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Photodegradation of the antifouling compounds Irgarol 1051 and Diuron released from a commercial antifouling paint

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Abstract

The antifouling compound Irgarol 1051 and its degradation product M1 (also known as GS26575), along with another antifouling compound Diuron, have recently been found in Japanese coastal waters. This study was undertaken to find the origin of these chemicals and investigate their aquatic fate. Five glass plates, each coated with 1 g of antifouling paint containing Irgarol and Diuron, were submerged in 250 mL of five different test waters and the plates removed after several months. The aqueous solutions were divided into two groups: one exposed to natural sunlight, and the other kept in the dark as a control. Irgarol and Diuron were detected in all aqueous solutions, suggesting leaching from antifouling paints is the origin of these antifouling biocides found in Japanese coastal waters. Under sunlight conditions, Irgarol underwent a rapid degradation to produce M1, which remained even after Irgarol had disappeared from the system. These compounds were persistent in any aqueous solutions tested under dark conditions, indicating high stability to hydrolysis. Diuron and M1 were more persistent than Irgarol under sunlight irradiation. Since these compounds have high herbicidal activities, their ultimate impact on aquatic ecosystems is closely related to their aquatic fate.

Keywords: antifouling compounds; aquatic fate; degradation; Diuron; Irgarol 1051; leaching.

1. Introduction

New antifouling compounds are intended as replacements for the widely used antifouling agents organotin biocides (tributyltin and triphenyltin), which were regulated internationally in the late 1980s and early 1990s. Recently, the environmental fate and behaviour of antifouling paint booster biocides was reviewed by Thomas (2001). Among eighteen compounds which are currently used as antifouling biocides, Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) is a herbicidal additive for use in copper- and zinc-based antifouling paints (Gough *et al*., 1994). Irgarol 1051 does not appear to undergo rapid biodegradation, and its residues have been detected in European estuarine, coastal, and lake waters and sediments (Readman *et al*., 1993; Gough *et al*., 1994; Toth *et al*., 1996; Scarlett *et al*., 1997; Thomas, 1998; Penalver *et al*., 1999; Sargent *et al*., 2000; Thomas *et al*., 2000). There are a few reports of Irgarol residues outside Europe, for example, in Japanese coastal waters (Liu *et al*., 1999b) and within Australian coastal-water sea grasses (Scarlett *et al*., 1999). There has been little information in the open literature on Irgarol's environmental persistence and degradation. Liu *et al*. (1997) demonstrated that Irgarol 1051 could be bio-transformed by the white rot fungus *Phanerochaete chrysosporium* via the mechanism of N-dealkylation to yield a stable metabolite named as M1, which is same as GS26575 (2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine). It was also found that this metabolite, M1, was produced from Irgarol 1051 via two other pathways: mercuric chloride-catalysed hydrolysis (Liu *et al*., 1999a), and sunlight degradation (Okamura *et al*., 1999). The Irgarol degradation product M1 has been positively identified in Japanese coastal waters with the highest concentration of 1870 ng/L (Okamura *et al*., 2000), and was also found at lower concentrations (13–99 ng/L) in coastal water at Southampton, UK (Thomas *et al*., 2000). It was also noted by Hall *et al*. (1999) that M1 accumulated up to about 100 ng/L for the first month and then declined in Irgarol-treated marine microcosm study.

According to a survey we undertook in 1999, a urea-based herbicide Diuron, 3-(3,4-dichlorophenyl)-1,1-dimethylurea, was detected, for the first time, in coastal waters of Western Japan, accompanied by residues of both Irgarol and M1 (Okamura and Aoyama, 2001). There are several reports on residue analyses of Diuron and Irgarol in seawaters outside Japan (Ferrer *et al*., 1997; Thomas, 1998; Ferrer and Barcelo, 1999; de Almeida Azevedo *et al*., 2000; Martinez, *et al*., 2000). However, there have been no data on Diuron residues in Japanese aquatic environments despite the compound having been used for weed control in ploughed fields for a long time. Diuron is a registered herbicide, but Irgarol 1051 has not been registered as a permitted agrochemical in Japan. It was reported that Irgarol 1051 and Diuron were included in 17 safe and effective antifouling compounds assessed by the Shipbuilding Research Association of Japan (Yonehara, 2000). In contrast with our situation, legislation has already been introduced in some European countries to restrict the use of Irgarol and Diuron in boats < 25m (personal communication). To our knowledge, information on chemical compositions, production and usage statistics of antifouling compounds used in Japan is not publicly available. It is, therefore, difficult to confirm that the origin of these antifouling agents detected in the

Japanese coastal waters can be ascribed to commercial antifouling paints used for ship bottoms and/or on fishing nets. One way to confirm this would be to find a commercial paint product, which contains Irgarol and Diuron, and to perform a leaching study using that paint. This report uses that approach to investigate the origin of these compounds and their aquatic fate in terms of photodegradation.

2. Materials and methods

2.1 Test compounds

Irgarol 1051 (95%) was donated by Ciba Specialty Chemicals K.K. Japan. The degradation product M1 was purified by mercuric chloride-catalysed hydrolysis of the parent compound as given in Okamura *et al*. (2000). Diuron (95%) was purchased from Tokyo Kasei Kogyo Co. Ltd. Acetonitrile (MeCN, 99.8%, HPLC Grade, Ishidzu Chemicals), dichloromethane (DCM, 99.8%, Pesticide Grade, Kanto Chemicals), and methanol (MeOH, 99.8%, Pesticide Grade, Kanto Chemicals) were used for extraction and HPLC analysis.

2.2 Selection of test paint

Three commercial antifouling paint products (AP1, AP2, and AP3) were purchased from a Japanese paint company on December 1998. A portion of well-mixed paint (0.5 g) was taken in a 50 mL glass centrifugal tube, and then DCM (20 mL) and water (10 mL) were added. The tube was mixed with a mechanical shaker for 20 min. The lower DCM layer was collected after the tube had been centrifuged at 3000 rpm for 20 min. Additional DCM (20 mL) was added to the remaining water and the DCM was collected after mixing and centrifuging again. Both the DCM extracts were combined and the DCM was evaporated *in vacuo* with a centrifugal evaporator at 40 ˚C. The resulting residue, dissolved in methanol (5 mL), was filtered through a 0.2 µm membrane and concentrated to 1 mL. The methanol extract was subjected to HPLC by the method given in Okamura *et al*. (1999). HPLC analysis demonstrated that AP3 contained 1.0% w/v of Diuron and 0.26% w/v of Irgarol, and two other paints tested contained 1.9% w/v of Diuron without Irgarol. Therefore, the commercial paint product AP3 was used for the leaching study.

2.3 Leaching study of antifouling compounds from a paint

The end of a glass plate (26 mm width x 76 mm length x 1 mm thickness, normally used as a microscope glass slide) was dipped in the thoroughly mixed AP3 paint. The plate coated with paint was dried at room temperature in the dark for a couple of days. The average dry weight of the paint was 1.09 g (with 0.17 g as standard deviation) per one glass plate, calculated from 30 pieces of the plates used. Five different aqueous solutions (1 L): seawater, river water, and buffered solutions (pH 5, 7, and 9 in 20 mM sodium acetate), prefiltered with 0.2 µm membrane filters, were prepared. Each solution was divided into four autoclaved TPX bottles (250 mL each), which were suitable for the photodegradation study due to their high transparency to ultraviolet radiation in sunlight (Okamura *et al*., 1999). One glass plate, coated with antifouling paint containing Irgarol and Diuron, was submerged in 250 mL of these different test waters in a TPX bottle.

The test solutions, in these tightly capped TPX bottles, were placed on the building roof of the Research Institute for Bioresources, Okayama University, Japan, for a period of 10 months starting from 1 June 1999. The aqueous solutions were divided into two groups: one with exposure to natural sunlight (three bottles for each test water), and the other was kept in the dark, covered in a white polystyrene foam box (one bottle for each test water). Water samples collected at 0, 0.5, 1, 2, 3, 4.5, 6, 8, and 10 month intervals were subjected to HPLC analysis to determine the concentrations of Irgarol 1051, its degradation product M1, and Diuron. Three water samples were collected from each of the light-exposed bottles, and three from the ones kept in the dark at each sampling time. The glass plates were removed after three months for the sunlight exposure and after six months for the dark exposure, respectively. At three, six, and eight months, the whole water samples exposed to sunlight were filtered through a 0.2 µm membrane and then transferred into new autoclaved bottles aseptically, because the light-exposed TPX bottles became fragile due to the long-term exposure to sunlight. There were visible materials trapped on the membrane filters in a few cases at bottle replacement. This is probably due to operational contamination by microbes or dust. No fragility of the bottles under dark conditions was observed.

2.4 Degradation study of M1

Irgarol's degradation product M1 (10,000 mg/L in MeCN) was dosed into the five different aqueous solutions (3 L) in the same manner as described in Section 2.3, above. The solutions containing 1.0 mg/L of M1 with 0.01% MeCN were then passed through a 0.2 µm membrane filter and stored in autoclaved TPX bottles. These solutions were used for the hydrolysis and photodegradation experiments. Degradation of M1 was evaluated using the same procedure as described by Okamura *et al*. (1999). Five different test solutions (10 mL each) in glass tubes were kept at 50 ˚C in the dark for one week. The test solutions were also autoclaved at 120 ˚C and 1.12 atom for 20 min. Five glass tubes per test water were employed for each treatment. The concentrations of M1 with and without treatment were determined by HPLC. Test solutions (250 mL) in the TPX bottles were placed on the building roof and the M1 concentrations were periodically determined in the same manner described in Section 2.3, above.

2.5 Analysis of antifouling compounds

The extraction procedure using a Sep-Pak C18 ENV column and analytical procedure using reversed-phase HPLC were identical to those used in our previous study (Okamura *et al*., 1999), except for a modified gradient program to accomplish better separation of target compounds from multiple peaks in the extract. The solvents used were: (A) 10 mM phosphate solution (pH 2.5), and (B) MeCN at a flow rate of 0.2 mL/min at 40 ˚C. The linear gradient elution employed was programmed to go from 20% B to 30% B in 10 min, and from 30% B to

100% B in 20 min, with a total 30 min run. M1, Diuron, and Irgarol were eluted at retention times 13.3, 21.6, and 22.6 min, respectively, under these conditions.

3. Results and discussion

3.1 Photodegradation of antifouling compounds released from a paint

Identification of antifouling compounds in the commercial paint AP3 was performed by GC/MS for Irgarol and M1 (Okamura *et al*., 2000), and by LC/MS for Diuron (Okamura *et al*., 1999). M1 was not found in the paint AP3 according to the GC/MS analysis. The DCM extract of the AP3 (0.5 mL in xylene) dissolved in MeOH (1.0 mL) was found to contain 5.2 mg of Diuron and 1.3 mg of Irgarol 1051 according to HPLC analysis. Therefore, the contents of Diuron and Irgarol in the AP3 were estimated to be 1.0% and 0.26% w/v, respectively. There was one report that a commercial antifouling paint purchased in Australia had been found to contain Irgarol 1051 (Scarlett *et al*. 1999), however, the concentration of Irgarol in the paint was not reported.

Leaching studies using the commercial paint AP3 were performed over 10 months, with the concentrations of three compounds in the test waters as shown in Figs. 1 to 3. Diuron was released from the paint coated on the glass plate into the test waters under dark as shown in Fig.1-B. The highest concentration was about 70 mg/L of the buffered solutions at pH 7 and 9, and the Diuron concentration in the paint was calculated as 1.8% w/w (=17.5 mg per 0.25 L water per 1 g dry paint). Diuron concentrations in water increased with time until removal of the plate, and remained stable thereafter. The amount released into the seawater was the lowest among the test waters, followed by river water and buffered solution (pH 5). On the other hand, changes in Diuron concentrations under sunlight conditions were different from the ones under dark control (Fig.1-A). Under sunlight irradiation, Diuron concentrations increased with time (up to about 20 mg/L in the waters except for seawater) and decreased to a certain level after the plate was removed. The difference in the concentrations clearly shows that Diuron released into buffered solutions is easily degraded by sunlight irradiation (Fig.1-A and B). Leaching rates (%) of Diuron were calculated using the concentrations at the third month on the basis of the maximum leached concentration 70 mg/L (Table 1). The leaching rates in buffered solutions kept under sunlight were much lower than those kept in the dark. There were no significant differences in leaching rates in natural waters for the first three months, regardless of sunlight. The leaching rate of Diuron in seawater was the lowest among the test waters. It is concluded that Diuron released into test waters was considerably stable to hydrolysis and also stable to sunlight irradiation to some extent. We could not assign any HPLC peaks in the extracts to metabolites of Diuron, although several photoproducts have been reported (Tanaka *et al*., 1986).

Irgarol 1051 was released rapidly from paint into water (Fig. 2) and in a different manner to Diuron (Fig. 1). Irgarol concentration in the paint was estimated to be 0.03% w/w (= 0.3 mg in 0.25 L per 1.0 g dry paint), and the highest concentration released was 1.2 mg/L in the buffered solution of pH 9. Under dark conditions, Irgarol released in the first three months remained stable for the following five months (Fig. 2-B). Irgarol concentrations released into seawater were, among the test waters, the lowest, and this was the same as shown for Diuron (Fig. 1). It is probably due to higher ionic strength of seawater to other test waters. Higher amounts of Irgarol were released into river water than into a buffered solution of pH 5. Under sunlight irradiation, Irgarol released into test waters was present in all test waters for the first three months, and then reached non-detectable levels after the paint was removed (Fig. 2-A). Leaching rate (%) of Irgarol was calculated using the concentrations at the third month on the basis of the maximum leached concentration of 1.2 mg/L (Table 1). The leaching rates in the test solutions under light were lower than those under dark except for the case in seawater. Irgarol in seawater was detected at the same levels for the first three months, regardless of sunlight irradiation. The results clearly demonstrated that Irgarol released into waters would rapidly undergo photodegradation if there was no source to supply Irgarol.

The concentrations of M1 in the test waters were also analysed for 10 months (Fig. 3), because it had been reported that M1 could be produced via sunlight degradation of Irgarol 1051 (Okamura *et al.*, 1999). M1 was detected both under sunlight and dark conditions and the concentrations found under sunlight were higher than those under dark, regardless of the test waters. Under sunlight irradiation, M1 concentrations were constant and no Irgarol residues were detected after the plate was removed. On the contrary, M1 in the dark remained constant after the third month. These results demonstrate that M1 is more persistent than Irgarol under both conditions tested. This also implies that M1 produced from Irgarol, which had been successively released from the paint into the water, accumulated in the waters. Fig.4

demonstrates the relationships between Irgarol concentration and M1 production in natural waters for the first three months. The maximum M1 concentration detected was 2.4 mg/L in river water, which was higher than that measured for Irgarol (0.8 mg/L). It is noteworthy that M1 concentrations observed from the first to the third month were higher than those of Irgarol in natural waters under sunlight condition. This is due to a higher persistency of M1 than the parent compound in natural waters to sunlight irradiation. This result is consistent with the observation by marine microcosm study, that is, M1 was present at higher level than Irgarol after three months of Irgarol administration (Hall *et al.*, 1999).

Unexpected production of M1 under dark conditions was also reported by our previous photodegradation study of Irgarol (Okamura *et al.*, 1999). This has not been completely explained, but probably occurred due to inadvertent exposure of the sample during experimental processing, since M1 itself was not detected in the paint AP3 by GC/MS analysis. There are a number of areas where the dark control may have received solar irradiation. For example, storage of the TPX bottles in a white-coloured polystyrene box which may not have been opaque enough, during transportation of the bottles from roof to laboratory, and when conducting subsequent sampling and concentration steps under ambient conditions.

Diuron and Irgarol concentrations in seawater under sunlight and in the dark conditions were significantly lower than those in the other test waters (Figs. 1 and 2). There were no remarkable differences in the concentrations in seawater between under sunlight and in the dark. This observation may be explained by salting-out effect of seawater. However, Fig.4

demonstrates that more amount of Irgarol released into seawater had been degraded to form M1 since M1 concentrations under sunlight was much higher than Irgarol. The effect of salting-out on leaching of antifouling compounds will be clarified by further experiments using different ionic strength waters.

As for the aquatic fate of Irgarol in natural environments, it is suggested that Irgarol is gradually released from antifouling paint into the surrounding water and reacts with sunlight in the upper water column to decompose itself rapidly, and to form a resulting product M1, which is more persistent than the parent compound. Environmental transformation data of Irgarol indicates that the principal degradation processes for Irgarol will be microbial metabolism under aerobic conditions and photolysis (Hall *et al*. 1999). According to Liu *et al* (1997), Irgarol could not be degraded by a mixed bacterial culture or natural aquatic bacteria form Lake Ontario even after an incubation period of five months. Hence, photodegradation of Irgarol was focused in this study, whilst biodegradation must be an important pathway to comprehend the aquatic fate of Irgarol in natural environments.

Both Irgarol and Diuron residues are simultaneously reported in environmental samples as mentioned, and this implies a high persistency in aquatic environments. There have been a few reports of M1 residues in environmental samples (Hall *et al*., 1999; Okamura *et al*., 2000; Thomas *et al.,* 2000), however, no data were available on the fate of M1 in aquatic environments except for our previous study (Okamura *et al*. 1999). These reports suggest that both Irgarol and Diuron are being used extensively for antifouling purposes worldwide. An experiment on the biodegradability of Irgarol and Diuron in seawater showed that both compounds were not biodegraded in eight weeks, as assessed by a bioassay using a ship-fouling diatom *Amphora coffeaeformis* (Callow and Willingham, 1996). Considering the fate of the paint itself, transfer of paint particles from ship hull into marinas and fishing harbours as a result of shore-side activities, such as high pressure hosing, can provide a source of any included biocide within the sediment. These paint particles will continue to release biocides, providing a constant source during the life of the paint particles and remain as a potential source for release into the surrounding environment (Thomas *et al.*, 2000). Therefore, more studies on the ultimate fate of the antifouling compounds released from paint are needed to establish a strategy for their management in aquatic ecosystems.

3.2 Degradation of M1

Purified M1 was dissolved in five different test waters and the solutions used for a degradation study. The recoveries of M1 (1 mg/L) from five different waters were 77 ~ 88%, which were slightly lower than those of Irgarol analysed by the same procedure (Okamura *et al*., 1999). No significant hydrolysis was observed after a seven-day incubation at 50˚C under dark conditions, except in the buffered solution at pH 5 (8% loss) as shown in Fig. 4. M1 was not significantly degraded by autoclaving at 1.21 atm for 20 min with the exception of M1 in seawater (11% loss). These data demonstrate that M1 is stable against hydrolysis and is heat-resistant under the conditions tested.

After a 10-month solar irradiation, more than 78% of M1 was degraded in any aqueous solutions tested (Fig. 5-A). M1 concentrations in the test waters remained stable for the first two months (from 1 June to 4 August 1999), and then decreased proportionally on a semi-logarithmic scale in the following 1–2 months (from August to September). M1 was not significantly degraded by the fourth month (from October 1999 until April 2000). The degradation rate of M1 at the end of exposure was highest (93%) in the buffered solution at pH 5, and ranged from 78% to 84% in the other waters. Photodegradation of M1 occurred at acidic pH rather than at neutral or basic pH and this was the same as for Irgarol (Okamura *et al.*, 1999). Under dark conditions, 75–89% of M1 remained in all waters tested at the end of the experiment (Fig. 5-B). The differences in degrees of degradation observed between sunlight and dark condition were clearly due to a photochemical reaction. The photodegradation rates of M1 in natural waters (pH 8.0 in either water) were no different from the buffered solutions of pH 7 and 9. It was speculated that natural photosensitizers in the river waters and seawaters were not involved in acceleration of M1's photodegradation, although Irgarol's photodegradation was significantly accelerated in natural waters (Okamura *et al*., 1999). It is difficult to compare the photodegradation study of M1 (Fig. 5) with the one for Irgarol performed in 1997, since the experiments were carried out in different years. These results provide an explanation of why M1, once produced in ambient waters, is more persistent than the parent compound. However, it was photodegraded with no formation of degradation products under the analytical conditions by HPLC. It is concluded that both compounds could be photodegraded in water to a certain extent under sunlight irradiation.

3. Conclusions

An antifouling paint containing Irgarol 1051 and Diuron was selected from several commercial products. A long-term field experiment with the paint submerged in five different aqueous solutions demonstrated that Irgarol and Diuron were released from the paint into all the solutions. Under sunlight conditions, Irgarol underwent rapid degradation to produce M1, which was more persistent than Irgarol. Irgarol was rapidly photodegraded if there was no source. However, Diuron remained at a certain level even after the paint was removed. The results strongly suggest that the antifouling paint tested, which is commercially available on the Japanese paint market, is one of the origins of the antifouling herbicides detected in Japanese coastal waters. M1 was stable to hydrolysis in aqueous solutions and was heat-resistant under the conditions tested. A long-term field experiment of M1 dissolved in five aqueous solutions indicated that 78–93% of M1 was degraded after ten months' exposure to sunlight, although 75–88% of M1 remained under dark conditions. It is concluded that both Diuron and M1 are more persistent than Irgarol 1051. The ultimate fate of those compounds in aquatic environments must be clarified.

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Figure captions

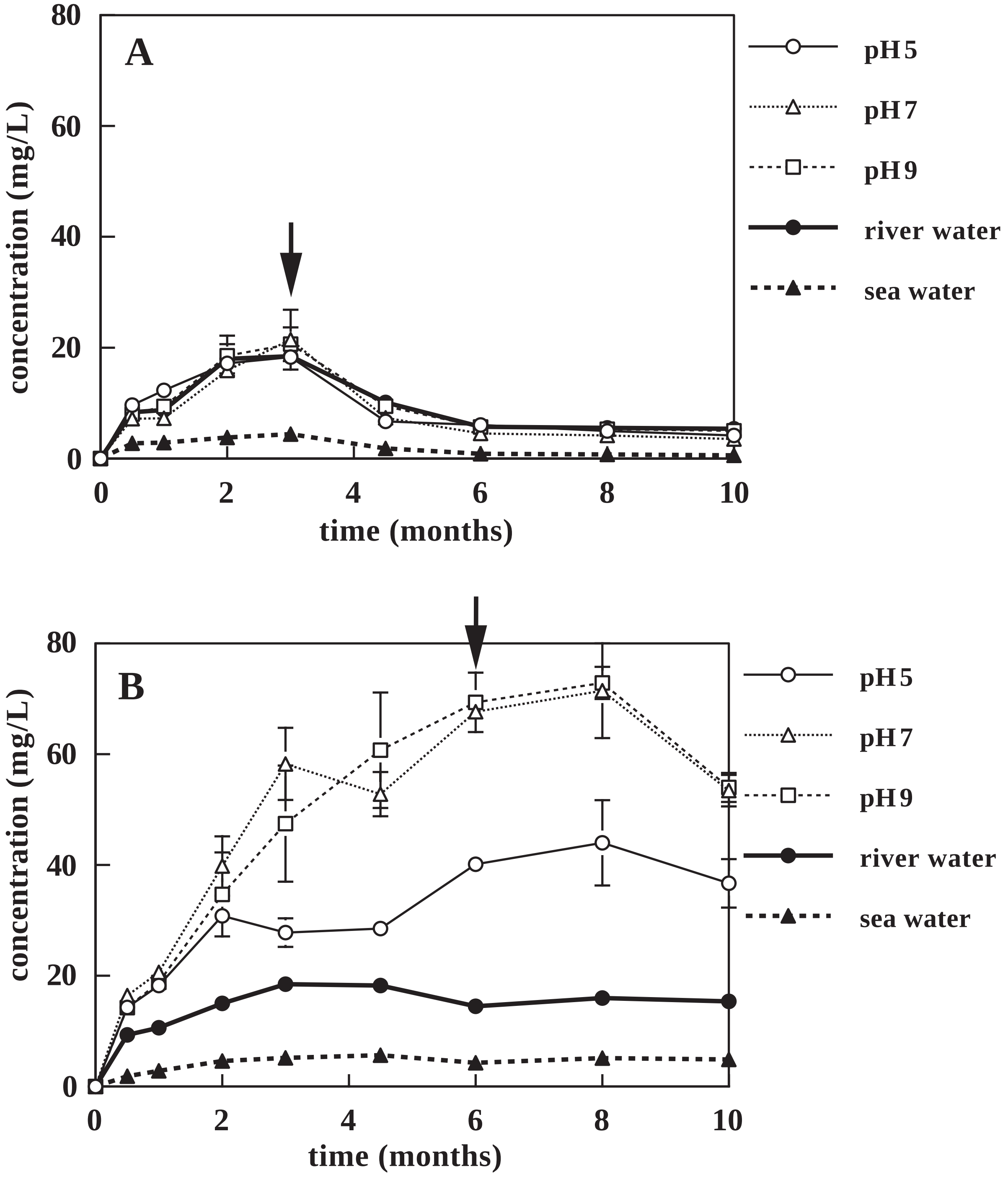

Fig. 1 Fate of Diuron released from paint into aqueous solutions under sunlight (A), and in the dark (B). The glass plate coated with paint was introduced on 1 June 1999 and was

removed from the bottle at the time indicated by an arrow.

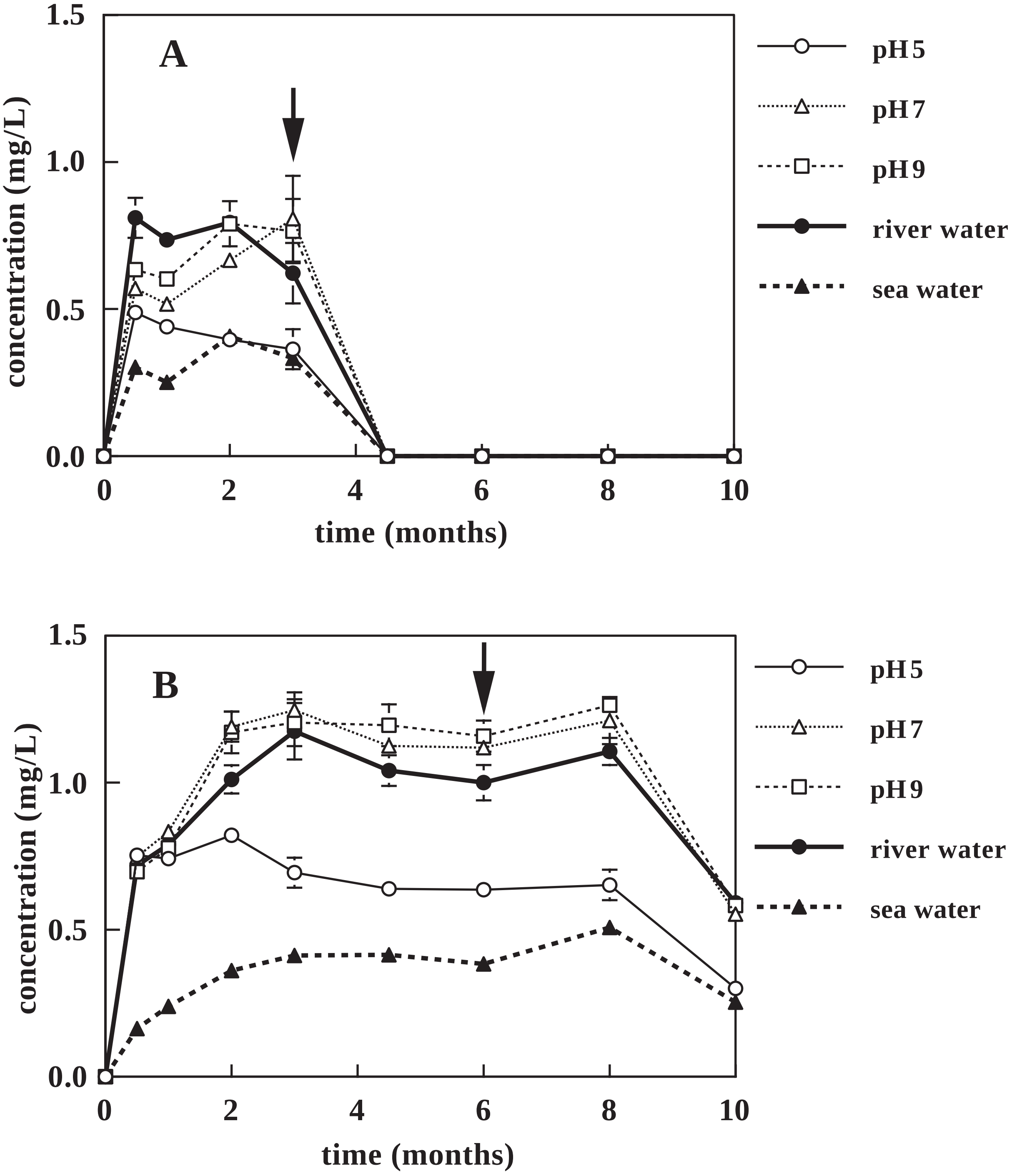

Fig. 2 Fate of Irgarol 1051 released from paint into aqueous solutions under sunlight (A) and in the dark (B). The glass plate coated with paint was introduced on 1st June 1999 and was

removed from bottle at the time indicated by an arrow.

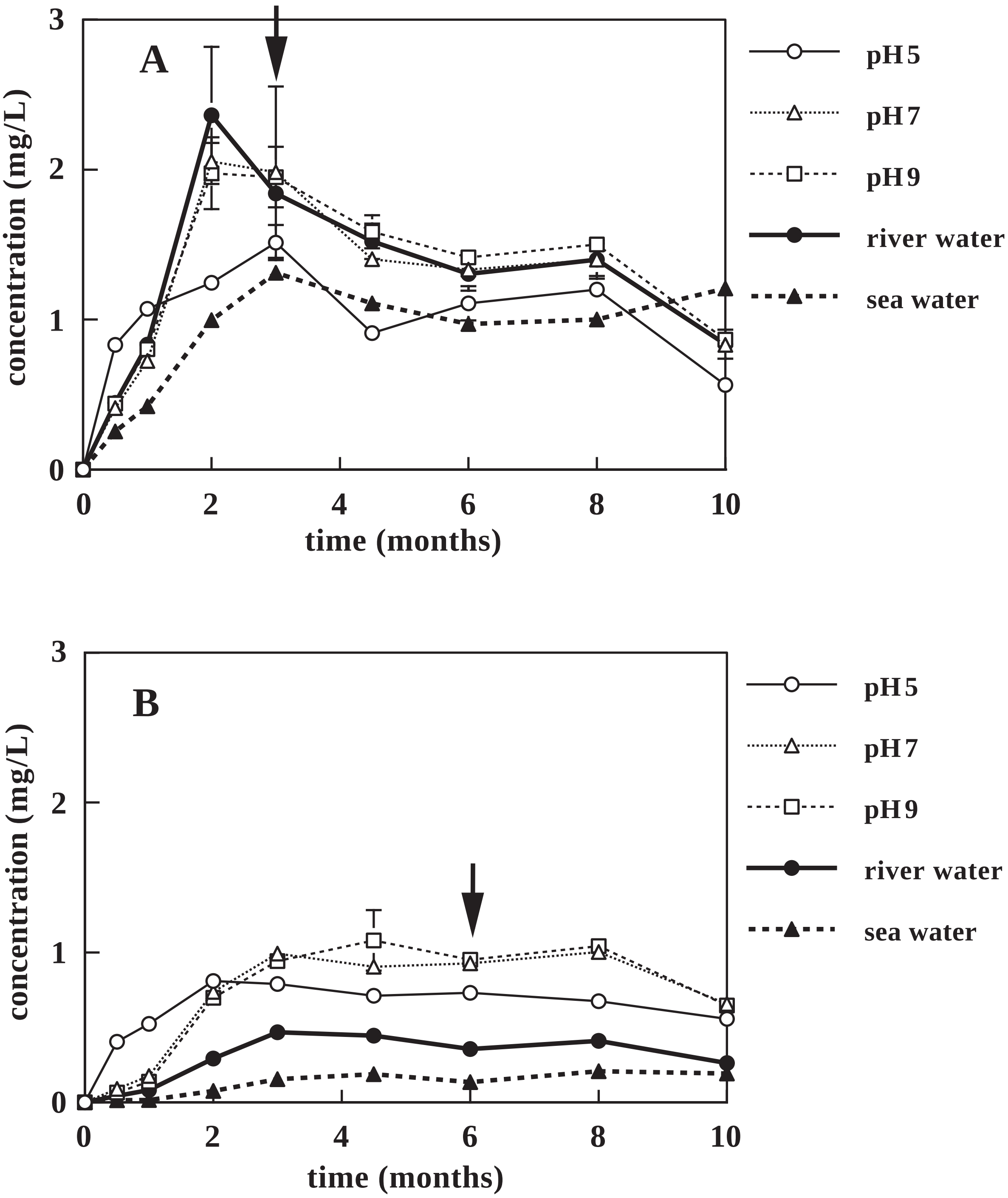

Fig. 3 Fate of M1 produced from Irgarol released from paint into aqueous solutions under sunlight (A), and in the dark (B). The glass plate coated with paint was introduced on 1

June 1999, and was removed from the bottle at the time indicated by an arrow.

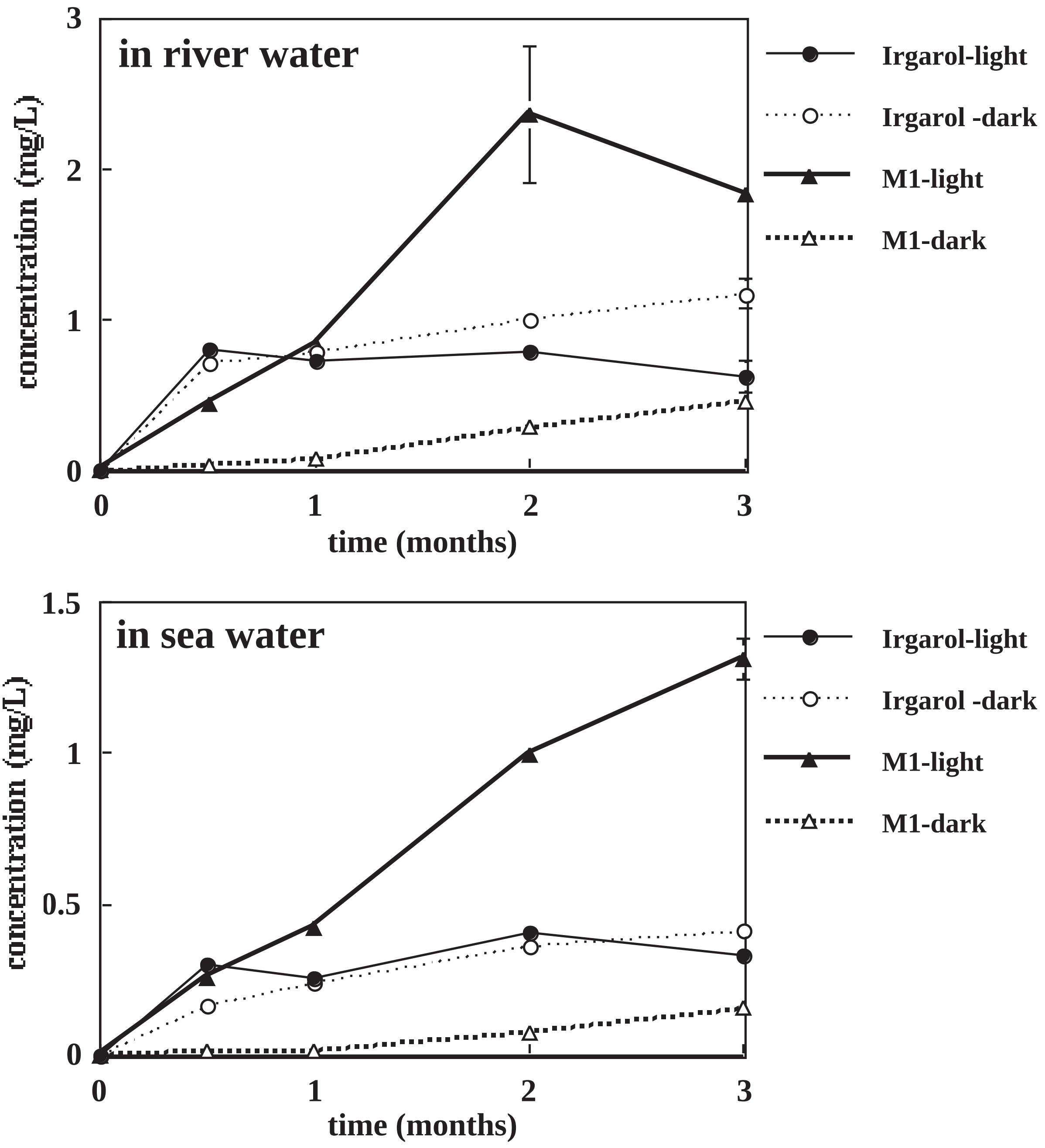

Fig. 4 Relationships between Irgarol concentration and M1 production in natural waters for the first three months.

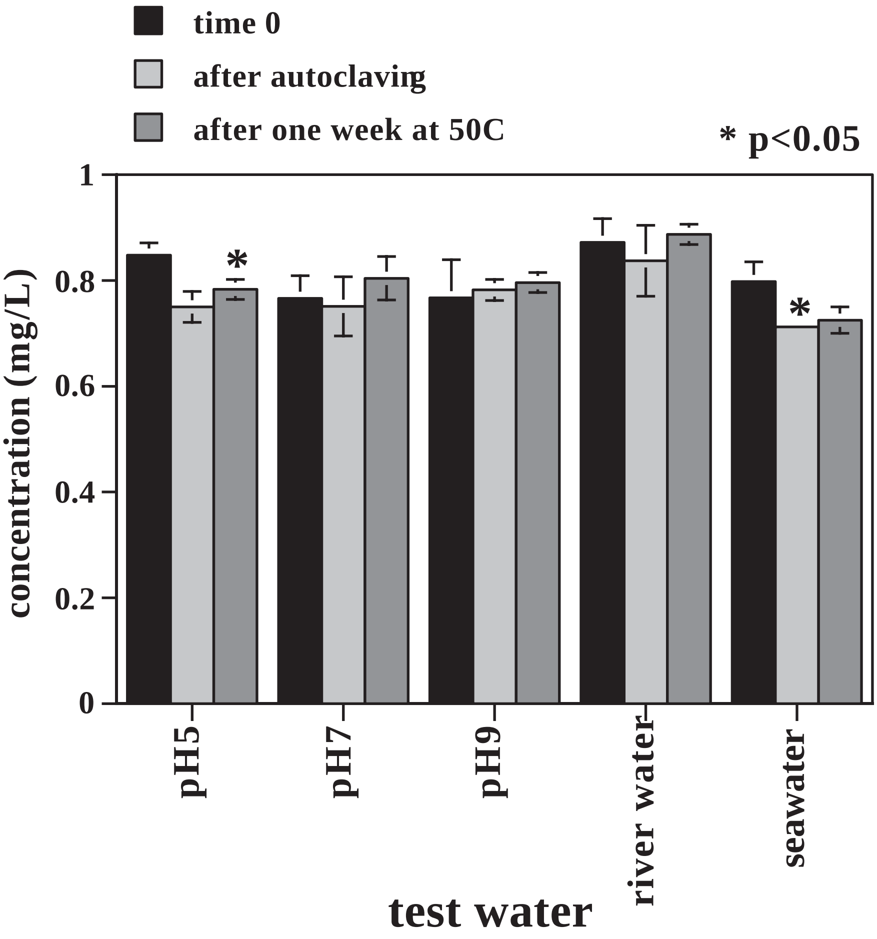

Fig. 5 Hydrolysis of M1 in aqueous solutions.

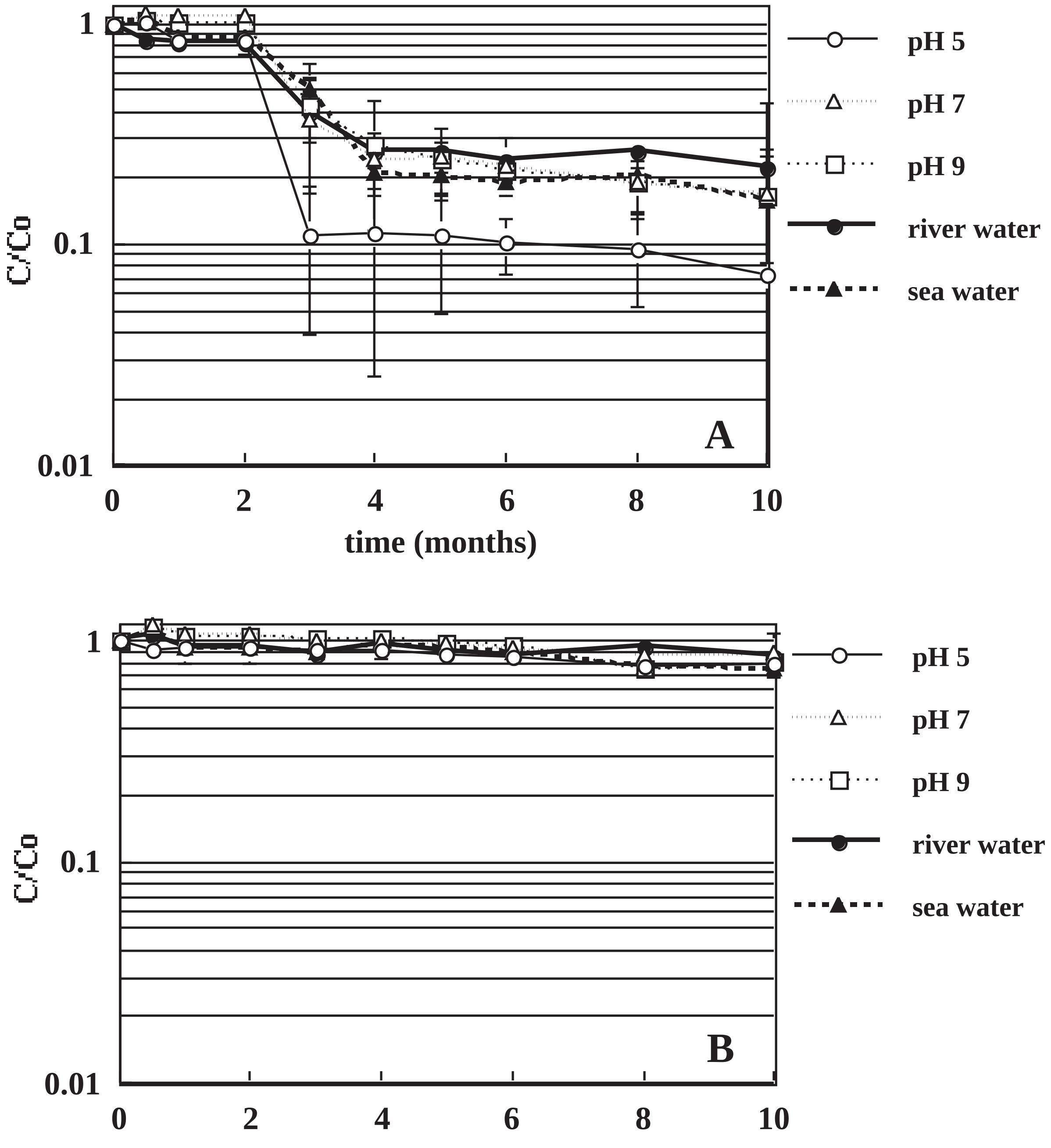

Fig. 6 Degradation of M1 dissolved in aqueous solutions under sunlight (A), and in the dark (B).

Table 1 Leaching rate (%) of the compounds from paint into water*

	Diuron		Irgarol 1051	
test water	Light	Dark	Light	Dark
pH 5	26	40	29	55
pH 7	31	83	65	100
pH 9	29	68	61	96
river water	26	26	50	94
sea water	6	7	27	33

* The rates were calculated using the concnetrations at the 3rd month on the basis of the maximum leached concentraions (70 mg/L for Diuron and 1.2 mg/L for Irgarol).