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Seasonal Distribution of the Antifouling Compound Irgarol® 1051 Outside a Marina in the Stockholm Archipelago

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Fouling, i.e. growth of algae and other organisms on the hulls of ships and boats, causes increased friction and higher fuel consumption. To prevent this, antifouling paints containing biocides are applied. Ciba Irgarol® 1051 [2-tert.butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine] is a photosynthesis inhibitor, which is included in formulations of antifouling paints to control growth of photosynthetic organisms. Copper, which controls growth of a number of aquatic organisms, is also typically included in such paint formulations. Irgarol® 1051 has a limited solubility in seawater (1.8 mg L^{-1} at pH 7 in 0.6 m*M* NaCl) and a $logP_{ow}$ of 2.8 (Hall et al. 1999). It has been suggested to bind to particulate matter in the water and is thus likely to eventually become localized to the sediment. Irgarol® 1051 has been detected both in water and in sediment in marine, brackish and freshwater environments (Readman et al. 1993; Gough et al. 1994; Dahl and Blanck 1996; Tolosa et al. 1996; Tóth et al. 1996; Zhou et al. 1996; Scarlett et al. 1997; Biselli et al. 2000). Irgarol® 1051 has a strong inhibitory effect on the photosynthesis and growth of algae. Typical NOEC values are in the range of 100-1000 ng L^{-1}. Its toxicity to aquatic animals is considerably lower (see review by Hall et al. 1999).

The aim of this study was to acquire data on the presence of Irgarol® 1051 in water and sediment and its variation over the season at different distances from a pleasure boat marina in the Stockholm archipelago. It shows both the temporal and spacial distribution of Irgarol® 1051 in a coastal area of the Baltic Sea, which is a unique brackish environment.

MATERIALS AND METHODS

The study was carried out at Karlslund marina located in the southern Stockholm archipelago. The marina is one of the biggest pleasure boat harbours in the Stockholm area, holding about 800 boats. In the area outside the marina there are several small boat clubs with a total number of boats approximately half that of the marina. The total number of boats in the study area was estimated to be 2100. Of these 850 were located in the inner area, Väsbyfjärden, and 1250 in the Sandemarsfjärd area. The latter area may be divided in two main areas: Gålö, with

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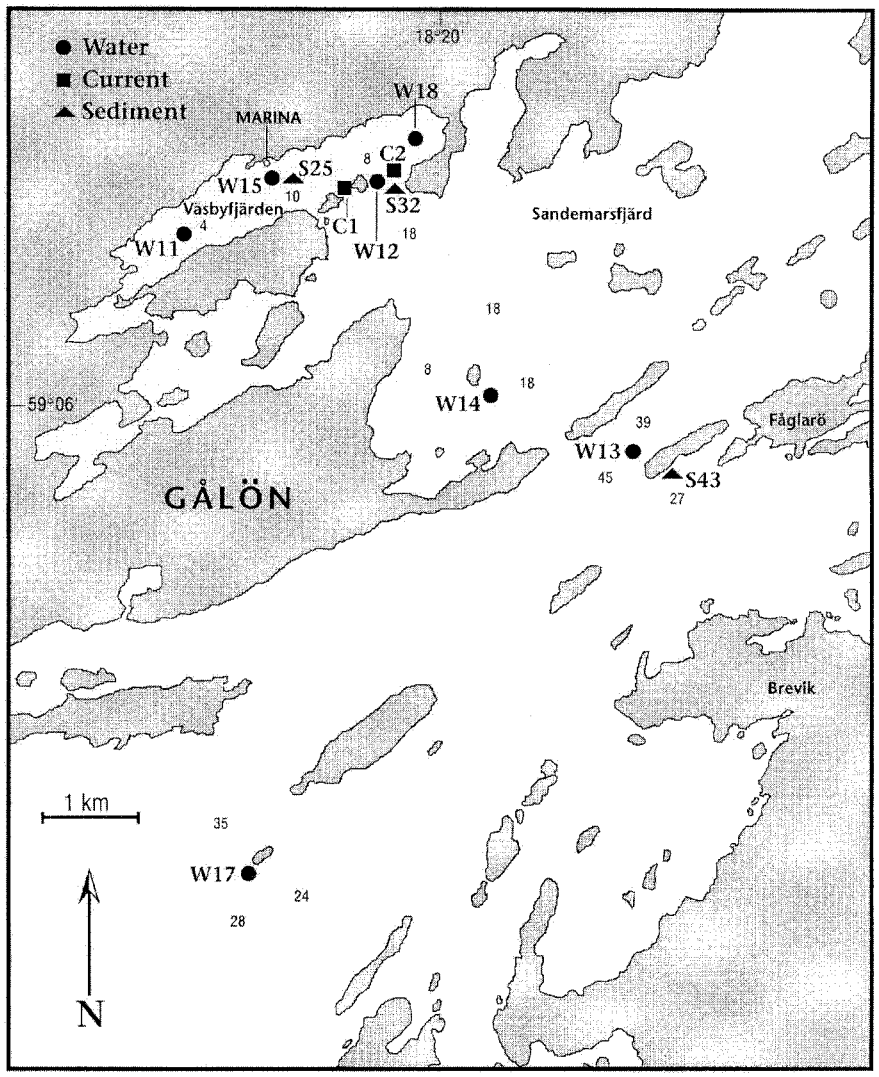

Figure 1. Map of the study area. The water sampling stations are marked with filled circles and the sediment sampling stations are marked with filled triangles. Locations for current meters are marked with filled squares.

450 boats and Dalarö with 800 boats. The proportion of boats painted with Irgarol® 1051 was investigated through interviews. It was estimated that all boat owners paint their boats, of these about 2/3 of the boat owners used Irgarol® 1051-containing paints and the remaining 1/3 used paints with copper only.

The study site was chosen due to its comparably well-defined geographical structure with three areas: an inner semi-closed area which adjoins a less enclosed area, which in turn adjoins more open waters (see Figure 1). The inner area

(Väsbyfjärden) is also connected to outer waters by a channel in the southwest. The study site is not likely to be influenced by physical and environmental factors such as freshwater outlets or heavy rainfall. The currents in the archipelago are normally very slow, although unpredictable. Since there is no tide, wind and air pressure are the main influencing factors on water movement.

The sampling period covered the entire season 1996 (April 29 - November 26), beginning in spring about 1 week after the ice had disappeared, and ending in autumn, just before the ice was formed. Water samples were taken at seven stations and sediment samples at three stations. Sampling points (stations) for water were denoted W11, W12, W13, W14, W15, W17, W18 and for sediment S25, S32, S43 (see Figure 1). In total, 10 water samples and 3 sediment samples were taken at each station. Three of the stations were located in the inner area (Väsbyfjärden), two in the middle area (Sandemarsfjärd) and two in the outer area (Ornöströmmen-Mysingen). The outer area has the most extensive water movement with currents normally going towards SW or occasionally NE.

Samples were taken from the bow of a small boat, anchored with the bow facing the current to avoid possible contamination with Irgarol® 1051 from the boat. Water samples in triplicate were collected in pre-cleaned 1-L glass bottles at about 0.3 m below the water surface. The samples were refrigerated, transported to the analysis lab and kept cold until analysis. Two replicates from each sampling point were analyzed and the third kept as a backup. If the time between sampling and analysis exceeded two days the samples were frozen until analysis. The backup replicates were frozen on arrival at the laboratory. Additional water samples for chemical and physical analyses were taken at the same time as the sediment samples.

Sampling points for sediment were selected with the aim of finding seabeds with accumulation bottoms having a homogenous, recent sediment where the sedimentation process had been relatively unaffected by erosion and transport processes. The sampling was done from a larger boat with a platform and a crane. Samples of surface sediment were taken from the uppermost 0-1 cm, using a core sampler of the Kajak type. Four replicate samples were transferred to pre-cleaned 0.5-L glass bottles. Three sediment cores were pooled for each replicate. The samples were refrigerated and kept cold during transport to the laboratory. All sediment samples were frozen on arrival to the laboratory and three replicates were freeze-dried for analysis. One replicate was saved frozen for backup. Analysis for TOC was done in triplicate using an elemental analyzer (Fisons NA-1500). Prior to analysis, the sample (5-20 mg) was treated with hydrochloric acid to convert any inorganic carbon to carbon dioxide, which was driven off.

Standard measurements of visibility, water depth and temperature were done at each water station on each occasion. Air temperature and predominant wind direction were registered at all sampling dates. The current at each station was measured at 0.5 m depth with a Haamer's pendulum type current meter. With this method only currents faster than 10 cm s^{-1} could be measured. Continuous

monitoring of the transport of water in and out of Väsbyfjärden was done from June 13 to September 15 using three datalogging current meters (SD-6000, Sensordata, Norway). Two meters were positioned at 2.7 m (C2high) and 4.4 m depth (C2low) in the major outlet northeast of Måbärsskär, with a total water depth of 6.0 m. The third was positioned at 2.3 m depth (C1) in the smaller outlet southwest of Måbärsskär, with a total water depth of 3.9 m (see Figure 1).

Water samples (1.5-2 L) with two added surrogate standards, terbutryn (0.06 μg L^{-1}) and ethion (0.05 μg L^{-1}; both Dr Ehrenstorfer), were passed through a previously activated and washed solid phase extraction (SPE) cartridge (Isolute ENV+, 200 mg, International Sorbent Technology). The sample was drawn through the cartridge with vacuum at a flow of approximately 50 mL min^{-1}. The cartridge was then rinsed twice with tap water (10 + 10 mL) to remove salts, after which the remaining water was removed by drawing acetone (400 μL) through the cartridge. The analyte was eluted with acetone:ethyl acetate (1:1). A first aliquot of the solvent mixture (2.5 mL) was allowed to penetrate into the sorbent and then left to stand for 5 min, after which the solvent passed through the cartridge with gravity. The elution was repeated twice with the same solvent mixture (2.5 + 2.5 mL). The combined eluents (7.5 mL) were passed through anhydrous sodium sulphate, the solvent evaporated to dryness, and the analyte redissolved in cyclohexane:acetone (9:1, 0.5 mL).

Two refrigerated or frozen replicate samples were analysed on separate days. If one of these replicates had unexpectedly high noise level and the other replicate showed the presence of Irgarol® 1051, or if a detectable concentration of Irgarol® 1051 was anticipated for other reasons, the third replicate was analysed. The limit of quantification (LOQ) and limit of detection (LOD) were check by spiking (4-25 ng/L) with authentic Irgarol® 1051 (Ciba Specialty Chemicals) tap water and water from the Fyris River in Uppsala, both with added sodium chloride (1 %). The LOQ was set to the lowest level of the spiked kontroll samples (4 ng L^{-1}) or at least more than 9 times the background noise level (for samples containing large amounts of particles the LOQ would be slightly higher than 4 ng L^{-1}). The LOD was set to three times the noise level. Concentration below the LOQ but above the LOD are reported as trace amounts.

Three of the four replicate sediment samples were analysed. The freeze-dried sample (1-1.5 g) was transferred to a supercritical fluid extraction (SFE) cell (2.5 mL volume) together with copper powder (app. 0.04 g) and sand (app. 0.2 g) at the bottom. Terbutryn (0.12 μg g^{-1}) was added as surrogate standard. The extraction was performed with an SFE system 2200 with SFX 2-10 extraction module (ISCO), using carbon dioxide modified with methanol (0.2 ml in the cell) as extraction fluid. Cell temperature 80 °C, pressure 300 atm, 5 minutes static extraction followed by 25 minutes dynamic extraction. The extract was collected in acetone:cyclohexane (1:1), the solvent evaporated to dryness and the extract redissolved in cyclohexane:dichloromethane (1:1, 1 mL). The extract was then purified by gel permeation chromatography on a Biobeads SX-3 (BioRad Inc.) column (40 x 1 cm), using cyclohexane:dichloromethane (1:1, 1 mL min^{-1}) as

eluent. The solvent was evaporated and the analytes redissolved in cyclohexane:acetone (9:1, 0.5 mL). The LOQ for Irgarol® 1051 in sediment was normally 5 ng g^{-1} dry weight or lower as set by the lowest spiking level of Irgarol® 1051-free sediment (5-40 ng g^{-1}), but was higher if the sediment had very low density. The LOD was 2 ng g^{-1}.

The extracts were injected into an HP-5890A gas chromatograph (Hewlett Packard) equipped with an HP-1 (25 m x 0.2 mm, 0.33 µm phase thickness) capillary column. Conditions were: splitless injection (60s); injection volume 3 µL; helium carrier gas; injector temperature 245 °C, temperature programme: 90 °C (1 min), 30 °C min^{-1} to 200 °C, 8 °C min^{-1} to 260 °C held 15 min. Detection was done with an HP 5970 MSD mass selective detector with electron ionisation (70 eV) with selected ion monitoring of m/z 182, 238 and 253(M+).

RESULTS AND DISCUSSION

Irgarol® 1051 concentration in water over the study period is shown in Table 1 and Figure 2. During the first 60 days there was an increase in Irgarol® 1051 concentrations at the four innermost sampling points up to a peak of 70-130 ng L^{-1} in early July. The concentrations in the outer area were close to the detection limit (4 ng L^{-1}) at this time. Hereafter, the concentrations at the four innermost sampling points decreased until the beginning of August when they started to increase again to a second peak, similar to the first, which occurred at the beginning of September. From mid-September to November Irgarol® 1051 concentrations decreased to 4-6 ng L^{-1} in the inner area. Irgarol® 1051 was detected in sediment at the station closest to the marina (S25) but not outside Väsbyfjärden. The Irgarol® 1051 concentration at this station was 5 ng g^{-1} DW (100 ng g^{-1} TOC) on May 12 (day 14), 9±1(s.d.) ng g^{-1} DW (190±20 ng g^{-1} TOC) on July 12 (day 66) and 2-5 (trace amounts) ng g^{-1} DW (45-120 ng g^{-1} TOC) on November 25 (day 211). The results from chemical and physical water analyses show normal values for all parameters over the study period. The surface salinity varied between 5.6 and 6.3 ‰ and the pH varied between 7.7 and 8.2. High TOC values were found at S25 and S32 in July and coincided with low water visibility, while a high value (9.8 mg L^{-1}) at station S32 in May had no clear explanation.

The ice disappeared in mid April. A rather cold, cloudy and windy period lasted until the end of July, and was followed by a warm and sunny period with 20-25°C until the end of August. Surface water temperatures increased slowly to 15°C in late June. The highest water temperature, 20°C, was recorded at the end of August. A comparison between surface water temperatures and the logged temperature data from the current meters at 2.3, 2.7 and 4.4 m depth in the mouth of Väsbyfjärden, indicates a possible thermal stratification until at the end of August when the water column was mixed. The principal current direction in the deeper water layers registered by the three current meters in the mouth of Väsbyfjärden was towards NNW and W, i.e. inwards to Väsbyfjärden. The current speeds were generally very slow, 0-1 cm s^{-1}, but up to 7 cm s^{-1} was registered

Table 1. Irgarol® 1051 concentration (ng L^{-1}) in water samples over the study period starting on April 29, 1996 (day 1). The values are means of two determinations with range (if any) given in brackets. For location of the sampling stations refer to the map in Figure 1. nd = not detected

date (day #)	W15	W11	W18	W12	W14	W13	W17	launched boats (%)
	inner area			middle area		outer area		
04/29/96 (1)	8 (5-10)	6 (3-8)	4 (3-5)	nd	nd	nd	nd	< 5
05/13/96 (15)	20	30	20	nd	4	nd	nd	20
06/06/96 (39)	30	30	55 (50-60)	50	10 (9-10)	nd	nd	90
06/27/96 (60)	75 (70-80)	70	125 (120-130)	125 (120-130)	40	6	6 (5-6)	100
07/08/96 (71)	50	40	60	60	15 (10-20)	nd	5	100
08/01/96 (95)	30	30	40	35 (30-40)	7 (6-8)	nd	nd	100
09/03/96 (128)	115 (110-120)	75 (70-80)	96	85 (80-90)	20	5	5	100
09/23/96 (148)	60	70	30	15 (10-20)	10 (9-10)	6 (5-6)	5	50
10/21/96 (176)	20	20	9 (8-10)	4	5	4	nd	10
11/26/96 (212)	6 (6-7)	6	5	4	4	nd	4	< 5

during the unstable weather period at the beginning of July. Figure 3 shows a projection of the water transport during the period June 13 to September 15 made by integrating logged current speeds for each direction. The integration does not show temporal variations during this period which, however, were minor. The current at the outer sampling station W17 was predominantly directed towards S and SW with speeds normally between 12 and 25 cm s^{-1}.

The distribution of Irgarol® 1051 in water outside the marina was consistent with water movements primarily caused by wind. In April and May the wind direction varied and Irgarol® 1051 was relatively evenly distributed in Väsbyfjärden, but not detected outside the mouth in Sandemarsfjärd. In June to early September the dominant wind was south to southwesterly and Irgarol® 1051 concentrations were higher in the northeastern part of Väsbyfjärden, and also outside the mouth to Sandemarsfjärd. In late autumn the wind varied but tended to be more northeasterly and Irgarol® 1051 was mainly distributed towards the southwest of Väsbyfjärden. Wind speeds were commonly 3-6 m s^{-1}. From mid-June to mid-September there was a slow current in the deeper water layers directed inwards to Väsbyfjärden. The warmer surface water was forced by southwesterly winds to the mouth of Väsbyfjärden creating a current of surface water outwards from this

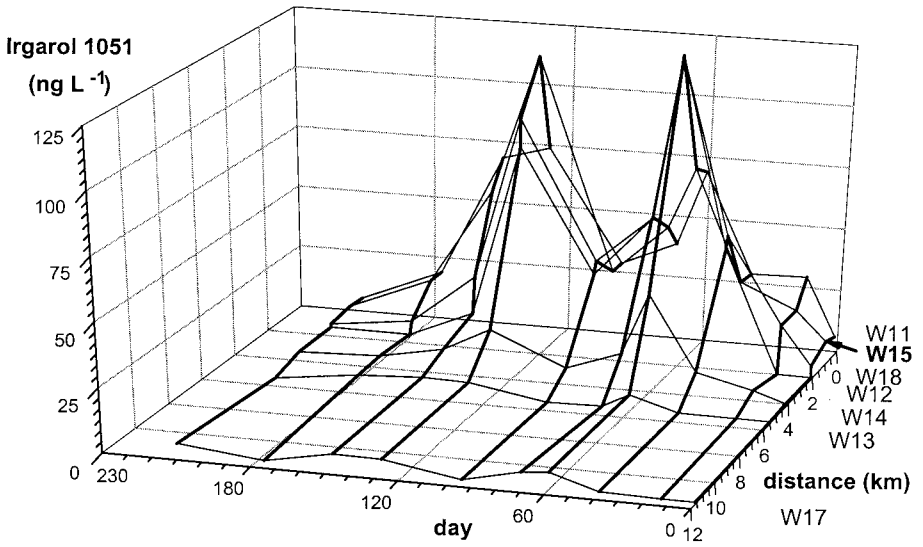

Figure 2. Mean values of Irgarol® 1051 concentrations measured in water samples over the study period. Station W15 (arrow) was closest to the marina.

area. It is assumed that this contributed to the observed gradients of Irgarol® 1051 concentration in Väsbyfjärden and Sandemarsfjärd. The decrease in Irgarol® 1051 concentration in this area in July and August coincided with a period with predominantly strong southwesterly winds, which caused transport of surface water out of Väsbyfjärden.

We assume that a major fraction of Irgarol® 1051 released from boats in the marina remained in the upper water layer for a time period long enough to be transported out of Väsbyfjärden and further out. Turnover of the entire water column due to breaking of the thermoclines occurred most probably in the end of August, which may explain the second Irgarol® 1051 peak in September.

Irgarol® 1051 in sediment was found only at the sampling point closest to the marina, which makes it difficult to relate Irgarol® 1051 levels in water to those in sediment. The highest Irgarol® 1051 concentration was found outside the marina in early July. At that time most boats had been in the water for at least one month. In November the Irgarol® 1051 concentration in the sediment had decreased, possibly as a result of mixing of the water and the upper sediment layer in Väsbyfjärden. The extent to which degradation contributed to the observed Irgarol® 1051 levels is not known.

The presence of Irgarol® 1051 in coastal waters close to marinas has previously been investigated and discussed. Several investigators have presented data on the content of Irgarol® 1051 in water, (Readman et al. 1993; Gough et al. 1994; Dahl and Blanck 1996; Tolosa et al. 1996; Tóth et al. 1996; Zhou et al. 1996; Scarlett et

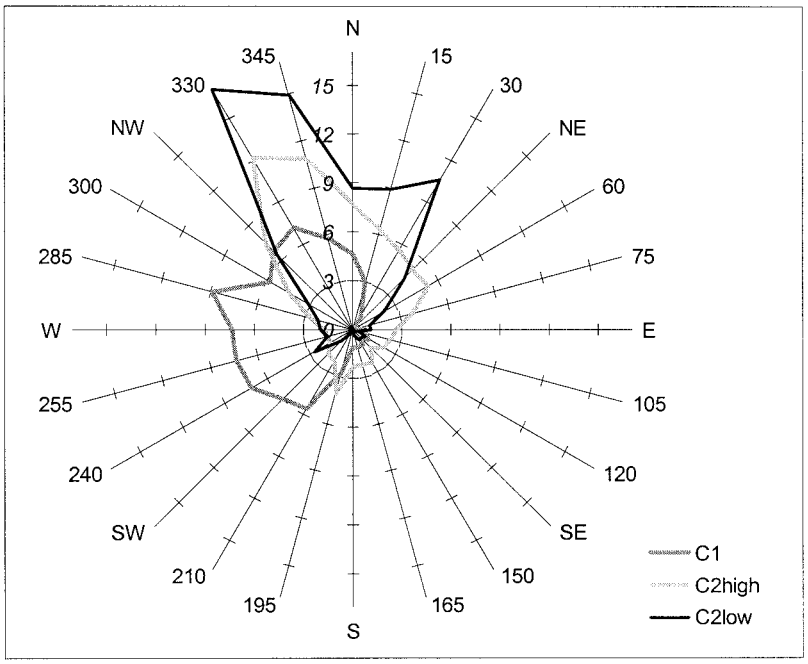

Figure 3. Projection of water transport in and out of Väsbyfjärden due to the currents registered by the three current meters during the period June 13 to September 15. The labels by the value axis show distance of water transport in km for each direction group, calculated from current speed and time. Each of the three projections is based on about 4500 measurements.

al. 1997; Steen et al. 1997; Biselli et al. 2000), whilst Irgarol® 1051 in sediment has been studied only in three of these (Gough et al. 1994; Tóth et al. 1996; Biselli et al. 2000). Concentrations of Irgarol® 1051 in coastal water have varied substantially depending on the distance of the sampling points from the marinas and the number of Irgarol® 1051-painted boats moored in the marina. Irgarol® 1051 concentrations up to 130 ng L^{-1} found in the present study were lower than the maximum concentration found in a marina in southern France (Readman et al. 1993) and in some marinas in the south Baltic Sea (Biselli et al. 2000). They were, however, similar to the majority of the Irgarol® 1051 concentrations found in other sites, whilst levels of Irgarol® 1051 in estuaries at the English east coast and the Dutch west coast were lower (Zhou et al. 1996, Steen et al. 1997).

The findings in this study that Irgarol® 1051 released into water from antifouling paints is found predominantly in water samples and to a lesser extent in the sediment is in agreement with the conclusions of Tolosa et al. (1996). It contrasts, however, with Bard and Pedersen (1992), who predicted that Irgarol® 1051 is adsorbed to particles in the aquatic environment and will be distributed mainly to the sediment. We conclude that reduction of Irgarol® 1051 concentration in this study is significantly dependent on dilution by water transport. Given that Irgarol®

1051 has been used in the Stockholm archipelago for many years, this study provides no evidence to suggest accumulation in water or sediment in this area.

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