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Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints

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Abstract

Two major antifouling biocides used worldwide, Irgarol 1051 and diuron, and their degradation products in Shoreham Harbour and Brighton Marina, UK were studied during 2003–2004. The highest concentrations of Irgarol 1051 were 136 and 102 ng L^{-1} in water and 40 and 49 ng g^{-1} dry weight in sediments for Shoreham Harbour and Brighton Marina, respectively. As the degradation product of Irgarol 1051, M1 was also widespread, with the highest concentration of 59 ng L^{-1} in water and 23 ng g^{-1} in sediments in Shoreham Harbour, and 37 ng L^{-1} in water and 5.6 ng g^{-1} in sediments in Brighton Marina. The target compounds showed enhanced concentrations during the boating season (May–July), when boats were being re-painted (January–February), and where the density of pleasure crafts was high. Overall, the concentration of Irgarol 1051 decreased significantly from late 2000 to early 2004, indicating the effectiveness of controlling its concentrations in the marine environment following restricted use. Diuron was only detected in 14% of water samples, and mostly absent from sediment samples.

Keywords: Antifouling paints; Irgarol 1051; Diuron; Metabolites; Seawater; Marine sediment

1. Introduction

The serious environmental problems caused by the extensive use of tributyltin in antifouling paints, e.g. imposex in dogwhelks, resulted in the introduction of alternative compounds for the protection of ship hulls. Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) and diuron (1-(3,4 dichlorophenyl)-3,3 dimethyl urea) are two of such substances, which have been used worldwide as active ingredients for this purpose. Prior to September 2000, eight organic compounds including Irgarol 1051 and diuron were allowed for use in antifouling paints in the UK. After September 2000, as a result of 98/8/EE directive implementation, restrictions concerning the use of such substances in antifoulants were instituted. According to these restrictions, antifouling paints for use in small vessels are allowed to contain only the substances dichlofluanid, zineb and zinc pyrithione. Irgarol 1051 was approved for use on larger (>25 m) vessels up to July 2003 (Bowman et al., 2003), whereas diuron is no longer approved for use as an active ingredient in antifouling paints on vessels of any size.

It is well known that the more stable in the environment a compound is the more effective the antifouling paint becomes because the protection of the vessels lasts longer. For this reason stable compounds are preferred in paint industries. As a result, even after a booster biocide is banned it may still be detected in the marine environment. Furthermore, degradation products of these compounds may also be detected as a result of natural transformation processes such as photodegradation and biodegradation (Lam et al., 2005).

Although Irgarol 1051 is not considered to be easily degraded in seawater with a half-life of approximately 100 days, recent studies (Liu et al., 1999) show that it can be degraded to form its main metabolite M1 (2-methylthio-4-*tert*-butylamino-*s*-triazine) through *N*-dealkylation. Concentrations of Irgarol 1051 in seawater worldwide vary between non-detectable and low parts

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per billion. Concentrations up to 4.2 μg L^{-1} have been detected in coastal areas (Basheer et al., 2002), whereas in the UK the highest concentration observed is 1.4 μg L^{-1} (Thomas et al., 2001). In sediment samples concentrations as high as 1 μg g^{-1} have been detected in marinas (Boxall et al., 2000). The levels of M1 are up to 1.9 μg L^{-1} (Okamura et al., 2000) and 0.003 μg g^{-1} (Ferrer and Barceló, 2001) for seawater and marine sediment respectively, which are generally lower than those of Irgarol 1051 indicating slow degradation rates of the parent compound.

Although considered to be relatively persistent in seawater, diuron may be degraded by *N*-dimethylation under aerobic conditions to metabolites including DCPMU (1-(3,4 dichlorophenyl)-3 methyl urea), DCPU (1-(3,4 dichlorophenyl) urea) and DCA (3,4 dichloroaniline). Diuron concentrations up to 6.7 μg L^{-1} (Thomas et al., 2001) and 1.4 μg g^{-1} (Thomas et al., 2000) have been detected in seawater and marine sediment samples, whereas among its degradation products only DCPMU and DCPU have been detected in seawater at concentrations ranging between 0.001 and 0.078 μg L^{-1} and between 0.001 and 0.006 μg L^{-1} respectively (Thomas et al., 2002). DCPMU has also been detected in sediments at concentrations below 0.025 μg g^{-1} (Martinez and Barceló, 2001).

The aim of this study was to investigate the levels of Irgarol 1051, diuron and their main degradation products (M1, DCPMU, DCPU and DCA) in Shoreham Harbour and Brighton Marina, UK, following the restrictions of their use in antifouling paints. Spatial and temporal variations of these compounds in seawater and sediment were investigated. Furthermore, the relationship between the physicochemical properties of seawater and marine sediment and the concentrations of the target compounds was also examined in order to identify geochemical controls.

2. Materials and methods

2.1. Chemicals

Analytical standards of Irgarol 1051, diuron and its degradation products were supplied by Dr. Ehrenstorfer (Germany). M1 was a gift of both the Centre for Environment, Fisheries and Aquaculture Science (Essex, UK) and Ciba-Geigy (NY, USA). Atrazine-d_5 from QMX Laboratories (UK) was used as the internal standard. Ultrapure and HPLC-grade water was prepared in the laboratory with a Maxima HPLC/LS system supplied by ELGA (UK) and a MilliQ/MilliRO Millipore system (USA). Stock solutions in methanol were prepared at 1000 mg L^{-1} for Irgarol 1051, diuron and their degradation products, and at 500 mg L^{-1} for atrazine-d_5. The organic solvents acetonitrile, dichloromethane, methanol, ethyl acetate and acetone were of glass-distilled grade (Rathburns, Scotland). HPLC grade acetonitrile and methanol were purchased from Merck (Germany).

2.2. Description of study areas

Shoreham Harbour (Fig. 1a) is situated on the South Coast of England in West Sussex and located 5 miles to the West of the city of Brighton and Hove. Inside the harbour and above the main channel is situated the Lady Bee Marina with berths for 120 vessels. Another small marina called Emerald Quay is situated on the West of the harbour. Brighton Marina (Fig. 1b) is situated half a mile from the centre of Brighton. It is the largest marina in the UK, at over 126 acres with berths for 1300 vessels. The marina is subject to winds causing sand banks to form, thus it requires annual dredging (Bowman et al., 2003).

2.3. Sample collection

Sub-surface (0.5 m) seawater samples were collected in pre-cleaned amber glass bottles (2.5 L). The bottles were placed in a stainless steel frame fitted with a spring-loaded PTFE stopper that was opened and closed underneath water so as to minimise surface microlayer. The samples were then filtered through 0.7-μm GF/F filter papers (Whatman), spiked with 100 ng of atrzine-d_5, and stored at 4 °C till further processing. Measurements of salinity, conductivity and pH were taken in situ using a WTW Multiline P4 Universal Meter with a Tetra Con 325 salinity probe and a SenTix 41–3 pH electrode. Surface sediment samples were collected using a hand held Van Veen sediment grab. The sediment samples were transferred to pre-cleaned glass sediment jars and stored at −18 °C till analysis.

Sample collection was performed from March 2003 to February 2004. Three sampling campaigns took place in Brighton Marina (03/2003, 12/2003 and 02/2004) where samples were collected from 15 sites throughout the marina, whereas in Shoreham Harbour 9 sampling trips were undertaken (03/2003, 05/2003, 07/2003, 08/2003, 10/2003, 11/2003, 12/2003, 01/2004, 02/2004) where samples were taken from 9 sites.

2.4. Characterisation of marine sediments

In order to measure the pH of marine sediments, each sample (4 g dry weight) was placed in a test tube to which 5 mL of pure water was added. The test tubes were closed and agitated vigorously for 5 min. Then, another 5 mL of pure water was added to the test tube and the samples mechanically agitated for 15 min. The samples were left for 10 min before the pH of the supernatant was measured using the WTW Multiline P4 Universal meter.

The particle size distribution of the sediment samples was accomplished by sieving. Samples (10 g dry weight) were sequentially passed through two sieves with pore size of 180 and 63 μm so as to obtain three size fractions: >180 μm, 180–63 μm and <63 μm respectively.

For the determination of organic carbon content appropriate tin boats (8×5 mm) were cleaned with chloroform, acetone and finally pure water. Sediment samples (10 mg) in triplicate were accurately weighed into the boats, and acidified with sulphuric acid for 24 h so as to remove carbonate. Then the tin boats were closed and placed into the autosampler of a Carlo Erba elemental analyser for the analysis. For the calibration of the instrument an external standard of acetanilide (Thermoquest, Italy) was used. Results were validated by the use of a Certified Reference Material (Mess-2) from the National Research Council of Canada, which is a marine sediment containing 2.14±0.03% organic carbon.

2.5. Sample extraction and analysis

Isolation of the target compounds from seawater samples was performed using a solid-phase extraction (SPE) procedure, following a method developed by Gatidou et al. (2005). Briefly, SPE cartridges (Isolute ENV^+, 1 g) were activated with 10 mL each of methanol and ultrapure water. The extraction was performed at a flow rate of 10 mL min^{-1}. Following extraction, the cartridges were washed with 4×2.5 mL of ultrapure water, dried for 3 min and eluted with 3×2 mL of methanol. The eluents were evaporated to dryness under a gentle stream of nitrogen (35 °C) and re-dissolved in 300 μL of ethyl acetate.

In order to increase the preconcentration factor, a volume of 2 L was extracted for the determination of Irgarol 1051 and M1 using SPE cartridges with a high sorbent mass (1 g). The recoveries of the two compounds at three levels (10, 100, 1000 ng L^{-1}) ranged between 82.0% and 96.4% for M1 and from 94.6% to 116% for Irgarol 1051. The method remained repeatable ($n=6$) and reproducible ($k=3$, $n=20$) with RSD ≤ 2.5%. The limits of detection (LODs) were found to be 0.5 and 3.1 ng L^{-1} for M1 and Irgarol 1051, respectively.

Sediment samples for the determination of Irgarol 1051 and M1 were extracted using microwave-assisted extraction as described previously (Gatidou et al., 2004b). Briefly, 3 g of marine sediment spiked with 100 ng of internal standard were extracted with 30 mL of water at 115 °C for 10 min using a MARS-X microwave accelerated extraction system. The LODs of the two compounds were 0.9 and 1.7 ng g^{-1} (dry weight) for M1 and Irgarol 1051.