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Screening of Antifouling Biocides around a Pleasure Boat Marina in the Baltic Sea after Legal Restrictions.

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Abstract

Copper, zinc, and Irgarol 1051 concentrations were determined around a pleasure boat marina in the Stockholm Archipelago. Copper concentrations in water were twice as high (6.62 μg L^{-1}) in 2004 as 1992-93, zinc concentrations six times higher (20.0 μg L^{-1}). Concentrations in bladder wrack (*Fucus vesiculosus*) had also risen. Irgarol concentrations in water were similar (~0.17 μg L^{-1}) in 1996 and 2004, while concentrations in bladder wrack halved from 1993 to 2004. The peak concentrations of copper and Irgarol in water have shifted indicating that the main source in the 1990s were local boats, but in 2004 visiting boats.

Key Words Irgarol 1051 - copper - zinc – water - bladder wrack - *Fucus vesiculosus*

Fouling, i.e., growth of algae and other organisms on the hull of ships and boats, causes increased friction and higher fuel consumption. To prevent this, the hull can be painted with an antifouling paint. Irgarol 1051 (2-*tert*-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine) is a herbicide included in formulations of anti-fouling paints. To get a broader antifouling effect it is often used as a booster biocide in combination with other compounds, e.g., copper. It was registered for use in Sweden in 1992, but may have been used earlier as no approval from regulating agencies was needed before that. Other antifouling compounds, such as organo-tin compounds and diuron have not been allowed on pleasure boats in Sweden since 1989 and 1992, respectively.

The Baltic Sea is the world's largest brackish water body (Sjöberg 1992). The surface water has a salinity gradient ranging from about 2‰ in the inner parts of the Bay of Bothnia to 10‰ in the southwest. The salinity has varied substantially in recent geological time as a consequence of the varying hydrologic conditions in the Baltic Basin after the latest glaciation some 8000-12000 years ago. This is reflected in the species composition with many species living under suboptimal salinity conditions making the Baltic a particularly vulnerable ecosystem. Recognising this and that problems with fouling are successively reduced with lower salinity, the Swedish Chemicals Agency has limited the use of antifouling compounds in Swedish waters. From January 1999 restrictions became more stringent gaining full effect 2002. Today no paints containing antifouling biocides are approved for use on pleasure boats that are used chiefly in the Baltic, defined as the coast east- and northwards from Trelleborg. Paint in stock at retailers could be sold until the end of 2001, and end users were allowed to use up paints already purchased.

This study was performed as a preliminary evaluation of the restrictions. The purpose was to investigate if there is future need of in depth environmental monitoring of antifouling compounds. Target compounds were primarily Irgarol and copper, but zinc was also included as this element is increasingly common in paints used on pleasure boats in the Baltic.

Materials and methods

The study was carried out around Bullandö Marina in the Stockholm Archipelago. Coordinates of the sampling locations are given in Table 1. The marina itself

(Station 1) is in a relatively secluded and shallow (app. 4-6 m) bay with limited water circulation, while the currents provide good water circulation in the sound outside the marina (Station 2). The boats are usually launched in late April or early May and taken up for winter in October or November. The natural harbour at Säck (Station 3) is even more secluded and much deeper (app. 22 m) than the marina with a narrow and shallow entrance and little water circulation during the summer months. Säck is a popular tourist harbour frequented by pleasure boats mostly during the peak of summer (late June to August). Fjärdgrundet (Station 4) is a shallow avoided by boats year round and surrounded by open water. The first samples were taken in early April, before the boats were launched and while the marina and the natural harbour at Säck were still largely ice covered. The final samples were taken in November when the majority of boats had been taken out of the water for winter storage.

Table 1 Station coordinates and range of auxiliary data collected. More details of auxiliary data are given in Kylin (2006).

Parameter	Station 1	Station 2	Station 3	Station 4
Latitude N	59° 17.77'	59° 17.70'	59° 23.47'	59° 24.06'
Longitude E	18° 38.97'	18° 39.48'	18° 47.88'	18° 43.12'
pH	7.90 – 8.74	7.91 – 8.83	7.83 – 8.66	7.91 – 8.84
Conductivity, mS m^{-1}	706 – 912	705 – 930	780 – 959	748 – 948
Ca^{2+} mequ L^{-1}	2.91 – 3.53	2.92 – 3.59	3.18 – 3.73	2.98 – 3.62
Mg^{2+} mequ L^{-1}	10.5 – 13.8	10.5 – 14.0	12.0 – 14.5	11.0 – 14.2
Alkalinity mequ L^{-1}	1.167 – 1.377	1.252 – 1.380	1.267 – 1.419	1.189 – 1.389
$NO_3^{-1} + NO_2^{-1}$ μg L^{-1}	1 – 5	1 – 5	1 – 5	1 – 4
NH_4^+-N μg L^{-1}	4 – 20	4 – 11	4 – 32	3 – 9
tot- N μg L^{-1}	253 – 821	258 – 462	235 – 423	258 – 423
PO_4-P μg L^{-1}	2 – 7	2 – 8	2 – 9	1 – 9
Tot-P μg L^{-1}	15 – 50	13 – 33	13 – 41	14 – 23
TOC mg L^{-1}	3.8 – 5.6	3.7 – 5.8	3.6 – 5.2	3.4 – 5.6

Samples of surface water were collected at 0.5 m below the surface. As specified by the Swedish Environmental Protection Agency (SEPA) for the Swedish national environmental monitoring programmes (SEPA 2002a), samples for inorganic parameters were transferred to plastic containers, while samples for determination of Irgarol were transferred to glass bottles. Samples of bladder wrack (*Fucus vesiculosus*) were taken at the same locations as the water samples with a high density polyethylene rake attached to a wooden shaft reaching the bottom. The tips, representing the latest seasonal growth, was cut off in the field on a polyethylene plate with a high purity stainless steel surgical blade and put in polyethylene containers (Forsberg et al. 1988). All samples were put on ice and transported to the lab within five hours and kept refrigerated (2°C, water) or frozen (-20°C, *Fucus*) until analysed.

The methods used for the inorganic auxiliary parameters (Table 1) were those used in the Swedish national environmental monitoring programmes (SEPA

2002a), as far as possible using standardised ISO methods (Kylin 2006). Copper and zinc were measured with graphite furnace atomic absorption spectrometry, in bladder wrack after microwave assisted wet combustion with nitric acid. All materials used were of analytical grade. For quality assurance/quality control (QA/QC) of copper and zinc in water standard reference material SLRS-4 (National Research Council of Canada, Ottawa) was used. In addition, standard additions at three levels of copper were performed for two samples, and duplicate analyses from different sampling vials were performed of five samples for copper and 16 samples for zinc. For copper and zinc in bladder wrack standard additions at five different concentrations were made. For further details of methods, uncertainties and reference materials se Kylin (2006).

Irgarol in water was determined as described by Haglund et al. (2001). In short, the water was extracted using solid phase extraction with ENV+ (IST, Mid Glamorgan, UK). The cartridges were washed with water to remove the salts, and the analyte eluted with acetone:ehtyl acetate (1:1). The Swedish Food Administration method for pesticides in vegetables (SFA 2998) was used to analyse Irgarol in bladder wrack. In short, the material was homogenised in acetone with an Ultra-Turrax (IKA, Staufen, Germany), partitioned between water and dichloromethane, large molecules removed with gel permeation chromatography (Biobeads SX-3, Bio-Rad, Hercules, Cal., USA). All quantifications were with gas chromatography- mass spectrometry as described by Haglund et al. (2001). Deuterated Atrazine (Dr. Ehrenstorfer, Augsburg, Germany) was added at extraction as surrogate standard, and ethion (Dr. Ehrenstorfer) was added prior to quantification to check procedural losses. Blank and reproducibility tests were performed throughout. The limits of detection (LOD, three times the noise) and quantification (LOQ, three times the LOD) were determined for each water sample individually by addition of low concentrations of the Irgarol to a subsample. For bladder wrack uncertainty was estimated by spiking at five different levels (n=3) and varied between 30% at 2 μg kg^{-1} to less than 10% at 50 μg kg^{-1}.

Results and Discussion

Bullandö Marina was selected for this study as it is the largest pleasure boat marina on the Baltic Sea, and an investigation of antifouling compounds was conducted there in 1992-93 (Öhrn 1995). In addition, an investigation of Irgarol was conducted at Karlslund Marina, some 25 km to the south of Bullandö, in 1996 (Haglund et al. 2001). Our main emphasis was on the seasonal concentration variations in the water, but as water samples will only give the momentary concentration the water samples were complemented with bladder wrack samples. These will accumulate the pollutants over time and give integrated values. Also, the SEPA has devised environmental quality criteria (EQC, SEPA 2002b) for heavy metals in seawater based on the concentrations in bladder wrack.

A summary of the seasonal concentration variations of copper, zinc, and Irgarol in the water samples are shown in Figure 1. Individual concentrations are reported by Kylin (2006) together with detailed auxiliary inorganic data. The auxiliary data (Table 1) varied over the year as could be expected from factors such as snow melt and runoff and could not explain any of the variation in the target analytes. For all three analytes the concentrations are clearly elevated in the marina and the natural harbour during the most intense boating season June-August. Although it seems that the peak for Irgarol in the marina comes somewhat earlier than for copper or zinc. There is also a concentration increase of Irgarol during the boating season in the sound outside the marina, while the seasonal variations of zinc and especially copper concentrations are less clear. Although the concentrations in the sound are somewhat higher than at the background during the boating season, they show essentially the same seasonal pattern.

Relatively high background levels in the Stockholm Archipelago complicate the interpretation of the metal concentrations. Monitoring data from the archipelago are few, but the area has been indicated as having fairly high levels of both copper and zinc compared to other parts of the Baltic (Grimås and Suarés 1989). A partial explanation, at least for copper, is that it comes from Lake Mälaren. There are ore deposits in the Lake Mälaren water shed, but in addition the outflow passes through central Stockholm before reaching the archipelago. This high background may mask any effects of low or moderate use of copper containing antifouling paints in all but the most frequented and sheltered harbours.

The zinc concentrations in the marina and at Säck increase more than the copper concentrations during the boating season. Also, the total concentration span was much larger for zinc than for copper, which is reasonable considering that the use of zinc compounds as formulators in boat paints is widespread and has increased since the legal restrictions against copper and Irgarol came into effect.

At Säck, the highest concentrations of all target analytes are found later in summer than in the marina coinciding with the end of the boating season. This possibly reflects a continuous build-up of the concentrations during the boating season due to the low water circulation at this station. If so, it is not until September when there are less boats and increased wind action that the water circulation in this deep secluded bay manages to transport the contaminants out of the harbour at a higher rate than they are released from visiting boats. In comparison, although the marina is also sheltered, there is a slight current passing the sampling station why the water circulation is less restricted than at Säck. Had this not been the case the differences between the marina and Säck would probably have been larger given the higher number of boats in the marina.

Copper concentration in water samples from Bullandö Marina were twice as high in 2004 as in 1992-93 when comparing the highest and lowest values, and the zinc concentrations were up to six times higher in 2004 than in 1992-93 (Kylin 2006). An increase of the copper and zinc concentration was also noted in the sound outside the marina although not to the same extent. A continuous monitoring programme is necessary before any firm conclusions can be drawn, as we presently know very little about the year to year concentration variations in the water.

The previous study at Bullandö (Öhrn 1995) covered mainly the metals. Irgarol was included only in the last stages and only in bladder wrack. Compared to 1993 the concentrations of Irgarol in bladder wrack in the marina and in the sound outside the marina have gone down to about half. On the other hand, the maximum water concentrations in the marina are similar to those found at Karlslunds Marina in 1996 (Haglund et al. 2001). However, comparing the variations over the boating season these differ markedly between 1996 and 2004. The highest concentrations of Irgarol in 1996 were when the boats belonging to the marina were launched or landed. In contrast, the highest concentrations in Bullandö 2004 were found in the middle of the summer when the number of visiting boats from areas where the use of Irgarol is still allowed was highest.

The concentrations of all analytes in the bladder wrack samples (Table 2) confirm that the levels are higher in the marina than at the other sites. However, although the concentrations are lower at the background than the other sites, the concentrations at the other three sampling stations are too similar to clearly detect any differences. Unfortunately, the first sampling of bladder wrack was made before the yearly growth of 2004 had started, and tissue already one year was sampled. As a consequence, concentrations at the first sampling were higher than in the second when younger tissue was sampled. According to the Swedish EQCs for metals in bladder wrack (SEPA 2002b) the concentrations of copper and zinc in the marina indicate a situation with ‘very large anthropogenic influence, while the other stations vary between ‘moderate’ and ‘large’ anthropogenic influence. Zinc was not determined in bladder wrack in 1992-93, but for copper the trend is the same as for the water samples with concentrations 2004 approaching twice those found 1992-93.

Table 2 Irgarol, copper, and zinc in bladder wrack on dry weight basis.

Station	Date yyyy-mm-dd	Irgarol $\mu g\ kg^{-1}$	Cu mg kg^{-1}	Zn mg kg^{-1}
Marina	2004-04-28	41	10.1	463
	2004-07-21	14	6.4	602
	2004-11-02	96	9.3	799
Sound	2004-04-28	22	5.4	202
	2004-07-21	16	3.1	175
	2004-11-02	24	4.1	175
Säck	2004-04-28	12	3.9	148
	2004-07-21	14	3.0	92
	2004-11-02	24	4.6	187
Background	2004-04-28	24	4.6	156
	2004-07-21	Trace*	2.0	65
	2004-11-02	17	3.0	92

*$0.5\ \mu g\ kg^{-1} < \text{trace} < 2\ \mu g\ kg^{-1}$

The increased copper concentrations in water and bladder wrack between 1992-93 and 2004 are cause for concern. Presently, the reason is not clear. For boats longer than 12 m copper containing paints are still approved in the Baltic, but the number of pleasure boats of this size is relatively small and it seems unlikely that these should be the main source of copper. It cannot be excluded that the increased copper concentrations are a result of illegal use of copper containing paints purchased outside of Sweden. It is interesting to note, though, that the highest water concentrations are found in August when the number of visiting boats from other areas is highest. Similarly to Irgarol, there is a shift in the timing of the peak concentrations between the previous study and this. In 1992-93 there are two peaks, one early and one late in the season (Öhrn 1995), while in 2004 there was only one peak in the middle of the summer. This strengthens that in the previous studies the main source of these antifouling compounds were local boats, while it was visiting boats in 2004.

The increase of zinc concentrations in the water from 1993 to 2004 is easier to explain, as zinc has become more common in paints used by pleasure boat owners in the Swedish Baltic. In addition, the seasonal patterns are similar in the two investigations peaking during summer, indicating that the zinc source in 1993 differed from the copper source.

Comparing with published ecotoxicity data, Gustavson et al. (1999) found toxic effects of copper on phytoplankton communities expressed as pollution-induced community tolerance (PICT) at 1 µg L^{-1}, a concentration found in this study more or less continuously even at the background site. The experiment was conducted in enclosures in natural seawater, where the bioavailability of copper is comparable to that of the water in the present study. For zinc, De Schamphelaere et al. (2003) reported a 72-h no effect concentration (NOEC) of 5.4 µg L^{-1} for the alga *Pseudokirchneriella subcapitata* and Masters et al. (1991) reported a 4-d NOEC of 14 µg L^{-1} for the crustacean *Ceriodaphnia dubia*. Thus, the copper and zinc concentrations found around Bullandö may have harmful effects on aquatic life.

Based on current knowledge it is difficult to estimate if ecotoxic effects may or may not be caused by the concentrations of Irgarol found in this study. Dahl and Blanck (1996) estimated a NOEC on periphyton of 0.016 µg L^{-1}, while an evaluation of the available literature data concluded that only the 10% most sensitive plant species in the aquatic environment should be affected by an Irgarol concentration of 0.14 µg L^{-1} (Hall et al. 1999), a concentration that was exceeded at least once during 2004. However, it is difficult to draw any firm conclusions on environmental effects based solely on laboratory data (Hall et al. 1999), why it is common practice by regulatory agencies to apply safety factors in risk assessment to compensate for uncertainties regarding how well laboratory data represent the environmental situation. It is even more difficult to draw any conclusions regarding synergistic effects or effects in brackish water ecosystems (Gustafsson et al. 2010).

The absence of long time-series of Irgarol, copper, or zinc in the Stockholm Archipelago makes it difficult to evaluate the concentration changes between the1990s and 2004 as the year-to-year variation is not known. The situation seems to be the same throughout the world; we have found no investigation of these analytes that can be used to gain additional knowledge how different usage patterns affects the environmental concentrations and possible ecotoxic effects. To draw firm conclusions on the long-term environmental implications and the efficacy of regulatory measures it is, therefore, necessary to acquire additional data, preferably by including these analytes in environmental monitoring programmes.

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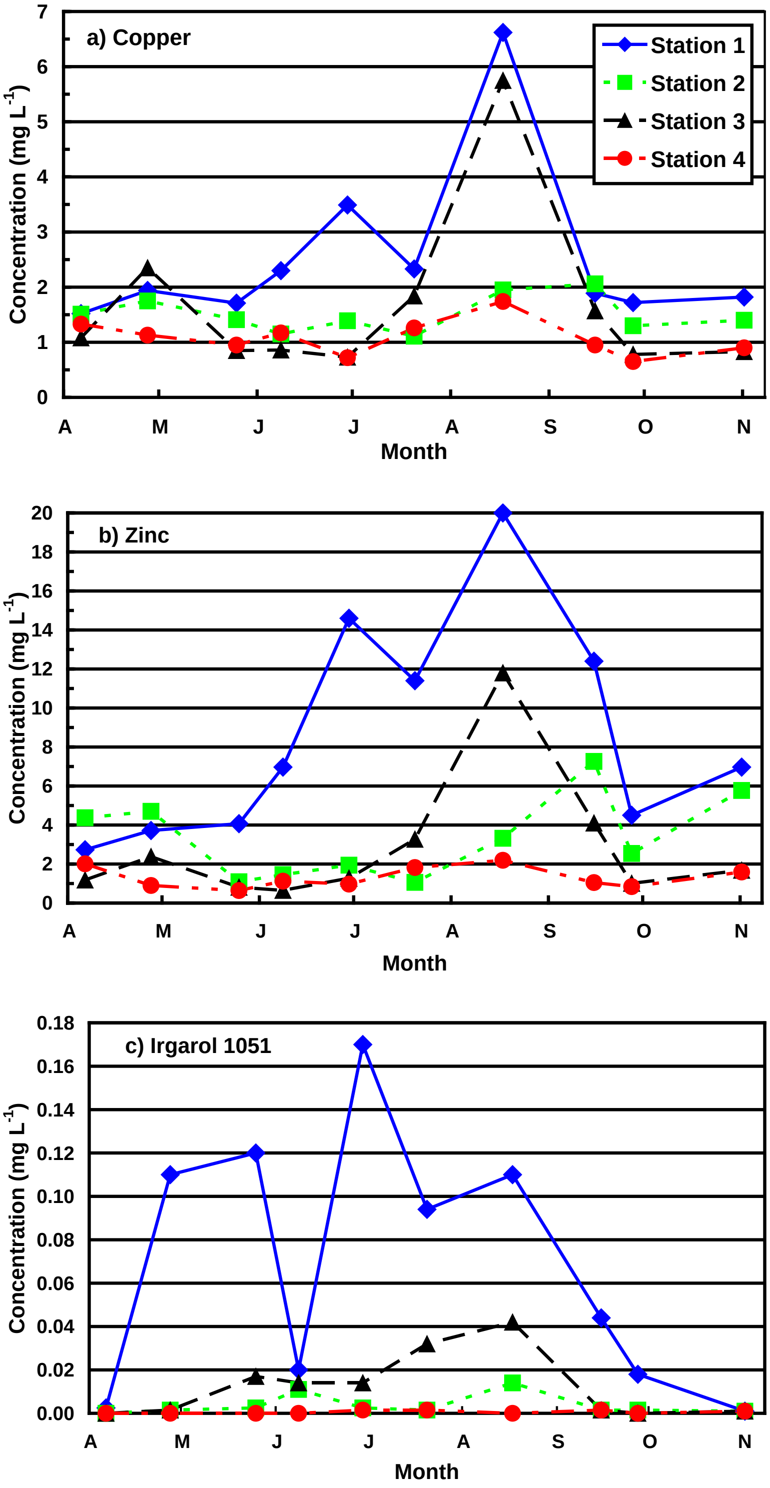

Fig. 1 Concentrations of a) copper, b) zinc, and c) Irgarol 1051 in the Stockholm Archipelago during the boating season April to November 2004. *Station 1* Bullandö Marina, *Station 2* sound outside the marina, *Station 3* natural harbour at Säck, *Station 4* Fjärdgrundet.