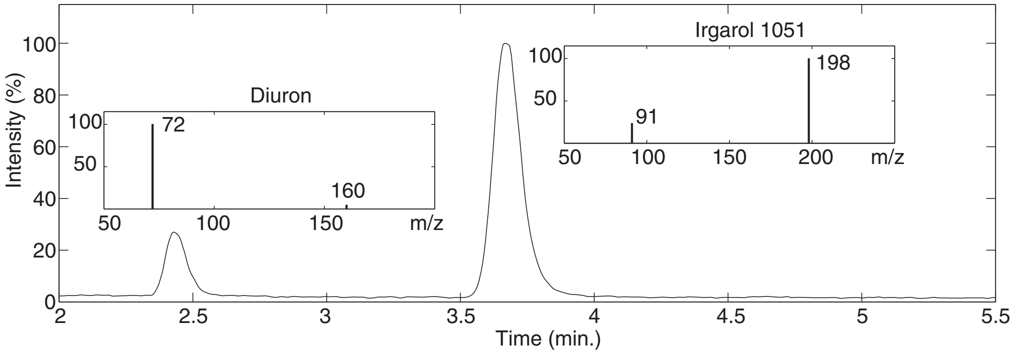

Figure 3. Total ion current (TIC) chromatogram corresponding to real samples coming from the Puerto Rico marina (point C1). The presence of Diuron and Irgarol 1051 can be observed as the, first and second peak respectively. The small boxes represent selected ions measured under the MRM mode present in each peak.

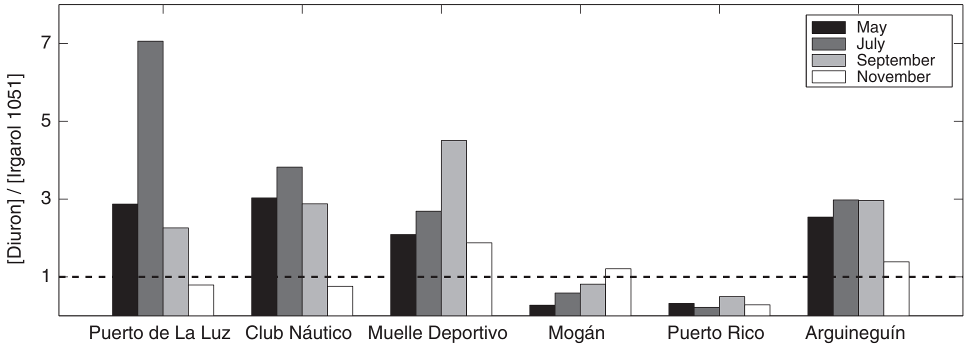

Figure 4. Evolution over time of the Ratio between Diuron and Irgarol 1051 (Diuron/Irgarol 1051) for each harbour.

in south-east Spain [10]. The concentrations measured in this study concord with values found in the Spanish Mediterranean region [44,45].

Figure 3 shows a TIC chromatogram and spectrum with selected ion monitoring under the MRM mode of the C1 sample collected in May. This figure denotes the presence of Diuron and Irgarol 1051.

The Puerto de La Luz is a commercial harbour with an area on a higher level where the pollutants possibly disperse. This may explain the low levels of both biocides found, although at point A1, opposite a shipyard, high values of Diuron were measured.

Irgarol 1051 levels gave highest values in November in the Puerto de La Luz (up to $51\,\mathrm{ng\,L^{-1}}$) and the Club Náutico (up to $72\,\mathrm{ng\,L^{-1}}$) (Table 3). As reported in previous studies, a strong polluting input may be derived from shipyard activities in the coldest months [46]. In contrast, the highest levels in Puerto Rico and Mogán were detected in the summer, when tourism increases.

With respect to the ratio between Diuron and Irgarol 1051 concentrations (Figure 4), values higher than 1 were obtained for all the ports, with the exception of Mogán and Puerto Rico. This does not tally with the results obtained in others work [22,25]. On the other hand, in November, the ratio decreases for the Puerto de La Luz, Arguineguín, the Club Náutico and the Muelle Deportivo from values higher than 1 to values close to 1.

Dichlofluanid and TCMTB were not found in the samples analysed. Dichlofluanid has been measured in seawater in other locations such as the coast of Spain [7] and in Greek marinas [47]. This compound offers a high degradation rate due to its instability in alkaline aqueous media such as seawater, and presents low solubility with an elevated octanol/water coefficient (log Kow = 3.7). These characteristics make it difficult to measure Dichlofluanid in real seawater samples, in spite of its widespread use. With respect to the occurrence of TCMTB, this compound has been previously investigated in other areas and has been not detected in seawater samples [7,9,25,36,38].

Several studies have proved the severe toxicity of Irgarol 1051 for aquatic autotrophs. Levels over 136 ng L^{-1} may cause serious damage to some phytoplanktonic algae such as the freshwater diatom *Navicula pelliculosa* [48], whereas concentrations as low as 63 ng L^{-1} may decrease the photosynthetic activity of periphyton communities [41]. Levels of 180 ng L^{-1} affect the photosynthetic efficiency of *Zostera marina* [49]. With respect to Diuron, concentrations in the range of 100 to 1000 ng L^{-1} significantly limit the photosynthesis in the seagrass species *Halophila ovalis* and *Zostera capricorna* [50]. In addition, the combination of both biocides may provoke synergic [51] or additive effects [16].The concentration found in the coastal waters of Gran Canaria exceeded these levels in some cases and, as summarised above, similar or greater concentrations are frequently given. For this reason, several countries have already limited or forbidden the antifoulant use of Irgarol 1051 and Diuron. The Dutch authorities have established a maximum permissible concentration (MPC) of 430 ng L^{-1} for Diuron and proposed 24 ng L^{-1} for Irgarol 1051 [35]. In our study, no sample presented a higher value than the MPC for Diuron, but 40% of the samples were over the MPC for Irgarol 1051.

4. Conclusions

The concentration of biocides leached from antifouling paint coatings have been monitored in many developed countries. Up to the present, no data have been available with respect to the concentration of booster biocides in the coastal waters of the island of Gran Canaria (the Canary Islands, Spain). The toxicity of these compounds may affect primary producers, thus making it necessary for them to be monitored and controlled.

In this study, a solid phase extraction (SPE) procedure coupled with LC/MS-MS was used to determine the presence of common booster biocides in the coastal waters of the island of Gran Canaria. The results of these measurements indicated that the levels of biocides found (Diuron and Irgarol 1051) are comparable with those detected in other locations. These concentrations often exceeded the limits fixed under the legislation of other countries. There was also an observed trend over time in the levels of booster biocides. High concentrations of Irgarol 1051 were measured in July in Mogán and Puerto Rico, and in November at the Puerto de La Luz and the Muelle Deportivo. The highest levels of Diuron, on the contrary, were found in the marinas of Las Palmas de Gran Canaria at the end of the summer.

Acknowledgements

This study was funded by the Spanish Ministry of Education and Science, Project No. CTM2006/06503. Our thanks go to the Las Palmas port authorities and to the Puerto Rico and Mogán port management for their support.

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