Antifouling biocides in water and sediments from California marinas

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Abstract

Irgarol 1051 is a common antifouling biocide and is highly toxic to non-target plant species at low ng/L concentrations. We measured up to 254 ng/L Irgarol in water and up to 9 ng/g dry weight Irgarol in sediments from Southern California recreational marinas. Irgarol's metabolite, M1, concentrations were up to 62 ng/L in water and 5 ng/g dry weight in sediments. Another antifouling biocide, diuron, reached up to 68 ng/L in water and 4 ng/g dry weight in sediments. The maximum Irgarol concentrations in water were greater than the Irgarol concentration recommended as the plant toxicity benchmark (136 ng/L), suggesting that Irgarol concentrations may be high enough to cause changes in phytoplankton communities in the sampled marinas. Irgarol concentrations measured in sediments were greater than calculated Environmental Risk Limits (ERL) for Irgarol in sediments (1.4 ng/g). Antifouling pesticide accumulation in sediments may present a potential undetermined risk for benthic organisms.

Introduction

Irgarol 1051 (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) is an antifouling booster biocide widely used in copper-based paints to prevent algal growth on submersed boat surfaces. It is a triazine-based herbicide, with relatively low water solubility (7 mg/L) (Konstantinou and Albanis 2004). Because of its intended activity as an antifouling biocide, Irgarol is continuously released into surrounding waters from the paints applied to boat hulls. Irgarol is relatively persistent in seawater with a reported half-life ranging from 100 to 350 days (Hall 1999, Thomas *et al.* 2002). It degrades in seawater forming its major metabolite, M1 (2-methylthio-4-tert-butylamino-6-amino-s-triazine) (Okamura *et al.* 2000). M1 is relatively stable as well, with a reported seawater half-life ranging from 82 (Thomas *et al.* 2002) to over 200 days (Okamura *et al.* 2000). Irgarol has a relatively high Log K_{ow} = 3.95 (Konstantinou and Albanis 2004), suggesting its tendency to accumulate in sediments. A modular estuarine mesocosm experiment showed 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). Irgarol's metabolite, M1, also accumulated in the mesocosm sediments with an average mass balance of 17% of the Irgarol amount added to the mesocosm. In general, 35 days after the exposure, mesocosm sediments contained Irgarol and M1 amounts approaching 100% of the initial Irgarol dose, suggesting that estuarine sediments may serve as a depository for these chemicals. M1 has been shown to have a long half–life in sediments of 260 days (Thomas and Brooks 2010).

Irgarol is the most widely detected antifouling booster biocide worldwide. Reported concentrations range from <1 ng/L to µg/L levels (Konstantinou and Albanis 2004). The highest concentration of Irgarol reported to date was 4,200 ng/L in water from Singapore in 2000 (Basheer *et al.* 2002). In the

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United States, up to 635 ng/L of Irgarol was reported from Florida (Zamora-Ley *et al.* 2006), and up to 1,816 ng/L from Maryland in 2004 (Hall *et al.* 2005). Previous studies reported Irgarol concentrations from San Diego area recreational marinas as high as 304 ng/L in 2005 (Sapozhnikova *et al.* 2007). In 2006, Irgarol concentrations up to 712 ng/L were recorded from recreational marinas throughout Southern and Northern California (Sapozhnikova *et al.* 2008). However, sediments were not analyzed in these studies from CA, FL and MD.

Irgarol is a photosystem II inhibitor, and highly toxic to non-target organisms at low ng/L levels (Hall 1999). Calculated Environmental Risk Limit (ERL) for Irgarol in water is 24 ng/L and in sediments is 1.4 ng/g (van Wezel and van Vlaardingen 2004). ERL represents concentration above which the potential risk of the chemical to the ecosystem may occur. Reported Irgarol's LC_{50} for green algae *Navicula pelliculosa* is 136 ng/L (Hall 1999), this value is used as the plant toxicity benchmark.

In 2003, three European countries (the United Kingdom, Sweden and Denmark) restricted Irgarol use on boats <25 m in length. The recent study showed that Irgarol and M1 aqueous concentrations from the United Kingdom significantly decreased in the following years (Gatidou *et al.* 2007), illustrating the effectiveness of the legislation. While concentrations in water decreased significantly, concentrations of both Irgarol and M1 remained relatively high in sediments (40 - 49 ng/g dry weight Irgarol, 5.6 - 22.7 ng/g dry weight M1). Irgarol is persistent in sediments, either bound to paint particles scrubbed from boats or adsorbed to sediments (Thomas *et al.* 2003). Using a linear nine-box model, Ranke (2002) calculated that residence time for Irgarol in marine systems is over 10 years (Ranke 2002). Zhou (2008) suggested that when paint residues containing Irgarol accumulate in organic rich sediments, the latter may serve as storage and release sites for Irgarol, and that Irgarol may be classified as a persistent organic pollutant due to its long half-life (Zhou 2008). Tolhurst *et al*. (2007) reported that disturbance of sediments contaminated with Irgarol can cause desorption of Irgarol and its release to surrounding water (Tolhurst *et al.* 2007). Desorption studies by Volvoulis *et al*. (2002) showed that Irgarol desorption rate from sediments is 1.9 to 2.4% per 24 hours (Voulvoulis *et al.* 2002).

The common agricultural herbicide, diuron, is also used as an organic booster biocide in some antifouling paint formulations. Diuron is a broad-spectrum herbicide typically used in agriculture, and applied to a variety of fruits and crops. It is also widely used for non-agricultural applications, such as vegetation control in industrial sites and rights of way along power lines, roads, railways, and buildings (Moncada 2004). Diuron is persistent in seawater with a reported half-life ranging from 43 to 2,180 days (Moncada 2004). The Dutch National Institute of Public Health and the Environment proposed a maximum permissible concentration for diuron of 430 ng/L (Lamoree *et al.* 2002). Previous studies showed diuron's low-level widespread contamination (5 - 27 ng/L) in recreational marinas from California (Sapozhnikova *et al.* 2007, 2008).

The purpose of this study was to evaluate Irgarol 1051, its major metabolite M1 and diuron concentrations in surface water and sediments from Southern California recreational marinas and to estimate the partition of these chemicals into marina sediments. To our knowledge, this is the first study reporting these antifouling biocides in sediments from recreational marinas in the United States.

METHODS

Chemicals

Methanol, acetone, and HPLC-grade water were purchased from Burdick & Jackson (Muskegon, MI, USA). Irgarol 1051 (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine, 99.0% purity), was purchased from Ciba Specialty Chemicals Inc. (Tarrytown, NY, USA). 2-methylthio-4-tert-butylamino-6-amino-s-triazine (M1 or GS26575) standard was a kind gift from Dr P. Gardinali, Florida International University. Diuron standard (purity 99.0%) was purchased from ChemService (West Chester, PA, USA). Chlorotoluron N,N-dimethyl-d_6 (purity 98.0%), used as an internal standard, was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Ammonium formate and formic acid were purchased from Sigma Aldrich (St. Louis, MO). Sodium sulfate, 10-60 mesh, ACS grade for pesticide and residue analysis was from Fisher Scientific (Pittsburg, PA).

Sampling

Forty-three samples of water and corresponding sediments were collected from ten recreational marinas from Southern California (Figure 1) in the summer of 2008. Water samples were collected

0.5 m below the surface using a Niskin bottle sampler. Sediment samples were collected using a modified Van-Veen grab, compositing the top 5 cm of undisturbed sediment (Schiff 2000).

Sample Preparation

Water samples (0.5 L) were spiked with 100 ng of the internal standard and extracted with C18 (1 g, 6 ml) Solid Phase Extraction (SPE) cartridges (Phenomenex, Torrance, CA) using a vacuum manifold as previously described (Sapozhnikova *et al.* 2008).

Sediment samples (10 g) were mixed and ground with anhydrous sodium sulfate (previously fired at 450°C), spiked with 100 ng of the internal standard and extracted using Accelerated Solvent Extraction (ASE, Dionex 200, Sunnyvale, CA) with 100% dichloromethane at 120°C and 2,000 psi (Sapozhnikova *et al.* 2009). The resulting extract was filtered through fired anhydrous sodium sulfate, evaporated to dryness, and reconstituted in 1 mL of methanol and HPLC water mixture for LC-MS-MS analysis.

Quality Assurance/Quality Control

For quality control, each batch of six unknown water samples contained one reagent blank (HPLC water), one replicate of an unknown sample, one matrix spike (a replicate of an unknown sample from the batch spiked with a known amount of antifouling chemicals), and one matrix spike duplicate. Matrix spike recoveries were 102 ±18% (Irgarol), 109 ±15% (M1) and 127 ±10% (diuron) for fortified water samples at 100 ng/L. The percent deviations of antifouling chemicals found in replicate water samples were: 2 - 16% (Irgarol), 1 - 18% (M1), and 5 - 18% (diuron).

Sediment samples were extracted in batches of 16 samples, plus one reagent blank, one replicate sample, one matrix spike, and one matrix spike duplicate. Matrix spike recoveries for fortified sediments were 89 ±16% (Irgarol), 99 ±8% (M1) and 91 ±13% (diuron) for a spike concentration of 10 ng/g wet weight. Concentrations of Irgarol and M1 found in replicate sediment samples were within 19% (Irgarol) and 21% (M1). Dry weights were determined gravimetrically. Instrument performance was validated by injecting a continuous calibration

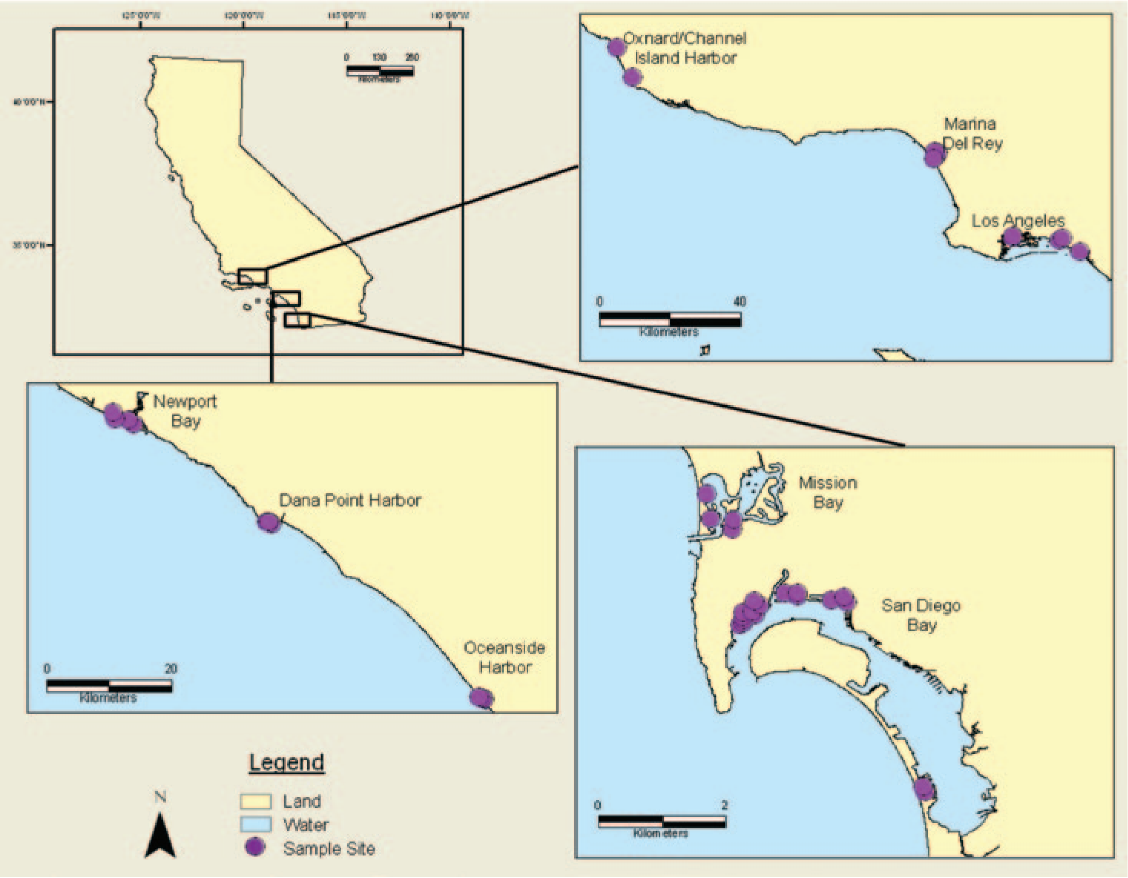

Figure 1. Sampling locations.

verification standard – a middle point of the calibration curve after every ten samples.

Method detection limits (MDLs) were calculated based on weighted least-squares regression (Zorn *et al.* 1997) and were: 1 ng/L (Irgarol and M1), 2 ng/L (diuron) in water samples and 0.3 ng/g dry weight for all analytes in sediment samples.

Statistical Analysis

Statistical data analysis was performed with SAS System for Windows version 9.1.3 (SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was conducted to determine possible differences among analyte concentrations. Levene's test of homogeneity was conducted to verify homogeneity of variance. Shapiro–Wilk W test was used to check for normality. Tukey–Kramer test was used for multiple comparisons with $\alpha = 0.05$ significance.

RESULTS AND DISCUSSION

Antifouling chemicals in water

Irgarol concentrations in water ranged from 2 to 254 ng/L (average 67 ng/L), M1 concentrations from <1 ng/L to 62 ng/L (average 18 ng/L) and diuron concentrations from <2 ng/L to 68 ng/L (average 6 ng/L) in water samples. The highest concentration of Irgarol was measured in Dana Point Harbor marina (254 ng/L). Dana Point Harbor is a relatively large marina with up to 2500 pleasure crafts, and there are no significant freshwater inputs into Dana Point Harbor other than storm drains servicing the local area.

The highest average Irgarol concentrations were measured in Dana Point Harbor marina (202 ±71 ng/L, n = 4), followed by Newport Bay marina (107 ±27 ng/L, n = 4), San Diego Bay marina (67 ±44 ng/L, n = 17) and Oceanside marina (54 ±64 ng/L, n = 3; Figure 2). Concentrations of Irgarol in Dana Point Harbor marina were significantly higher than in the other marinas ($p \leq 0.05$) except Newport Bay Marina.

The highest concentration of Irgarol metabolite, M1, was also measured in Dana Point Harbor marina at 62 ng/L. Concentrations of M1 were lower than the parent compound, but followed the same trend as Irgarol with highest average measured in Dana Point Harbor marina (52 ±17 ng/L), followed by Newport Bay marina (28 ±6 ng/L), San Diego Bay marina (19 ±13 ng/L) and Oceanside marina (13 ±14 ng/L; Figure 2). Concentrations of M1 in Dana Point Harbor marina were significantly higher than in Marina del Rey ($p = 0.001$), Mission Bay ($p = 0.001$), Oxnard/Channel I. Harbor ($p=0.002$), San Diego Bay ($p = 0.001$), and Oceanside Harbor ($p = 0.007$).

Diuron's highest concentration was measured in San Diego Bay marina (68 ng/L), with the second highest in Los Angeles/Long Beach marina (39 ng/L). In contrast to Irgarol and M1, average diuron concentrations were greatest in Los Angeles/Long Beach marina (35 ±6 ng/L), followed by San Diego marina (8 ±16 ng/L), Huntington Harbor marina (6 ng/L) and Newport Bay marina (4 ±2 ng/L; Figure 2). Diuron concentrations in Los Angeles/Long Beach marina were significantly greater than in Marina del Rey ($p = 0.043$) and Mission Bay ($p = 0.032$).

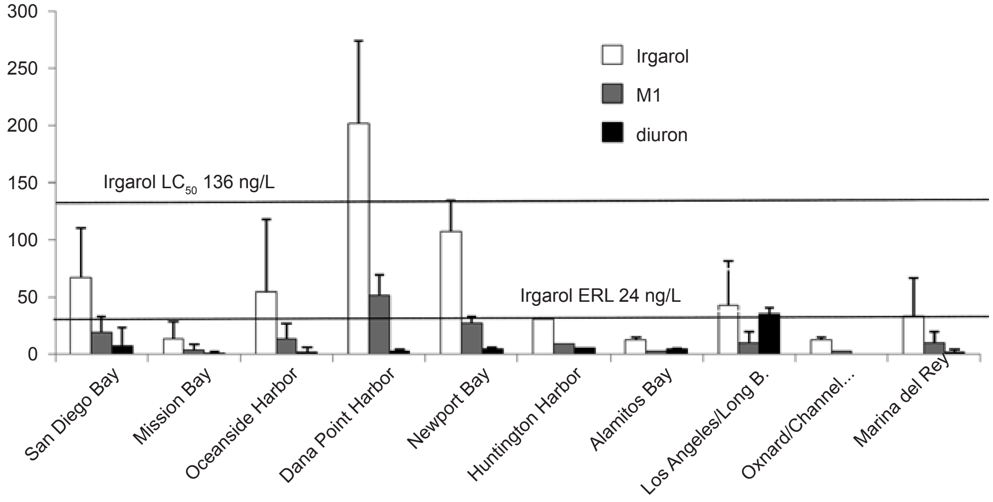

Figure 2. Antifouling chemical average concentrations in water samples, ng/L, error bars represent standard deviation.

Fourteen percent of water samples analyzed in this study had Irgarol concentrations exceeding the proposed plant toxicity benchmark 136 ng/L (Hall 1999) and seventy percent of Irgarol concentrations measured in water samples were greater than the suggested ERL of 24 ng/L, suggesting possible environmental risk in eight out of ten marinas in this study.

Temporal variations 2005 and 2008

In 2005, the maximum concentration of Irgarol was measured from Dana Point Harbor (304 ng/L) (Sapozhnikova *et al*. 2007), which was comparable with maximum concentrations of Irgarol from 2008 (254 ng/L). In 2005, antifouling chemicals were analyzed from four marinas in Southern California. The current study showed the same order of Irgarol concentrations among the four marinas as measured in 2005: the highest concentrations were found in Dana Point Harbor marina (average 202 ±71 ng/L), followed by San Diego Bay marina (average 67 ±44 ng/L), Oceanside Harbor marina (average 54 ±64 ng/L) and Mission Bay marina (average 14 ±15 ng/L; Figure 3).

In San Diego Bay marina, concentrations of Irgarol were 28 ng/L in 2005 and 67 ng/L in 2008; and not statistically different (p = 0.080; Figure 3). San Diego Bay is a deep water harbor, with the majority of shipping traffic related to military operations, tourism, and fishing. In the Mission Bay marina, Irgarol concentration increased slightly from 6 ng/L in 2005 to 14 ng/L in 2008. In Oceanside Harbor marina, Irgarol concentration increased from 44 to 54 ng/L. In Dana Point Harbor marina, the Irgarol average concentration remained relatively similar; 218 ng/L in 2005 and 202 ng/L in 2008. For Irgarol's metabolite, M1, the average concentration significantly increased (p = 0.037) from 2005 (7 ng/L) to 2008 (19 ng/L) in San Diego Bay marina (Figure 4). Average M1 concentrations were slightly higher in Dana Point Harbor and Mission Bay Harbor in 2008 compared to 2005, and slightly decreased in the Oceanside marina (Figure 4). M1 concentrations reflected Irgarol concentrations and showed the same order for four Southern California marinas: Dana Point Harbor > San Diego Harbor > Oceanside Harbor > Mission Bay Harbor marina. In general, M1 was measured at concentrations lower than the parent compound, with no statistical increase from 2005 to 2008. While toxicity thresholds and ERL values are available for Irgarol, there are no known studies to date describing M1 environmental effects, therefore, it is hard to predict whether measured concentrations could have any effects on marine ecosystems.

Diuron concentrations were below the detection limit (2 ng/L) in Mission Bay Harbor, and were relatively low for Oceanside Harbor, San Diego Bay and Dana Point Harbor marinas with a maximum average concentration of 8 ng/L (Figure 5).

Diuron concentrations in water samples ranged from <2 ng/L to 68 ng/L in this study. These concentrations are greater than diuron concentrations reported from our previous studies <2 to 12 ng/L in 2005 (Sapozhnikova *et al.* 2007) and 5 to 27 ng/L in 2006 (Sapozhnikova *et al.* 2008). Compared to the previous study of 2005, where diuron was detected in every water sample analyzed, this study had a 79% frequency of diuron detection; however, maximum measured concentrations were greater in 2008,

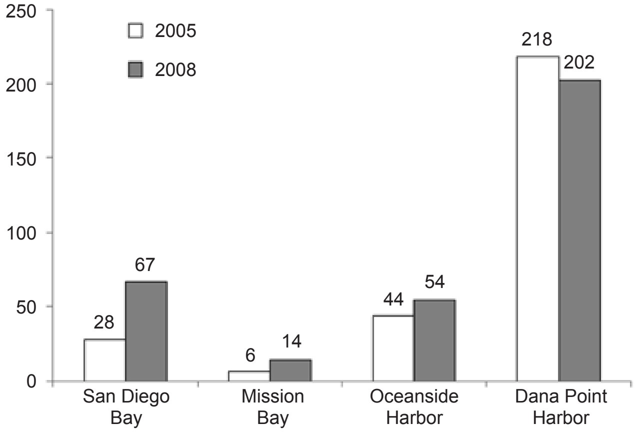

Figure 3. Comparison of Irgarol water concentrations from San Diego region marinas, ng/L.

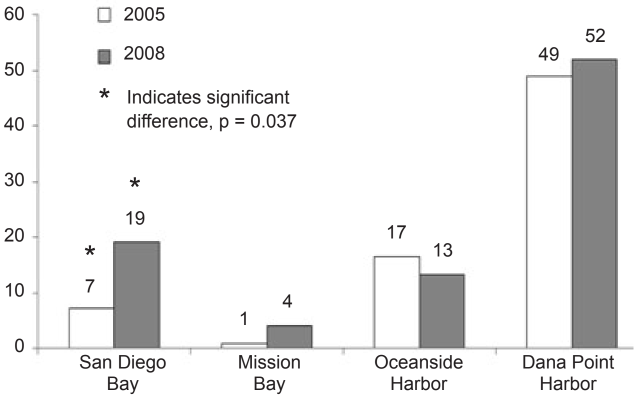

Figure 4. Comparison of M1 water concentrations from San Diego region marinas, ng/L.

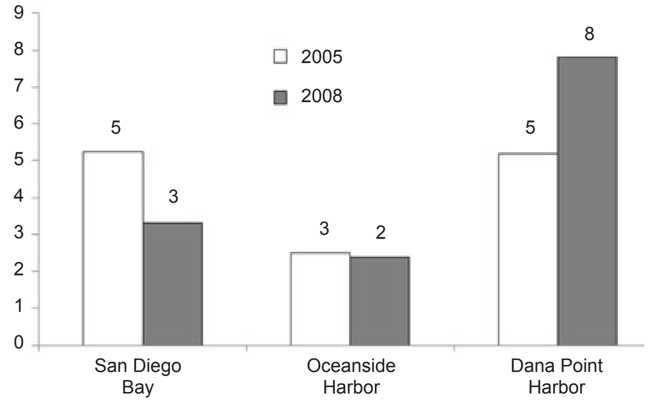

Figure 5. Comparison of diuron water concentrations from San Diego region marinas, ng/L.

indicating that diuron concentrations in California marinas increased from 2005. Diuron was the third most heavily used herbicide in California, with nearly 1.4 million pounds (634 000 kg) being reported in 2004 (PAN Pesticide Database – California Pesticide Use). A study by Huang *et al*. (2004) reported relatively high runoff rates for diuron - 4.4%, that resulted in high surface water concentrations (0.01 to 30.6 µg/L; Huang *et al.* 2004). The relatively long half-life (43 - 2180 days), DPR Pesticide Chemistry Database (http://www.cdpr.ca.gov/dprdatabase.htm) and heavy application of diuron probably contribute to its high detection frequency and relatively high and general trend of increasing concentrations.

Antifouling Chemicals in Sediments

Irgarol concentrations in sediments ranged from <0.3 to 8.9 ng/g dry weight, M1 concentrations ranged from <0.3 to 5.3 ng/g dry weight, and diuron concentrations ranged from <0.3 to 4.2 ng/g dry weight.

The three highest sediment concentrations of Irgarol were measured in Dana Point Harbor marina (8.9 ng/g dry weight), Oceanside Harbor marina (7.3 ng/g dry weight) and Newport Beach marina (7 ng/g dry weight). Average Irgarol concentrations measured in sediments of Dana Point Harbor marina were significantly greater ($p \leq 0.05$) than in all other marinas, except for Oceanside marina ($p = 0.098$) and Oxnard channel marina ($p = 0.062$). Average concentrations of Irgarol in sediments were: Dana Point Harbor marina (7.4 ±1.8 ng/g dry weight), Oceanside Harbor marina (3.5 ±3.1 ng/g dry weight) and Newport Beach marina (3.0 ±3.0 ng/g dry weight; Figure 6).

The highest M1 concentrations in sediments were measured in Oceanside Harbor marina (5.3 ng/g dry weight), and both Dana Point and Newport Beach marinas (4.2 ng/g dry weight). M1 concentrations measured in sediments from Dana Point Harbor marina were significantly greater ($p = 0.035$) than in sediments from San Diego Bay marina. Average M1 sediment concentrations followed the same order as Irgarol concentrations with highest in Dana Point marina (2.7 ±1.8 ng/g dry weight), Oceanside Harbor marina (2.0 ±2.8 ng/g dry weight) and Newport Beach marina (1.6 ±1.9 ng/g dry weight; Figure 6).

The highest diuron concentrations were measured in sediments from Los Angeles/Long Beach marina (4.2 ng/g dry weight) and Newport Beach marina (2.3 ng/g dry weight; Figure 6). In all other marinas, diuron concentration in sediments were lower than 1 ng/g dry weight. Following the same trend observed for water samples, average diuron concentrations were greatest in Los Angeles/Long Beach marina sediments (2.5 ±2.4 ng/g dry weight) followed by Newport Bay marina (1 ±0.9 ng/g dry weight). Diuron concentrations measured in sediments of Los Angeles/Long Beach marina were significantly greater ($p \leq 0.05$) compared to diuron concentrations measured in all other marinas in this study (Figure 6).

Concentrations of antifouling chemicals measured in sediments in this study were comparable to concentrations reported by other researchers. For example, up to 9 ng/g Irgarol in sediments were reported from Sweden (Haglund *et al.* 2001), which is similar to the highest Irgarol concentration in our study (8.9 ng/g dry weight). Thomas *et al*. (2002) reported up to 3.5 ng/g of Irgarol, up to 0.3 ng/g of M1 and 6.2 ng/g diuron in sediments from the UK collected in 2000 (Thomas *et al.* 2002). We measured up to 5.3 and 4.2 ng/g dry weight of M1 and diuron, respectively, in sediments from California marinas. Harino *et al*. (2005) reported up to 8.2 ng/g dry weight of Irgarol and up to 2.9 ng/g dry weight of M1 in sediments from Japan (Harino *et al.* 2005). These concentrations are also similar to sediment concentration in marinas from California. However, concentrations of diuron reported by Harino *et al*. (2005; 1,350 ng/g dry weight) are much higher than diuron concentrations measured herein. Gatidou *et al*. (2007) reported that Irgarol concentrations in sediments in Brighton marina, UK after restriction, were up to 49 ng/g, which is also higher than reported in our study. Irgarol use in the US began later than in Europe following the

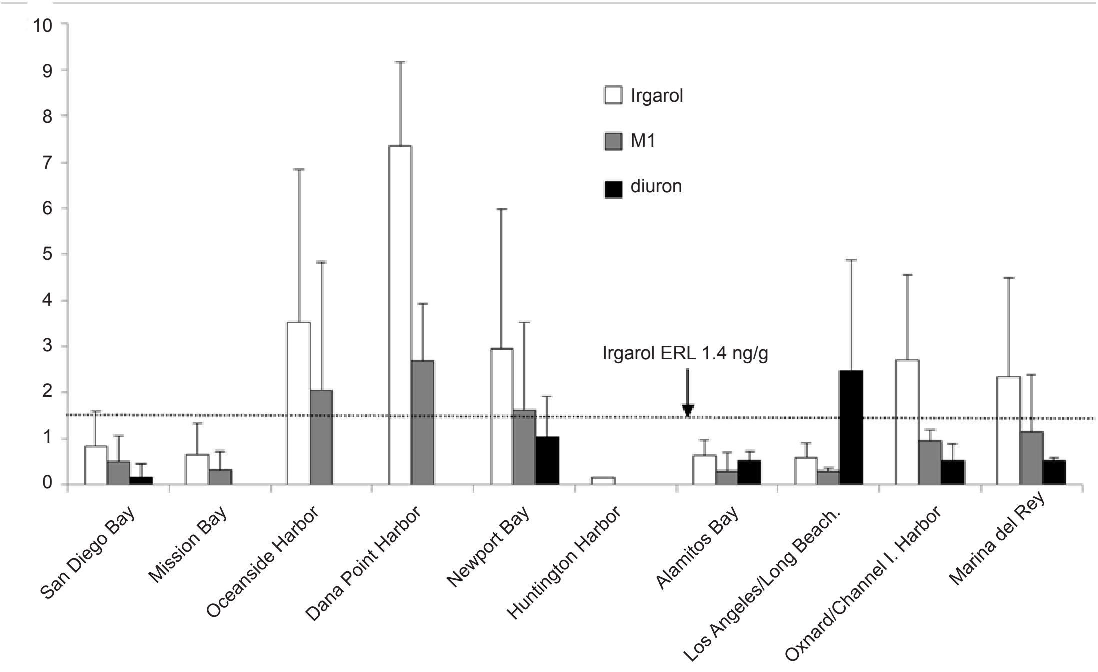

Figure 6. Antifouling chemical average concentrations in sediment samples, ng/g dry weight, error bars represent standard deviation.

ban of tributyltin use, and it is possible that Irgarol concentrations will continue to rise in US marinas. In contrast, M1 concentrations in sediments in our study (4.2 ng/g dry weight highest) were similar to those reported by Gatidou *et al*. (2007; 5.6 ng/g) in Brighton marina, UK.

Irgarol concentrations measured in sediments from our study were greater than Environmental Risk Limits (ERL) for sediments (1.4 ng/g). Thus, sediment concentrations may present potential risk to the ecosystem. For example, 35% of sediment samples analyzed in this study had Irgarol concentrations exceeding the suggested ERL.

Water – Sediment Partitioning

The water – sediment partitioning coefficient, or distribution coefficient K_d, was previously reported for Irgarol reaching up to 3,100 kg/L (Tolosa *et al.* 1996). In this study, we calculated K_d for Irgarol and M1 as a ratio of concentrations in sediments and water multiplied by 1000. In this study, calculated K_d ranged from 5 to 356 kg/L for Irgarol, and from 4 to 1,704 kg/L for M1. Based on the fraction of organic carbon measured in sediments, we calculated the organic carbon normalized partition coefficient, K_{oc}. K_{oc} is the ratio K_d and fraction of organic carbon. We compared K_{oc} from this study with values from previous studies (Table 1). The average Irgarol Log K_{oc} calculated in this study was 3.4 and was very similar to the theoretical value by Thomas *et al*. (2002; 3.3) and calculated by Tolosa *et al*. (1996; 3.0). Gatidou *et al*. (2007) estimate of Log K_{oc} ranged from 3 to 5. The average Log K_{oc} calculated for M1 in this study was 3.6, which was greater than the theoretical value by Thomas *et al.* (2002; 1.5), but similar to the value calculated by Gatidou *et al.* (2007; 3 to 5). While Log K_{oc} values estimated in our study were not based on a laboratory experiment, and therefore are limited by the results of this study, the calculated values agreed well with previously reported theoretical (Tolosa *et al.* 1996, Thomas *et al.* 2002) and field-based (Gatidou *et al.* 2007) values.

Thomas *et al*. (2003) showed that Irgarol is persistent in sediments when either in paint particles scrubbed from boats or adsorbed by sediments (Thomas *et al*. 2003). Tolhurst *et al*. (2007) reported that disruption of sediments contaminated with Irgarol can cause desorption of Irgarol and its release to surrounding water. Desorption studies by Voulvoulis *et al* estimated Irgarol sediment

Table 1. Log K_{oc} comparison.

Log Koc	This Study	Theoretical by Thomas et al. 2002	Calculated by Gatidou et al. 2007	Calculated by Tolosa et al. 1996
Irgarol	3.4 ± 0.4	3.3 ± 0.9	3-5	3
M1	3.6 ± 0.5	1.5 ± 0.23	3-5	NA

desorption rate as 2.4% (Voulvoulis *et al.* 2002). Using this desorption rate, we can calculate that 9 ng/g of Irgarol measured in sediments from Dana Point Harbor marina would result in a water concentration of 216 ng/L. Actual Irgarol water concentration measured from the Dana Point marina was 230 ng/L, very close to the calculated value, perhaps indicating active adsorption/desorption processes occurring in the contaminated sites.

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