# Photosensitized degradation of Irgarol 1051 in water

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Abstract

Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) is a herbicide analogue that is added to antifouling agents used on ships. Our former study on its degradation in sunlight suggested that unknown photosensitizers in natural waters accelerated the photodegradation to the degradation product, M1. In this study, the photodegradation of Irgarol in water was investigated in the presence of some photosensitizers. Test water containing Irgarol or M1, with or without photosensitizers, was irradiated with light from a UV-A fluorescent lamp for 48 h. The concentrations of Irgarol and M1 in the test water were determined by HPLC after solid-phase extraction. M1 was more stable than Irgarol when irradiated in the presence of photosensitizers such as acetone, benzophenone, tryptophan, and rose bengal. Hydrogen peroxide (HP) accelerated the photodegradation of Irgarol, and the product M1 was degraded in the presence of more than 100 mg $L^{-1}$ HP after 10 h. Natural humic substances (NHS) also accelerated the photodegradation of Irgarol, but in this case, the product M1 persisted even when Irgarol was completely degraded. Photosensitized degradation of Irgarol by NHS may result in the accumulation of M1 in aquatic environments.

Keywords: biocide, degradation, fulvic acid, humic acid, humic substances, hydrogen peroxide, UV-A

## 1. Introduction

Effective antifouling compounds that prevent the settlement and growth of fouling organisms on submerged structures will always be needed. Some compounds are used as alternatives to organotin biocides, which have been regulated internationally since 1990 due to their severe impact on aquatic ecosystems. Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine) is a herbicidal additive used in copper-based antifouling paints. Several studies since 1993 have demonstrated the presence of Irgarol in European coastal environments. More recently, workers have reported the residue in waters from Bermuda, USA, Singapore, Australia, and Japan. The occurrence and effects of Irgarol and some other biocides have been reviewed by some researchers (Thomas et al., 2002; Voulvoulis et al., 2002; Yamada and Kakuno, 2003; Konstantinou and Albanis, 2004).

Irgarol is known to be stable to biodegradation, hydrolysis, and heat. Liu et al. (1997) demonstrated that Irgarol 1051 was 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: also called GS26575). Recently, it was clarified that manganese peroxidase, one of the major ligninolytic enzymes produced by *P. chrysosporium*, was involved in the biotransformation mechanism (Ogawa et al., 2004). Degradation of Irgarol and simultaneous production of M1 were also reported by mercuric ion-catalyzed hydrolysis (Liu et al., 1999). The same reaction occurred by photolysis with natural sunlight (Okamura et al., 1999), and with natural and artificial sunlight in the presence of titanium dioxide suspensions (Konstantinou et al., 2001; Sakkas et al., 2002). Among these degradation mechanisms, the photochemical process with solar irradiation plays a critical role in the degradation and removal of Irgarol 1051 from the aquatic environment. Photodegradation of triazine herbicides under simulated solar irradiation occurs very slowly

(Minero et al., 1992). The fates of organic micropollutants are largely influenced by the presence of dissolved organic matter, such as humic substances, that is widespread in water–soil–sediment systems and which readily absorb light, leading to the formation of reactive oxygen species such as hydroxyl radicals. Degradation of *s*-triazine herbicides has been tried using hydroxyl radicals generated by ozone, $TiO_2$/UV, photodecomposition of $Fe(OH)^{2+}$, and $H_2O_2$/UV (Chui et al., 2002). Sakkas et al. (2002) demonstrated that natural humic substances isolated from Suwannee River water were responsible for the photolysis of Irgarol using simulated solar irradiation with a xenon arc lamp. They reported qualitatively that several intermediates, including M1, were produced. There are insufficient data on the photolysis of Irgarol and M1 in natural environments (Okamura et al., 1999; Okamura, 2002; Sakkas et al., 2002). This study was intended to investigate the effects of some photosensitizers on the photolysis of Irgarol and M1 in water when irradiated with environmentally relevant intensities of UV-A.

## 2. Materials and methods

### 2.1 Chemicals

Irgarol 1051 and its metabolite M1 were target compounds. Acetone, benzophenone, DL-tryptophan, rose bengal, and hydrogen peroxide (HP) were used for photodegradation experiments. All the chemicals used were of reagent grade. Six kinds of natural humic substances (NHS) were also used for photodegradation experiments. Two sets of fulvic acid (FA) and humic acid (HA) isolated from soils were obtained from the Japan Humic Substances Association (JHSA). HA-D and FA-D were prepared from Dando soil, Japan and HA-I and FA-I from Inogashira soil, Japan. The soil NHS are standard samples supplied by JHSA. Two water-borne fulvic acids, FA-T1 and FA-T2, were prepared from water collected

in the middle and lower reaches of the Takahashi River at Okayama, Japan, in July 1999 and September 2000, respectively. Both water FAs were purified from 250~300 L of the river water according to the method of Ertel et al. (1986).

For photodegradation experiments, benzophenone, DL-tryptophan, and rose bengal were set to 10 mg $L^{-1}$, and acetone was used at 2%. HP was used at 0.01, 0.1, 1, 10, 100, and 1000 mg $L^{-1}$. All NHS were adjusted to 10 mg $L^{-1}$, which corresponds to ca. 5 mg $L^{-1}$ as total organic carbon.

## 2.2 Photodegradation experiments

Stock solutions (10 g $L^{-1}$ dissolved in $CH_3CN$) of Irgarol 1051 or M1 were added to aqueous solutions in a test container (50 mL centrifuge glass tube with glass cap) to a final concentration of 1.0 mg $L^{-1}$. The concentration of the solvent $CH_3CN$ was 0.01%. The test containers, with or without photosensitizers, were irradiated horizontally by UV-A fluorescent lamps (20 W x two bulbs combined horizontally, National Co. Ltd., Tokyo, Japan) at ambient temperature for up to 48 h. The UV-A intensity at the center of the test glass tube was adjusted to 20 W $m^{-2}$ by controlling the distance between the lamps and test container. The intensity was in the range observed on fine summer days in west Japan. The UV-A intensity was measured using a digital UV meter attached to a UV-A detector (Model UV-103, Macam). Samples of the water (5 mL) were collected periodically over 48 h to analyze the concentrations of Irgarol 1051 and M1 during irradiation. Every experiment included a dark control, and the pH of the solution was measured. Photolysis rates were analyzed using pseudo first-order kinetics using concentrations measured at several intervals. The photolysis rate constant (k) and half-life ($t_{1/2}$) were calculated from the regression curve.

2.3 HPLC analysis

Aliquots (5 mL) collected during photo-degradation experiments were passed through a Sep-Pak $C_{18}$ ENV column (Waters) and the compounds retained on the resin were desorbed by methanol. The methanol extract was taken to dryness by a centrifugal evaporator under 40 ºC and the residue was dissolved in 400 µL of $CH_3CN$. Irgarol 1051 in the extract was analyzed using a Hitachi D-7000 HPLC system equipped with a photodiode array detector. A column (Develosil ODS UG5, 2.0 mm x 150 mm, Nomura Chemical) mounted with an ODS precolumn was used. The solvents used were: (A) 10 mM phosphate solution (pH 2.5), and (B) acetonitrile at a flow rate of 0.2 mL $min^{-1}$ at 40 ºC. Linear gradient elution was employed with programming from 30% B initially to 100% B in a 30 min run. Analytical data were shown as average with standard deviation from triplicate experiments

3. Results and discussion

3.1 Photodegradation of Irgarol and M1

The concentrations of Irgarol in river water and pure water under UV-A irradiation are shown in Fig. 1. After 48 h of irradiation, Irgarol in river water was degraded with simultaneous production of M1, whereas Irgarol in pure water was not degraded significantly and the degradation product M1 was not produced. This observation supports the reproducibility of our former study (Okamura et al., 1999). Irgarol or M1 solutions were irradiated in the presence of some photosensitizers for 48 h. The recovery of Irgarol was as follows: 0% for benzophenone, 40% for acetone, 47% for tryptophan, 63% for rose bengal, and 80% when no photosensitizers were present. At the same time, the recovery of M1 was as follows: 26% for benzophenone, 60% for acetone, 92% for tryptophan, 82% for rose bengal, and 90% when no photosensitizers were present. The recovery of more M1 than Irgarol in the

presence of each photosensitizer indicates the higher stability of M1 to UV-A irradiation.

### 3.2 Effects of hydrogen peroxide

Irgarol was degraded and M1 was produced in the presence of HP as shown in Fig. 2. HP concentrations lower than 1 mg $L^{-1}$ had no significant effect on Irgarol degradation, whereas HP concentrations higher than 10 mg $L^{-1}$ caused remarkably rapid degradation. Higher concentrations of HP (100 and 1000 mg $L^{-1}$) caused complete degradation of Irgarol after 24 h. At 10 mg $L^{-1}$ HP, high concentrations of M1 (0.07~0.08 mg $L^{-1}$) were produced after 24~48 h. At 100 mg $L^{-1}$ HP, M1 was present after 10 h, but had degraded after 24 h. No M1 was detected at the highest concentration of HP (1000 mg $L^{-1}$). This is probably due to very rapid degradation of M1 once it had been produced in the solution.

Photolysis rate constants (k) and half-lives of Irgarol and M1 when HP is present are shown in Table 1. The half-lives of Irgarol and M1 decreased with increasing HP concentrations. At HP concentrations of 10 and 100 mg $L^{-1}$, the half-lives of Irgarol were much shorter than for M1. Thus, it was clearly shown by the results from the $H_2O_2$-assisted photolysis reaction that M1 was more persistent than Irgarol.

### 3.3 Effects of natural humic substances

Four FAs and two HAs purified from natural soils and river waters were used as photosensitizers at a concentration of 10 mg $L^{-1}$. Degradation of Irgarol and simultaneous production of M1 were observed in the presence of each of the natural humic substances tested (Fig. 3). Degradation of Irgarol was most marked in the presence of a soil humic acid HA-I. Photolysis rate constants and half-lives of Irgarol when NHS were present are shown in Table 2. The half-lives of Irgarol ranged from 20 to 39 h except when HA-I was present, when

it was 6.8 h. M1 was produced simultaneously with the degradation of Irgarol; the maximum concentration was 0.35 mg $L^{-1}$ in the presence of HA-I. The concentration of M1 produced was much higher than when HP was present at 10 mg $L^{-1}$, and so the photochemical reaction assisted by NHS may lead to accumulation of more M1 in natural aquatic environments.

The changes in pH of the aqueous solutions including HP or NHS were ranging within 1.0 during 48 h irradiation. The irradiated solutions contained some small additional peaks on the HPLC chromatograms but none of these, except for M1, could be identified by HPLC–DAD methods. Ten compounds were identified by GC–MS as major photoproducts produced from Irgarol in $TiO_2$ suspensions under simulated solar light (Konstantinou et al., 2001). It was estimated that three dealkylated derivatives, including M1, were abundant among these 10 photoproducts. Sakkas et al. (2002) reported that M1 was a major photoproduct among five intermediates identified in HA/FA solutions under simulated solar light. The UV-A system with HA/FA used in this study also indicated M1 was the major photoproduct. The presence of M1 produced from Irgarol in the upper part of the water column must receive attention in terms of the persistence of ecological toxicity in sediments.

## 4. Conclusions

Irgarol 1051 is known to be stable to biodegradation, hydrolysis, and heat. Against environmentally relevant UV-A irradiation, Irgarol was stable in distilled water and was unstable in river water. Irgarol was degraded more rapidly than its degradation product M1 under UV-A in the presence of rose bengal, DL-tryptophan, acetone, benzophenone, hydrogen peroxide, and natural humic substances. The amount of M1 transformed from Irgarol in the presence of humic substances was much higher than in the presence of hydrogen peroxide. It is obvious that the natural humic substances purified from river waters and natural soils

accelerated the photodegradation of Irgarol and simultaneous production of M1. The photosensitized degradation of Irgarol with natural humic substances may result in greater accumulation of M1 in the upper water column. Thus, natural humic substances are one of the key components determining the fate of Irgarol in the aquatic environment.

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Figure Captions

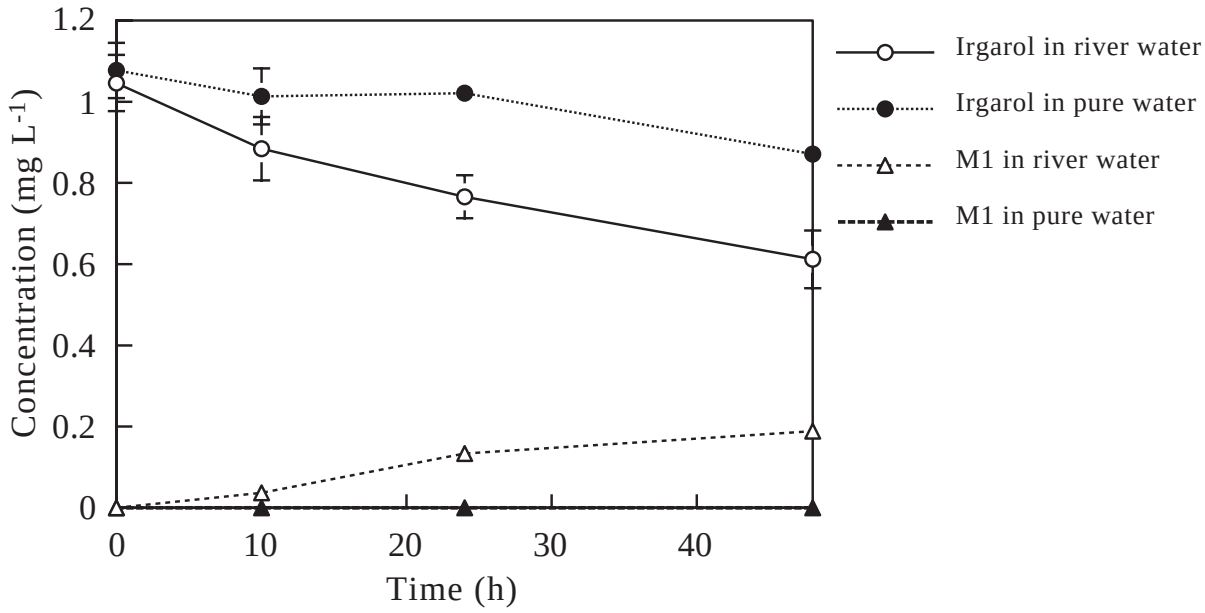


Fig. 1 Photodegradation of Irgarol 1051 and M1 in water under UV-A.

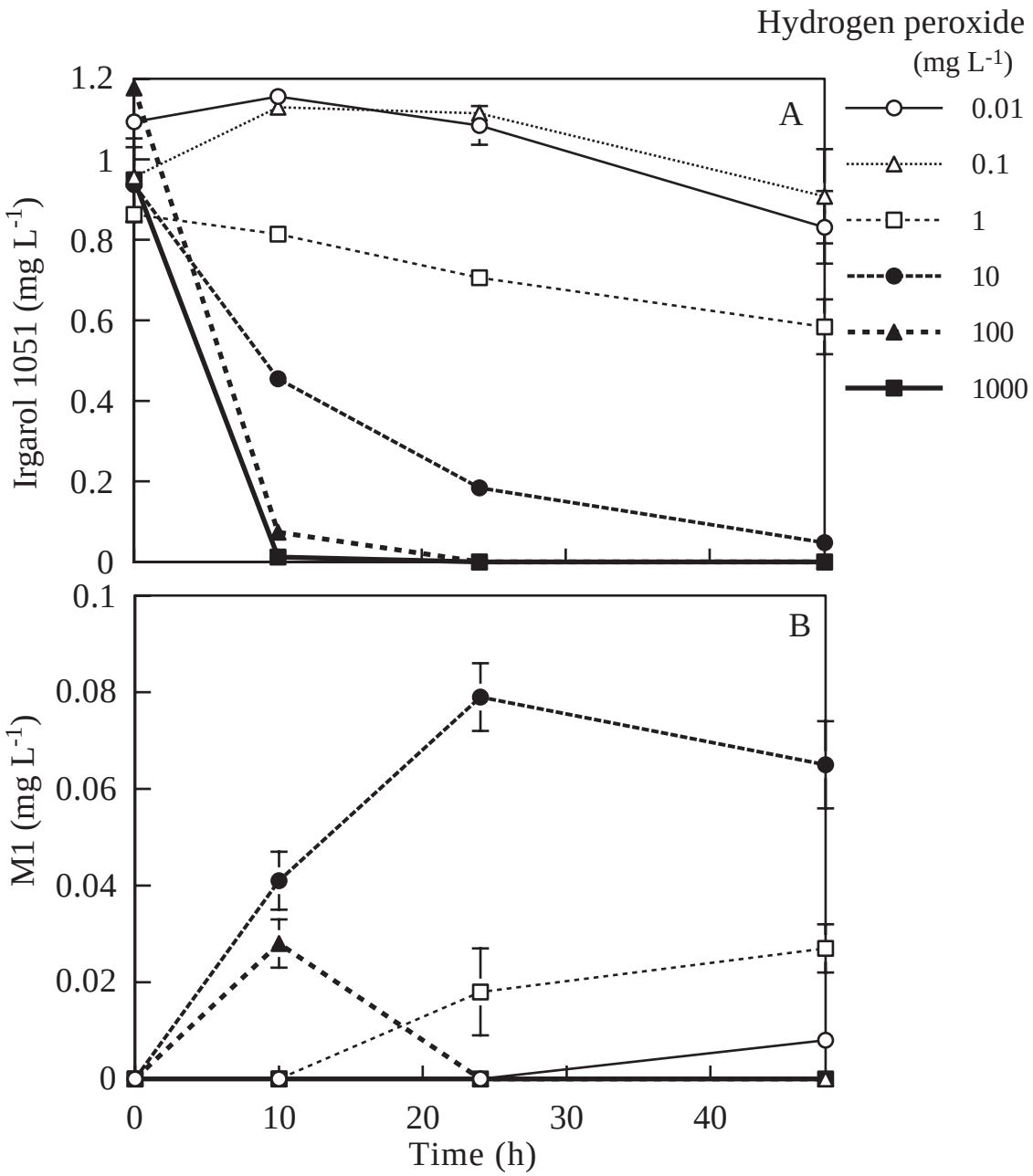


Fig. 2 Effects of hydrogenperoxide on the photodegradation of Irgarol 1051 (A) and the formation of M1 (B).

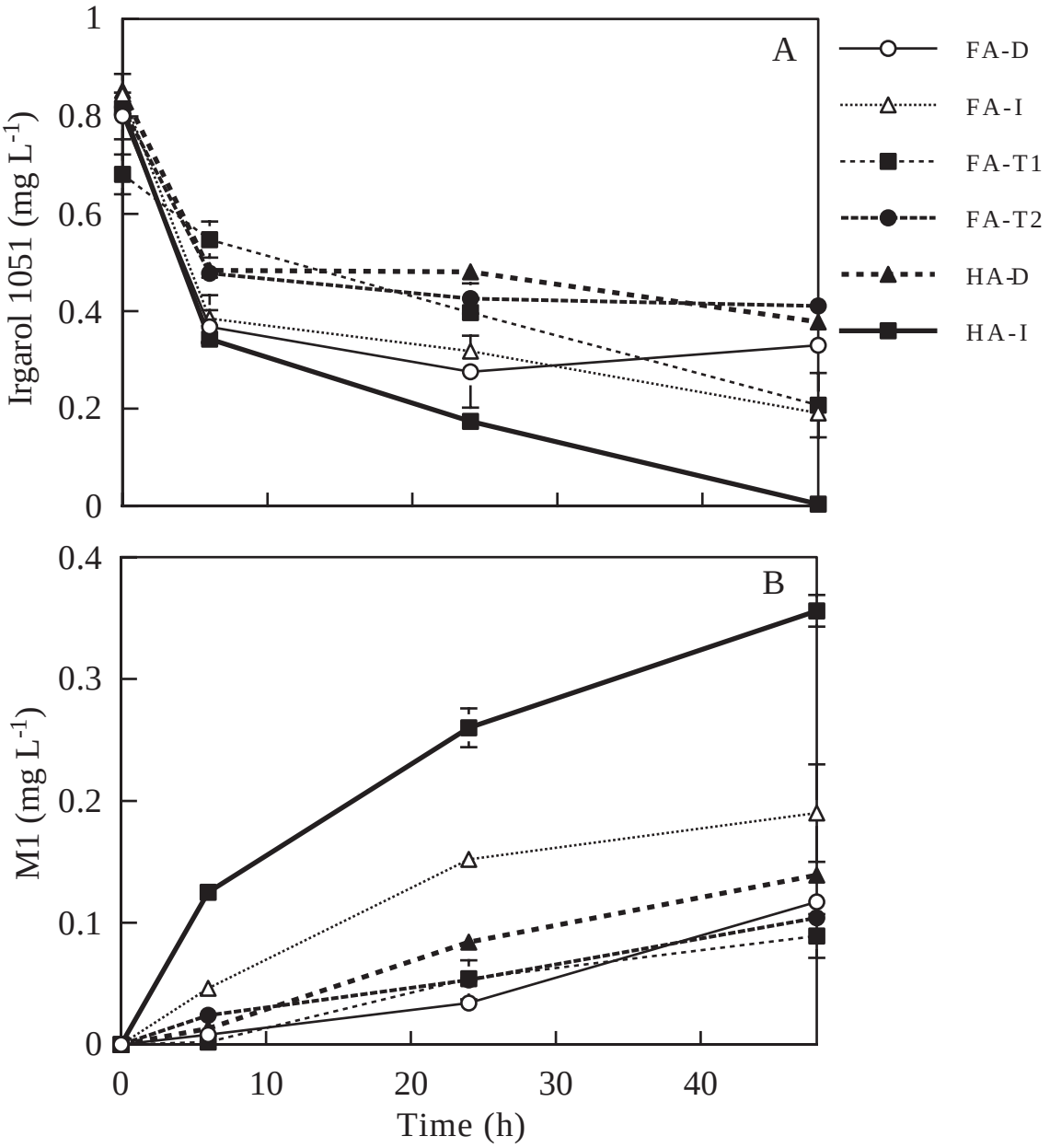


Fig. 3 Effects of humic substances on the photodegradation of Irgarol 1051 (A) and the formation of M1 (B).

Table 1 Photolysis of Irgarol or M1 with hydrogen peroxide (HP)

| | Irgarol | | | M1 | | |
|---|---|---|---|---|---|---|
| HP (mg $L^{-1}$) | k ($h^{-1}$) | $t_{1/2}$ (h) | $r^2$ | k ($h^{-1}$) | $t_{1/2}$ (h) | $r^2$ |
| 0.01 | - | - | - | - | - | - |
| 0.1 | - | - | - | - | - | - |
| 1 | 0.0081 | 86 | 0.997 | - | - | - |
| 3 | - | - | - | 0.00035 | 1980 | 0.120 |
| 10 | 0.059 | 12 | 0.993 | 0.0034 | 204 | 0.420 |
| 30 | - | - | - | 0.014 | 50 | 0.900 |
| 100 | 0.281 | 2.5 | 1.000 | 0.036 | 19 | 0.972 |
| 1000 | 0.437 | 1.6 | 1.000 | - | - | - |

Table 2 Photolysis of Irgarol with humic substa

| HS | Irgarol | | |
|---|---|---|---|
| ( 10 mg $L^{-1}$) | k ($h^{-1}$) | $t_{1/2}$ (h) | $r^2$ |
| FA-D | 0.025 | 27 | 0.720 |
| FA-I | 0.034 | 20 | 0.898 |
| FA-T1 | 0.025 | 27 | 0.996 |
| FA-T2 | 0.018 | 39 | 0.779 |
| HA-D | 0.019 | 36 | 0.825 |
| HA-I | 0.102 | 6.8 | 0.967 |