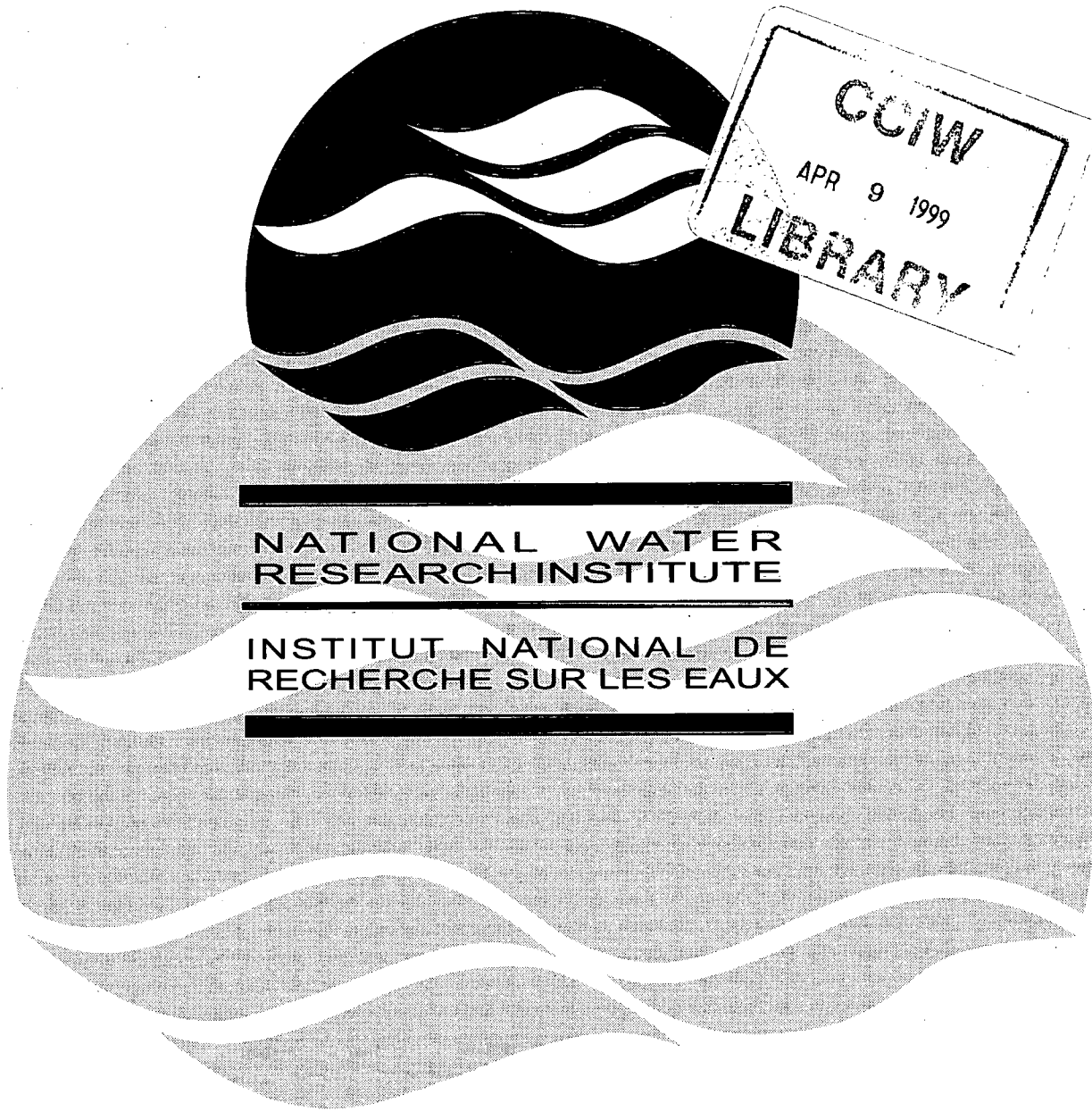


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VOLATILITY OF IRGAROL 1051

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NWRI Contribution No. 98-178

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MANAGEMENT PERSPECTIVE

Irgarol 1051 (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) is a newly developed herbicidal additive for use in copper-based antifouling paints. It is intended as a replacement for the widely used antifouling agent tributyltin (TBT) which has been regulated internationally since about 1990, primarily due to its severe impact on the aquatic ecosystem. For example, it has been estimated that, in the Arcachon Bay of France alone, the use of TBT caused a loss in revenue of 147 million U.S. dollars through reduced oyster production. Very recent studies have shown that TBT can cause sexual changes in gastropods. Females, upon exposure to levels in parts per trillion range, developed male characteristics such as penises (the so-called imposex problem), thus seriously reducing the population of gastropods in the marine environment.

Irgarol 1051 is a new chemical and information on its persistence and degradation is rather scarce, a fact that hinders the assessment of its ultimate impact on the environment. It is not presently registered for use in Canada under the Pest Control Products Act. In anticipation of its registration, and because it is registered in some other countries, we have been conducting research on the mechanisms and processes involved in its degradation to further our understanding of its impact and to obtain knowledge which will be useful for its management.

Although Irgarol 1051 is generally considered to be non-volatile, there are no data in the published literature on its volatility. Therefore, we have conducted experiments to test the volatility of this chemical. The results show that Irgarol 1051 cannot always be considered as non-volatile. When the temperature is high and the water motion is rapid, significant losses can occur through volatilization. These results will assist in the assessment of the fate and pathway of Irgarol 1051 in the aquatic environment.

SOMMAIRE À L'INTENTION DE LA DIRECTION

L'Irgarol 1051 (2-méthylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) est un nouvel additif herbicide destiné aux peintures antisalissures à base de cuivre. Il a été élaboré pour remplacer le tributylétain (TBT), un agent antisalissure largement utilisé qui est réglementé à l'échelle internationale depuis environ 1990, principalement à cause de son impact important sur les écosystèmes aquatiques. Par exemple, on a estimé que, dans la seule baie d'Arcachon (France), l'utilisation du TBT a entraîné des pertes de revenu de 147 millions de dollars américains dues à la réduction de la production d'huîtres. Des études très récentes ont montré que le TBT peut causer des changements sexuels chez les gastropodes. Chez les femelles exposées à des concentrations de l'ordre des nanogrammes par litre, on voit apparaître des caractères mâles, comme des pénis (problème de l'imposexe), ce qui a pour effet de réduire considérablement la population de gastropodes dans le milieu marin.

L'Irgarol 1051 est une nouvelle substance chimique et on dispose de peu d'informations sur sa persistance et sa dégradation, ce qui complique l'évaluation de son impact final sur l'environnement. Il n'est pas actuellement homologué au Canada en vertu de la Loi sur les produits antiparasitaires. En prévision de son homologation, et parce qu'il est homologué dans d'autres pays, nous avons effectué des recherches sur les mécanismes et les processus de sa dégradation pour mieux comprendre son impact et pour acquérir des renseignements utiles pour sa gestion.

Bien que l'Irgarol 1051 soit généralement considéré non volatil, il n'existe pas de données publiées sur sa volatilité. C'est pourquoi nous avons effectué des tests concernant la volatilité de cette substance. Les résultats montrent que l'Irgarol 1051 ne peut pas toujours être considéré non volatil. Quand la température est élevée et que le mouvement de l'eau est rapide, des pertes importantes peuvent se produire par volatilisation. Ces résultats faciliteront l'évaluation du devenir de l'Irgarol 1051 et des voies qu'il emprunte dans le milieu aquatique.

ABSTRACT

An experimental investigation into the volatility of the new anti-fouling compound Irgarol 1051(2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) was conducted. Organic-free water was spiked with Irgarol and the concentration was monitored over a period of fifty nine days. The test solutions were subjected to different stirring rates and temperatures. Concentration profiles from the water samples showed that the loss of Irgarol depended on environmental conditions and that Irgarol cannot always be assumed to be non-volatile.

RÉSUMÉ

On a effectué une étude expérimentale de la volatilité de l'Irgarol 1051 (2-méthylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine), un nouveau composé antisalissure. On a ajouté de l'Irgarol à de l'eau exempte de substances organiques, et suivi sa concentration durant 59 jours. Les solutions des essais ont été soumises à divers taux d'agitation et températures. Les profils de concentration des échantillons aqueux ont montré que la perte d'Irgarol était fonction des conditions environnementales et qu'on ne peut toujours considérer que l'Irgarol est non volatil.

INTRODUCTION

Irgarol 1051(2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine) is a newly developed herbicidal additive for use in copper and zinc based antifouling paints (Gough *et al.*, 1994). It is intended as a replacement for the highly toxic antifouling organotin biocides (e.g., tributyltin and triphenyltin) which were regulated internationally in the late 1980s and early 1990s, mainly due to their high toxicity and severe impact on the aquatic ecosystem. Irgarol 1051 has emerged as a new aquatic contaminant and has been found in many of the coastal waters of Europe (Readman *et al.*, 1993; Gough *et al.*, 1994; Dahl and Blanck, 1996; Ferrer *et al.*, 1997a and 1997b; Scarlett *et al.*, 1997; Steen *et al.*, 1997), the Seto Inland Sea in Japan (Liu *et al.*, in press) as well as in the fresh waters of Lake Geneva in Switzerland (Toth *et al.*, 1996).

Information in the open literature on the environmental persistence and degradation of Irgarol is rather scarce. A bioassay using a ship-fouling diatom indicated that Irgarol 1051 in natural sea water was not degraded over an 8-week period (Callow and Willingham, 1996). Liu *et al.* (1997) demonstrated that Irgarol 1051 can be biotransformed by the white rot fungus *Phanerochaete chrysosporium* via the mechanism of N-dealkylation to yield a stable metabolite M1 (2-methylthio-4-tert-butylamino-6-amino-s-triazine). Recently, it was found that the metabolite M1 was also produced from Irgarol 1051 through hydrolysis catalyzed with mercuric chloride (Liu *et al.*, in press) and through photodegradation (Okamura *et al.*, in press).

The volatility of Irgarol is considered to be low (Ciba Geigy, 1995) and it has been assumed to be non-volatile in modelling studies (Rogers *et al.*, 1996). However, there are no published data on the subject of Irgarol volatility. In this report, some data from volatility experiments are presented which show that Irgarol often cannot be regarded as non-volatile.

MATERIALS AND METHOD

Chemicals

Irgarol 1051 [(2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine), identification no. 84611.0] of high grade (95%) was a gift of Ciba-Geigy Canada Ltd., Mississauga, Ontario. All the test inorganic and organic chemicals were obtained from BDH Chemicals (Toronto, Canada). Pesticide grade organic solvents were obtained from Caledon Laboratories, Georgetown, Ontario. The sodium sulphate used for drying organic extracts was heated to 500°C for 24 h before use. All glassware were also rinsed with pesticide grade solvents before use. All other chemicals used in the experiments were reagent grade or better.

Laboratory experiment

Four one-litre glass beakers containing organic-free water were spiked with Irgarol to a concentration of approximately 70 µg/L. Three of the beakers were at a room temperature of approximately 20°C. Water movement was created in two of these beakers using magnetic stirrers. One was stirred slowly so that there was a gentle current which did not ruffle the water surface. The other one was subjected to fast stirring which created a noticeable vortex in the middle of the beaker. The fourth beaker was immersed in a water bath which was maintained at a constant temperature of 35°C. The test conditions are summarised in Table 1. The solutions were sampled periodically to measure any changes in concentration. Before each sampling, the beakers and contents were weighed and distilled water was added to account for water loss through evaporation. After a brief mixing period, samples were taken for chemical analysis.

Sample preparation and chemical analysis

Three 10 mL samples were withdrawn from each beaker at every sampling and then 10 mL of dichloromethane (DCM) were added to each sample. The samples were extracted with 3 x 10 mL aliquot of DCM. All resulting DCM extracts were dried through anhydrous sodium sulfate. A toluene keeper was added to each and the entire extract was concentrated to 5 mL on a rotary evaporator. Further concentration and solvent exchange into a final volume of 0.5 mL of toluene was performed under a stream of nitrogen.

The toluene extracts were analyzed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a nitrogen-phosphorus detector (300°C) and a flame ionization detector (300°C) utilising an oven program with a 2-min hold at 80°C and a temperature ramp of 10°C/min to 150°C followed by a temperature ramp of 4°C/min to 280°C and a final temperature ramp of 8°C/min to 300°C. The columns used were dual DB5 coated capillary columns (0.25 mm x 27 m) which had been installed into the injector (200°C) in the splitless mode with a constant helium carrier flow of 0.8 mL/min. Mass spectral analysis was performed using the same temperature program and column stationary phase (0.25 mm x 30 m) on a Hewlett Packard 5971A mass selective detector (MSD), and MS Chem Station. The MSD was operated in electron impact (EI) mode with an ionization potential of 70 eV and a source temperature of 190°C. The scan range was 50-500 amu and quantification of Irgarol 1051 was obtained using selective ion monitoring (SIM). Three selective ions, m/z 182, 238 and 253, were used to confirm the presence of Irgarol 1051.

RESULTS AND DISCUSSION

Concentrations of Irgarol 1051 in the experimental samples are summarized in Table 2. These data are plotted against time in Figure 1 to yield the profiles of Irgarol disappearance. From Table 2 and Figure 1 it can be seen that there were hardly any losses of Irgarol 1051 from beakers no. 1 and no. 2 (20°C, no motion and small current) as the Irgarol content remained practically constant over the fifty nine days of the experiment. However, for beakers no. 3 and no. 4 (20°C, fast stirring and 35°C, no motion), there were significant losses. At the end of the experiment, the Irgarol content in these beakers had decreased by about fifty percent. No degradation products were detected in any of the samples, which is not unexpected as Irgarol 1051 is not considered to be readily biodegradable and its degradation in seawater and freshwater is slow, with half-lives of about 100 and 200 days, respectively (Ciba Geigy, 1995; Liu *et al.*, 1997). Therefore, the loss of Irgarol in beakers no. 3 (20°C with fast stirring) and no. 4 (35°C with no motion) can be attributed to volatilization.

It should be recognized that calm conditions such as those occurring in beakers no. 1 and 2 seldom exist in a real marine environment, where wave action can generate ocean spray and air entrainment, conditions which will favour volatilization. This loss of Irgarol would be further enhanced by the strong winds frequently encountered in an ocean environment. Wind speed has been demonstrated to be one of the dominating factors affecting the volatilization of lipophilic chemicals from the aquatic environment (Cohen *et al.*, 1978). Thus, it is conceivable that a marine environment can provide conditions where the volatilization of Irgarol 1051 is not negligible.

Fouling pressure (i.e., potential to develop fouling) is much greater in the tropical marine environment than is in the temperate zone. Consequently, ships sailing in tropical oceans need more frequent applications of antifouling paint (U.S. Naval Institute, 1952). The higher water temperature in tropical oceans will no doubt lead to a greater loss of Irgarol from the water phase.

Transport of chemicals from water bodies to the atmosphere via volatilization or evaporation is an important environmental pathway for many chemical substances, particularly for those of low molecular weight and high vapor pressure. (Smith *et al.*, 1980). Now, our study has demonstrated that a chemical such as Irgarol 1051 with very low vapor pressure (8.8×10^{-5} Pa at 25°C) may also be volatile under given environmental conditions, thus implying the important role of volatilization in dictating the fate of a chemical in the aquatic environment.

CONCLUSIONS

Data from the present experiments show that Irgarol 1051 can be considered as non-volatile only at normal room temperatures and with low turbulence levels in the water. For tropical climates or when there is high turbulence level in the water, loss of Irgarol through volatilization must be considered.

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Table 1. Summary of test conditions

Beaker number	Temperature	Water movement
1	20 ^o C	no motion
2	20 ^o C	gentle stirring
3	20 ^o C	fast stirring
4	35 ^o C	no motion

Table 2. Summary of experimental data

Amount of Irgarol in sample (ng) *				
Days	Beaker no. 1	Beaker no. 2	Beaker no. 3	Beaker no. 4
0	70.78	67.04	66.83	64.18
1	70.26	66.23	64.97	68.5
3	68.34	68.13	66.91	67.45
5	64.47	69.01	66.06	62.48
13	63.00	64.49	66.28	62.23
20	62.21	66.35	59.37	58.15
29	69.37	65.99	59.69	no data
42	60.81	66.85	no data	47.82
49	63.07	60.65	40.05	46.53
59	65.58	52.19	32.7	35.66

* average of three samples

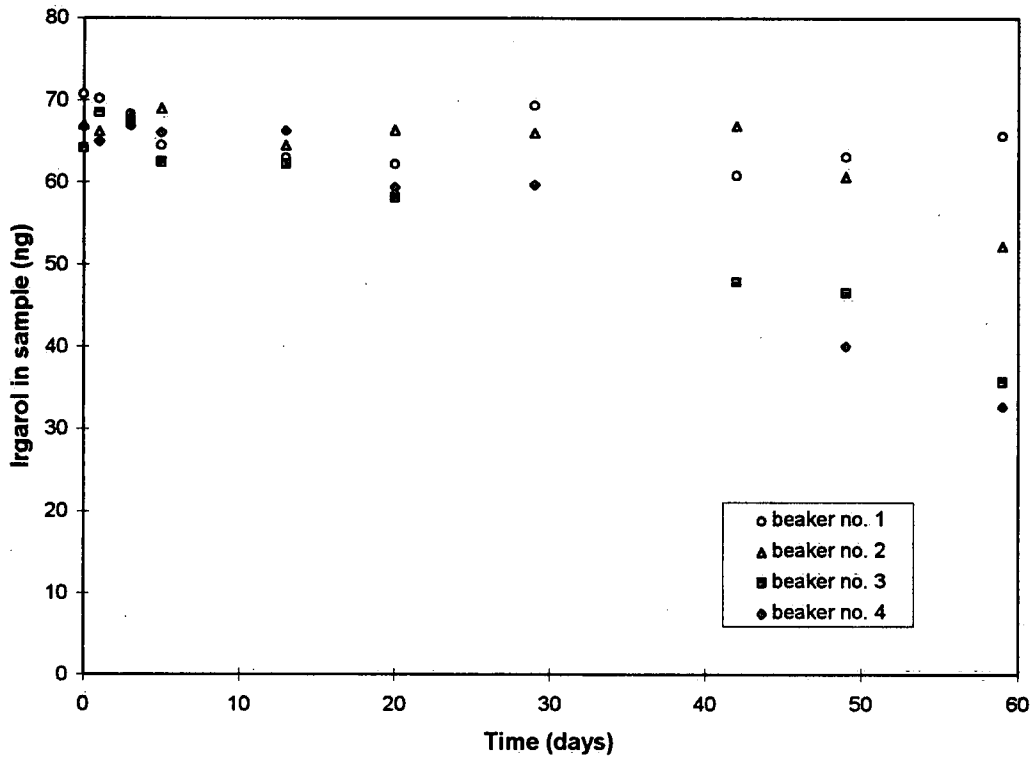
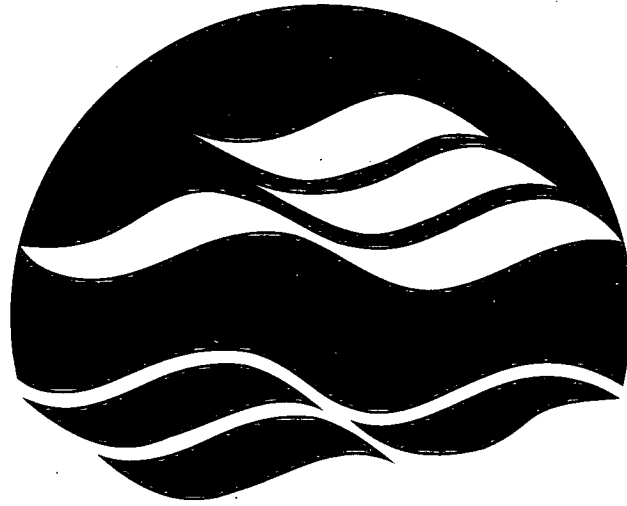


Figure 1. Change in Irgarol concentration with time.



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