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Antifouling paint booster biocides (Irgarol 1051 and diuron) in marinas and ports of Bushehr, Persian Gulf

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ABSTRACT

In the present study, antifouling paint booster biocides, Irgarol 1051 and diuron were measured in ports and marinas of Bushehr, Iran. Results showed that in seawater samples taken from ports and marinas, Irgarol was found at the range of less than LOD to 63.4 ng L^{-1} and diuron was found to be at the range of less than LOD to 29.1 ng L^{-1} (in Jalali marina). 3,4-dichloroaniline (3,4-DCA), as a degradation product of diuron, was also analyzed and its maximum concentration was 390 ng L^{-1}. Results for analysis of Irgarol 1051 in sediments showed a maximum concentration of 35.4 ng g^{-1} dry weight in Bandargah marina. A comparison between the results of this study and those of other published works showed that Irgarol and diuron pollutions in ports and marinas of Bushehr located in the Persian Gulf were less than the average of reports from other parts of the world.

Organic booster biocides are used as additives in copper-based antifouling paints to prevent the settlement and growth of marine organisms on submerged structures (Konstantinou and Albanis, 2004). Biofouling produces some negative environmental and economical consequences, such as increases in fuel consumption and corrosion processes as well as the potential for the introduction of foreign species in new ecosystems (Lewis et al., 2003). Worldwide, around 18 compounds are currently used as antifouling paint booster biocides with differing degrees of regulation. These chemicals are alternatives to organotin-based antifoulants whose use has been completely banned in 2004 due to their high toxicity and their effects on aquatic organisms (Mackie and Lloyd, 2002). Irgarol 1051 (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) and diuron (3-(3,4-dichlorophenyl)-1,1-dimethyl urea) have been widely used among others because of their high effectiveness as a growth inhibitor of marine and freshwater algae (Readman, 1999).

Diuron has been predominately used for weed control on land as a substituted urea herbicide since the 1950s. It is also widely applied for non-agricultural applications including vegetation control in industrial sites and rights of way along power lines, roads, railways, and buildings (Moncada, 2004). Irgarol and diuron (with aqueous solubility values of 7 and 36.4 mg L^{-1} and log K_{ow} 3.95 and 2.85, respectively) exert their antifouling action by inhibiting photosynthesis and impairing electron transport within chloroplasts (Dahl and Blanck, 1996; Alyuruk and Cavas, 2013). Both compounds are much more toxic to phytoplankton than other aquatic species (Dahl and Blanck, 1996; Malato et al., 2002). Irgarol appears to be especially toxic to the freshwater diatom (5 day EC_{50} 136 ng L^{-1}) and the freshwater macrophytes (14 day EC_{50} 0.017 ng L^{-1}) (Lambert et al., 2006). The environmental risk limits for Irgarol in water (ERL_{water}) and sediment ($ERL_{sediment}$) are 24 ng L^{-1}

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and 1.4 ng g^{-1}, respectively (Wezel and Vlaardingen, 2004). The Dutch National Institute of Public Health and the Environment suggested a maximum permissible concentration for Irgarol and diuron of 29 and 430 ng L^{-1}, respectively (Lamoree et al., 2002). Due to the Irgarol and diuron harmful effects on the marine ecosystem, some countries, such as the United Kingdom, Denmark and Sweden, have forbidden the use of Irgarol, whereas diuron has been also prohibited in UK and Netherlands (Thomas and Brooks, 2010).

In an overview, elimination (volatilization, chemical hydrolysis, biodegradation, photo-degradation) and accumulation rates (sedimentation and uptake by biota) of chemicals are the two phenomena affecting observed levels. Irgarol and diuron are resistant to hydrolysis and they are stable during 17 days of sunlight irradiation (Arai et al., 2009). Moreover, bacterial biodegradation of Irgarol 1051 and diuron are of minor importance (their initial concentration of 0.1 mg L^{-1} scarcely changed after 60 days) (Arai et al., 2009). 2-methylthio-4-tert-butylamino-6-amino-s-triazine (M1) and 3,4-dichloroaniline (3,4-DCA) are the main metabolites of Irgarol and diuron, respectively (Arai et al., 2009). Nevertheless, results of different studies indicate that generally Irgarol (with half-life ranging from 100 to 350 days) and diuron (with half-life ranging from 43 to 2180 days) are fairly stable compounds in seawater (Hall et al., 1999; Thomas et al., 2002; Moncada, 2004). On the other hand, sorption of these organic pollutants onto settling particulate matters is not only responsible for their concentration reducing in the water column, but also is the principal pathway of their accumulation in sediments. A modular estuarine mesocosm experiment revealed that after 35 days of Irgarol exposure, only 7% of parent compound remained unchanged in the water column and 75% accumulated in the mesocosm sediments (Sapozhnikova et al., 2009). Generally, in sediments, it has been demonstrated that degradation is slow even under aerobic conditions, resulted in booster biocides' elevated persistency in sediments. As a result, the sediments may serve as storage and release sources of pollutants (Thomas et al., 2003; Zhou, 2008). Studies conducted by Tolhurst et al. (2007) and Voulvoulis et al. (2002) showed that disturbance of sediments contaminated with Irgarol can cause desorption of Irgarol with the rate of 1.9–2.4% per 24 h.

Environmental monitoring of Irgarol 1051 and diuron has been extensive worldwide, in order to assess the risks to the environment. Since Irgarol and diuron have also agricultural uses, as a result their presence in the aquatic and estuarine environments cannot be attributed solely to the use of antifouling paints. Various studies on detection and distribution of Iragrol and diuron have been conducted in different areas including Northern Europe (Netherlands, Germany, England and Sweden) (Lamoree et al., 2002; Biselli et al., 2000; Thomas et al., 2001; Haglund et al., 2001), Mediterranean Sea (Spain, France and Greece) (Hernando et al., 2001; Tolosa et al., 1996; Sakkas et al., 2002), America (Bermuda and USA) (Konstantinou and Albanis, 2004; Sapozhnikova et al., 2013), and Australia (Konstantinou and Albanis, 2004). Moreover, some studies have been performed in Asia such as South Korea (Kim et al., 2014), Japan (Balakrishnan et al., 2012), Singapore (Basheer et al., 2002) and Malaysia (Rashid Ali et al., 2013) but to date no monitoring survey of these new antifouling biocides has yet been reported in the Persian Gulf (Iran). This study therefore presents the baseline data for occurrence and distribution of Irgarol 1051, diuron and its metabolite (3,4-DCA) in ports and marinas of Bushehr (northwest of the Persian Gulf, Iran).

Bushehr peninsula is located in a humid subtropical region. It lies near the head of the Persian Gulf at the northern part of a flat connected with the mainland by tidal marshes (Sheppard et al., 2010). The wide range of seasonal variation of seawater temperature and elevated salinity are important environmental stressors, which could enhance effects of pollution on sensitive marine ecosystems of this area (Schiedek et al., 2007). Bushehr (28.58 N and 50.50 E) is one of the most important ports in the Persian Gulf with a remarkable situation since it is an export market for the agricultural crops of Iranian southern provinces (e.g. Bushehr and Fars provinces) and is one of the largest regional fishing ports of Iran.

Table 1
Sampling location information.

Location	Latitude	Longitude	Depth (m)
Jalali marina	28° 55.233′N	50° 48.506′E	3.7
Jalali marina	28° 55.172′N	50° 48.442′E	3.1
Open seawater 1 (Persian Gulf)	28° 52.908′N	50° 49.922′E	4.7
Open seawater 1 (Persian Gulf)	28° 52.698′N	50° 49.690′E	6.0
Bandargah marina	28° 49.228′N	50° 54.525′E	0.6
Bandargah marina	28° 49.382′N	50° 54.484′E	2.0
Open seawater 2 (Persian Gulf)	28° 56.956′N	50° 48.299′E	5.6
Open seawater 2 (Persian Gulf)	28° 56.831′N	50° 47.781′E	6.2
Jofre marina	28° 58.298′N	50° 49.359′E	0.7
Jofre marina	28° 58.372′N	50° 49.363′E	1.6
Jabri marina	28° 58.822′N	50° 50.733′E	1.6
Bushehr port internal canal	28° 59.777′N	50° 49.978′E	12.3
Sadra Ship building factory	28° 58.869′N	50° 51.681′E	4.4
Sadra Ship building factory	28° 58.549′N	50° 51.452′E	4.7
Solhabad marina	28° 58.740′N	50° 50.997′E	2.3
Bushehr port internal canal	28° 58.873′N	50° 50.879′E	5.1

Water and sediment samples were collected from 16 stations located in the marinas and ports of Bushehr peninsula, northwestern Persian Gulf in October of 2013 at the end of the peak of the shrimp fishing (Table 1). Various sampling sites such as Bushehr port internal canal, marinas and ports for small fishing boats' and dhows' mooring spaces, and shipyards were deliberately chosen as study areas because contamination from antifouling biocides was expected to be high. In locations in which it was possible, samples were collected from the areas dedicated to small boats (<10 m) and dhows (10–30 m). However, not both vessel classes were present in every location. Three individual water samples were collected at each station. Water samples were taken from approximately 0.5 m below the surface using a Niskin bottle sampler (2 L) and transferred into the pre-cleaned 1 L amber glass bottles. The samples were then kept under 4 °C and brought to laboratory for analysis. Three replicate sediment samples were collected at each site, at 1 m distance from each other and analyzed individually. Surface sediment samples at a water depth between 0.6 and 12.3 m were collected using a Van-Veen grab sampler and transferred into the pre-cleaned aluminum containers (500 g) and stored in a freezer at −25 °C until analysis. Measurements of salinity, conductivity, pH and dissolved oxygen (DO) were taken in situ using a Hach HQ40d multimeter with related probs.

Total organic matter (TOM) was measured for each sediment sample as described elsewhere (Gaspare et al., 2009). For grain size assessments, 10 mL of tetra sodium diphosphate decahydrate (3% *w*/*v*) was added into the 1 g of homogenized and freeze-dried sediment. After 20 min of stirring, the mixture was introduced into a laser scattering particle size distribution analyzer (HORIBA, LA-950, Japan & France).

Irgarol 1051, diuron and 3,4-dichloroaniline were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Analysis of water samples was performed using microfunnel-supported liquid-phase microextraction method (MF-LPME) as previously explained by Saleh et al. (2014). Briefly, a volume of 300 mL of seawater sample was introduced into the glass vessel. A small magnetic rod was inserted into the vessel. The vessel was closed with the stopper through which passed the glass microfunnel. The upper part of the funnel was filled with a 400 μL of toluene by using a syringe. The sample compartment was stirred at 240 rpm with a magnetic stirrer. After the extraction, the extractant was withdrawn by using a syringe and its solvent evaporated under the gentle stream of nitrogen at room temperature. The residual re-dissolved in 50 μL methanol, diluted to 100 μL with deionized water and injected into the HPLC loop followed by analysis.

Samples of sediment were freeze-dried by an Operon freeze-dryer (5503-Korean) for 72 h. Analysis of sediments was carried out using ultrasound-assisted extraction (UAE) followed by dispersive liquid–liquid microextraction (DLLME) according to the procedures of Lambropoulou et al. (2003) and Rezaee et al. (2006) with some