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Aquatic phototransformation study of the antifouling agent Sea-Nine 211: identification of byproducts and the reaction pathway by gas chromatography–mass spectroscopy

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Abstract

The photochemical behaviour of the biocide Sea-Nine 211 was carried out in order to investigate several transformation products formed in different environmental matrices and under different conditions. Sea-Nine 211 photodecomposition was performed under laboratory conditions using a xenon light source and under natural sunlight conditions in sea, river, lake as well as in distilled water. In order to examine the effect of dissolved organic matter (DOM), the phototransformation of the tested biocide was studied also in the presence of various concentrations of humic and fulvic acids. The phototransformation was shown to proceed via pseudo-first-order reaction in all cases and the presence of humic and fulvic acids enhanced the photolysis reaction. Kinetic experiments were monitored with GC–ECD and the half-lives ($t_{1/2}$) varied between 6 and 433 h. Irradiation of the aqueous Sea-Nine 211 solutions gave rise to a great number of transformation products that were isolated by means of SPE using SDB extraction disks while six of them were tentatively identified using GC–MS techniques. Based on this byproduct identification a possible transformation pathway is proposed for the decomposition of Sea-Nine 211 in aqueous media. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phototransformation; Sea-Nine 211; Antifouling biocide

1. Introduction

As a result of the restriction imposed by European Union regulations on antifouling paints containing organotin biocides due to their negative impact on marine environment [1–3], new alternative formulations have been developed based mainly on organic biocides including Sea-Nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one, $C_{11}H_{17}NOSCl_2$) [4,5]. Due to their widespread use considerable coastal

concentrations of these biocides have been found in areas of high yachting activity, particularly in marinas and sportive harbors [6–9]. To date, little information about Sea-Nine 211 environmental fate have been reported and few data concerning its contamination at the marine environment are available. Recently considerable concentrations ranged from 5 ng/l to 3.3 μ g/l in the coastal environment of the Mediterranean region [8–10] have been reported.

Photoalteration processes are known to play an important role in regards to pesticides degradation. Moreover, the study of a contaminant photochemical behavior is a key issue in terms of the formation of

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toxic transformation products. Although modeling of pesticide behavior under laboratory conditions (usually using xenon arc lamp) [11–13] is a very useful tool for environmental studies, there is a need to conduct phototransformation studies in natural conditions taking into consideration factors such as temperature variation, daily and seasonal variation of natural sunlight intensity [14]. Being the primary light-absorbing species in surface water dissolved organic matter (DOM) plays an important role since it can either inhibit [15,16] or enhance [17,18] the phototransformation rate of a pollutant.

In the present study the determination of the transformation kinetics was followed by liquid–liquid extraction as it is a simple and reliable method for quantification of pesticides in water especially when using low extraction volumes [19]. For the isolation and the identification of the transformation products a SPE–GC–MS technique has been developed using SDB extraction disks. The objectives of the present study were the determination of (i) the transformation kinetics of Sea-Nine 211 in different natural waters under natural and simulated solar irradiation, (ii) the effect of dissolved organic matter on the reaction rate and (iii) the identification of intermediate products involved in the phototransformation pathway. To our knowledge this work represents the first phototransformation study of Sea-Nine 211 in environmental waters under laboratory and natural sunlight conditions.

2. Experimental section

2.1. Chemicals

Sea-Nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) was offered by Rohm & Haas (Philadelphia, PA, USA). Humic and fulvic acid (isolated from Suwannee River) standards were purchased from Fluka and International Humic Substances Society (IHSS), respectively. Pesticide grade *n*-hexane, dichloromethane and ethylacetate were provided from Pestiscan (Labscan, Dublin, Ireland). Sodium sulfate (pro-analysis) was from Merck (Darmstadt, Germany). SDB (styrenedivinylbenzene) extraction disks (47 mm) were supplied from 3M Empore (St. Paul, USA), and a conventional filtra-

tion apparatus was purchased from Supelco (Bellefonte, USA). Total organic carbon (TOC) analysis was performed on a total carbon analyser (TOC-5000 Shimadzu) using the high temperature catalytic oxidation method (HTCO), while nitrate and chloride measurements were carried out by suppressed ion chromatography using a Shimadzu 500 apparatus. UV absorption spectra were obtained by Jasco UV–Vis spectrophotometers.

2.2. Water sampling

Natural waters used in experiments were collected from the Epirus region of Greece (NW Greece) and were as follows: sea water (Ionian Sea), lake water (Pamvotis Lake) and river water (Kalamas River). The natural water samples were collected from the top meter of each water body in 2.5-l precleaned amber glass bottles sealed with screw caps lined with aluminum foil and stored at 4 °C prior to use. All water samples were used without previous treatment, filtration or sterilization. Their physicochemical characteristics are given in Table 1.

2.3. Chromatographic conditions

2.3.1. GC–ECD

Chromatographic analysis of Sea-Nine 211 was performed using a Shimadzu 14B gas chromatograph equipped with ⁶³Ni electron capture detector (ECD) at 300 °C. Analytes were separated with a DB-1 capillary column (J&W Scientific, Folsom, CA, USA), 30 m×0.32 mm I.D., containing dimethylpolysiloxane with a phase thickness of 0.25 μm. The temperature program used for the analysis was: from 150 °C (held for 2 min) to 210 °C (held for 14 min) at 5 °C/min and to 270 °C at 20 °C/min. The injector temperature was set to 240 °C. Helium was used as the carrier (1.5 ml/min) and nitrogen as the make-up gases (35 ml/min). The injector mode was splitless and the injection volume was of 1.0 μl.

2.3.2. GC–MS

A GC–MS, QP 5000 Shimadzu instrument

Table 1
Characteristics of selected environmental waters

Water type	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS ^a (mg/l)	TOC ^b (mg/l)	Salinity (‰)	NO ₃ ⁻ (mg/l)
Distilled	5.72	1.1	n.d. ^c	b.d.l. ^d	n.d.	n.d.
Ionian sea	7.72	52 800	219	2.53	36.5	0.95
Kalamas river	7.90	318	198	5.11	1.70	4.29
Pamvotis lake	7.67	326	358	10.34	0.51	7.82

^a Total dissolved solids.

^b TOC, total organic carbon.

^c n.d., not determined.

^d b.d.l., below detection limit.

equipped with capillary column DB-5-MS, 30×0.25 mm×0.25 μm , containing 5% phenyl–95% dimethylpolysiloxane (J&W Scientific) was used for the identification of the transformation products under the following chromatographic conditions: Injector temperature 250 °C, oven temperature program from 55 to 200 °C at 5 °C/min, from 200 to 210 °C (held for 2 min) at a rate of 1 °C/min and to 270 °C (held for 3 min) at 10 °C/min. Helium was used as the carrier gas at 1 ml/min. The interface was kept at 290 °C. The MS was operated in electron impact mode with an ionization potential of 70 eV and the spectra were obtained in full scan mode. The injector mode was splitless and the injection volume was of 3.0 μl .

2.4. Photolysis in natural waters

Irradiation experiments of Sea-Nine 211 at 1 mg/l under natural sunlight in three different natural waters (sea, river and lake) as well as in distilled water, were carried out in capped duran glass reservoirs in the Ioannina area (University Campus, roof terrace of the Department of Chemistry) during the period May–June 2000. The concentration was below its solubility level (6.5 mg/l) in water but of sufficient concentration to carry out the kinetic studies performed by GC with electron capture detection (ECD). Three samples were employed for each water.

Laboratory experiments were carried out in a 6.5-cm diameter cylindrical duran glass UV-reactor by exposing 50 ml of the aqueous solutions of Sea-Nine 211 (1 mg/l) in environmental waters, under artificial solar irradiation. The irradiation was carried out

using a Suntest CPS+ apparatus from Atlas (Gelnhausen, Germany), equipped with a xenon arc lamp as reported previously [19]. In all cases dark controls were run at the same concentration and conditions as those of the corresponding phototransformations in natural and simulated solar irradiation.

2.5. Photolysis in the presence of humic and fulvic acids

In order to examine the effect of dissolved organic matter (DOM), irradiations were also conducted in the presence of various concentrations of humic (HA) and fulvic acids (FA) using the suntest apparatus, the same reactor and initial concentration of Sea-Nine 211. HA and FA were used at the concentrations of 4, 8, 16 and 24 mg/l, respectively.

2.6. Quantification and extraction procedure

For the determination of the kinetic rate constants liquid–liquid extraction was chosen as it is a simple and reliable method for quantification of pesticides in water especially when using low extraction volumes [19]. At specific time intervals samples of 5 ml were withdrawn from the duran glass reservoirs and the UV-reactor. The samples were extracted twice with 2.5 ml *n*-hexane for 1 min using a vortex, dried with a small amount of Na₂SO₄ and finally analyzed by GC–ECD, quantified after the addition of the external standard chlorothalonil (tetrachloroisophthalonitrile). Calibration standards at the range of 0.1–1.0 mg/l for Sea-Nine 211 were linear with excellent correlation coefficients.

For the identification of transformation products,

the remained solutions (≈ 700 ml) of natural sunlight irradiation experiments and 50 ml of aqueous solutions irradiated under simulated solar light were extracted by an off-line solid-phase extraction (SPE) system at the end of total irradiation time. SDB extraction disks were used as the sorbing phase since they provide good recoveries for medium polar pesticides and due to the efficiency in the analysis of intermediates resulting from photolysis processes [19–21].

Prior to extraction the disks were activated with 10 ml of acetone for 2 h while 3.5 ml (outdoor experiment) and 0.25 ml (suntest experiment) of methanol modifier was added to the residues to allow better extraction. The SDB extraction disks were then placed on a sintered glass filter funnel apparatus attached to a vacuum source. A 5-ml volume of solvent mixture, dichloromethane–ethyl acetate (1:1, v/v) was added to the filter funnel and the disks were dried for 3 min. Then 5 ml of methanol were added and after almost all the methanol was drawn through the disk [22] 10 ml of deionized water was added. Then 50 and 700 ml volume of the water samples were added at flow-rate of 2.5 and 20 ml/min, respectively. After the water sample had passed through, the vacuum was left on for 10 min to allow the disk to become dry. The filtration system was put in a reservoir to receive the extract containing Sea-Nine 211 as well as the transformation intermediates. The extraction was done in the opposite way to the sample application (back-flush desorption) with 3×10 ml of solvent mixture dichloromethane–ethyl acetate (1:1, v/v) as eluting system. The solvents and sample were drawn through the disks at a rate of approximately 1 ml/min. The extracts were then dried over anhydrous sodium sulfate, concentrated to 0.1 ml under a gentle stream of nitrogen and further analyzed into the GC–MS instrument. The use of GC–MS is advantageous in that it is highly sensitive (even the minor peaks are identified through their MS spectra) and less time consuming since it allows a rapid analysis of the photolysis samples.

2.6.1. Calculation of half-life

The calculation of half-life time was performed using the first-order rate equation

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration at time t , and C_0 represents the initial concentration and k is the rate constant (slope).

The phototransformation constants in the case of outdoor experiment (natural solar irradiation) were calculated by subtracting the exponents of different degradation curves representing the apparent degradation and the degradation owed to hydrolysis, volatilization and biodegradation (dark experiment). In this way the considered k_{phot} constants and the half-lives $t_{1/2}$ refer to the real photochemical reaction excluding the contribution of other factors. Quantitative recoveries from dark controls sampled over the entire exposure period of simulated solar irradiation (30 h) have shown that Sea-Nine 211 did not undergo dark reactions (hydrolysis and biodegradation).

3. Results and discussion

3.1. Phototransformation kinetics

Sea-Nine 211 was irradiated in different types of environmental waters both under natural and artificial sunlight conditions. The results are presented as natural logarithmic values of Sea-Nine 211 concentration $\ln[C_s]$ versus the irradiation time (h). The phototransformation rate of Sea-Nine 211 follows a pseudo-first-order degradation curve in all cases as confirmed from the linearity of the plots of the natural log of Sea-Nine 211 concentration against time. The first-order rate constants (k_{phot}) and the half-lives ($t_{1/2}$) for natural and simulated solar irradiation are presented in Table 2.

Phototransformation of Sea-Nine 211 in natural waters was significantly enhanced following the order: lake water > river water > sea water > distilled water showing a strong dependence on the constitution of the irradiated media (Figs. 1 and 2). One can see that as the TOC and nitrate concentration in natural waters increases the slope of the rate plots increases, indicating an increasing reaction rate. This rapid phototransformation in both experiments is attributed to the presence of naturally occurring photosensitizers in natural waters. DOM and other reactive chromophores in natural water such as riboflavin and flavin absorb sunlight energy and are

Table 2
Photolysis kinetic parameters of Sea-Nine 211 in different aqueous media

Photolysis	$t_{1/2}$ (h)	k_{phot} (h^{-1})	R^2
<i>Natural solar irradiation (outdoor)</i>			
Distilled water	433	0.0016	0.995
Sea water	315	0.0022	0.997
River water	154	0.0045	0.991
Lake water	131	0.0053	0.989
<i>Simulated solar irradiation (suntest)</i>			
Distilled water	14	0.0483	0.994
Sea water	10	0.0677	0.992
River water	8	0.0823	0.995
Lake water	6	0.1079	0.983
<i>Simulated solar irradiation (suntest)^a</i>			
HA ^b , 4 mg/l	10	0.0690	0.977
HA, 8 mg/l	9	0.0776	0.990
HA, 16 mg/l	8	0.0835	0.981
HA, 24 mg/l	7	0.1008	0.978
<i>Simulated solar irradiation (suntest)^a</i>			
FA ^c , 4 mg/l	11	0.0624	0.989
FA, 8 mg/l	10	0.0664	0.992
FA, 16 mg/l	10	0.0726	0.981
FA, 24 mg/l	9	0.0771	0.987

^a Distilled water.

^b Humic acids.

^c Fulvic acids.

known to provide a rich variety of photochemical reactions initiating indirect photodegradation of organic contaminants [23,24]. Energy, electron and hydrogen atom transfer reactions as well as reactions with photochemically generated free radicals may be very significant in the environmental phototransformation of Sea-Nine 211 that does not absorb strongly above 290 nm (Fig. 3). Although from the UV–Vis absorption spectrums (Fig. 3) it seems that DOM present in natural waters absorbs most of the available photons emitted the sensitization effect provided by DOM and other naturally occurring photosensitizers is stronger than its “inner-filter” effect. In addition to dissolved organic matter (such as humic and fulvic acids), $\cdot\text{OH}$ radicals that are generated in natural waters by the photolysis of nitrate and nitrite as well as in waters containing sufficiently high metal ion concentration—through ligand to metal charge transfer reaction and photo Fenton chemistry—have been shown to sensitize the phototransformation of organic contaminants in aqueous solutions [25–28].

Although the irradiance of the sun energy measured by the radiometer and the one given for the Xe lamp are not comparable, the phototransformation rates calculated under simulated sunlight irradiation

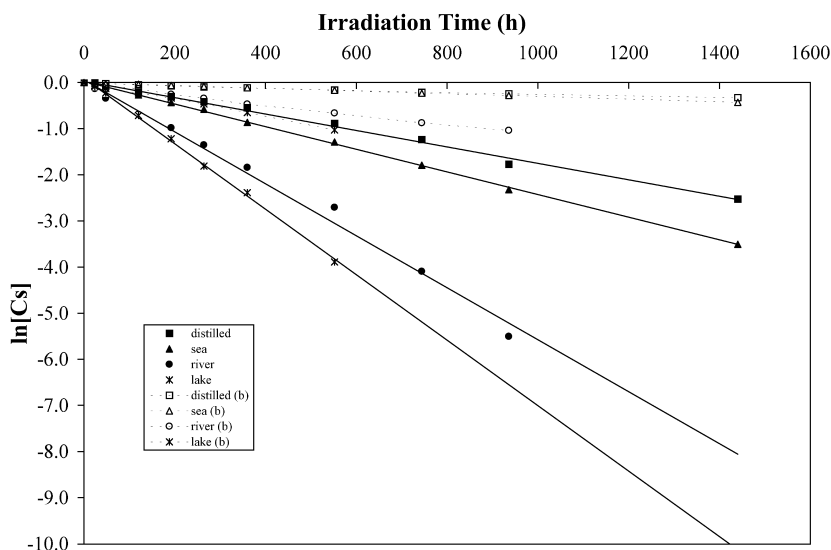


Fig. 1. Phototransformation of Sea-Nine 211 in different natural waters under environmental conditions. b, blank experiment.

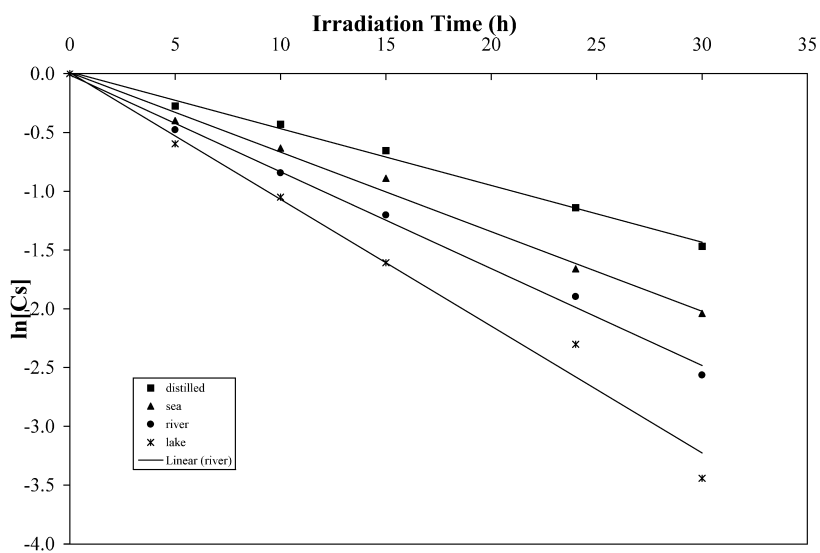


Fig. 2. Phototransformation of Sea-Nine 211 in different natural waters under simulated solar irradiation.

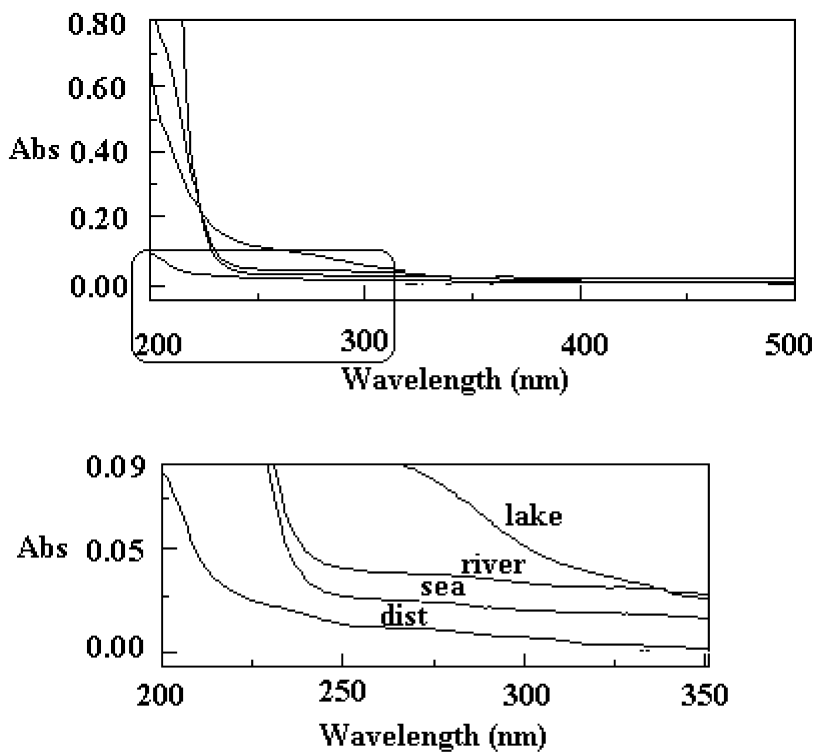


Fig. 3. UV-Vis absorption spectrum of Sea-Nine 211 aqueous solution in distilled, sea, river and lake water ($5.7 \times 10^{-6} M$).

were 20–30 times greater compared to the photo-transformation rates of natural sunlight irradiation; however, this will provide more realistic environmental transformation rates [29]. Greater photolysis rate constants (2–12 times) have been also observed during simulated solar irradiation for the photodegradation of pesticides [11,12].

In order to verify the sensitization effect of DOM, experiments with the same initial concentration of Sea-Nine 211 and various concentrations of HA and FA were conducted. Linear plots as shown in Figs. 4 and 5 were produced, allowing the calculation of the rate constants. When the concentration of DOM increases the slope of the rate plot increases, confirming the sensitization properties of both HA and FA. Photosensitized reactions involving electronic energy transfer from triplet states of humic and fulvic acids to organic molecules as well as photosensitized oxygenations via the singlet oxygen pathway have been widely described. In our study HA have shown greater ability to sensitize the photolysis of Sea-Nine 211. Due to the lack of data relating to structural composition of humic and fulvic acids such as carbon, nitrogen and oxygen content, no comparison could be made concerning their photochemical properties. The differences in the photosensitization properties could be explained by the presence, in variable amounts, of deactivators of

excited states. Paramagnetic metallic cations could deactivate the excited states of humic and fulvic acids but the efficiency depends not only on the amount but also on the localization and the chemical form of the metals in the macromolecules [30,31]. Photochemical behavior of humic and fulvic substances result from complex phenomena and depend on many factors, the origin of each substance being the most important [32]. However, the effect of HA and FA concentrations was not proportional since 6-fold increases in TOC resulted in only 20–30% increases in the reaction rate. This could be explained by a combination of “inner-filter” effect coupled with internal scavenging of reactive transients by the DOM phase. The above observation confirms the sensitization properties provided also by other constituents (such as nitrate) in natural waters initiating indirect photodegradation processes.

3.2. Transformation products

A total ion chromatogram (TIC) obtained by GC–MS for a SPE extract of Sea-Nine 211 solution after 23 days of solar irradiation in lake water is shown in Fig. 6. Similar chromatograms were obtained also for the other sample matrices. Up to nine compounds could be detected as possible transformation intermediates. Six of them were tentatively identified

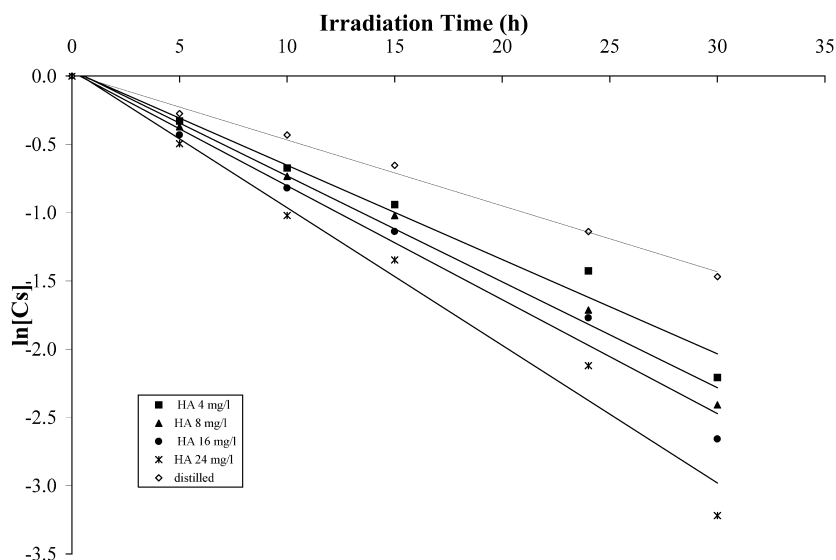


Fig. 4. Phototransformation of Sea-Nine 211 in various concentrations of humic acids in distilled water under simulated solar irradiation.

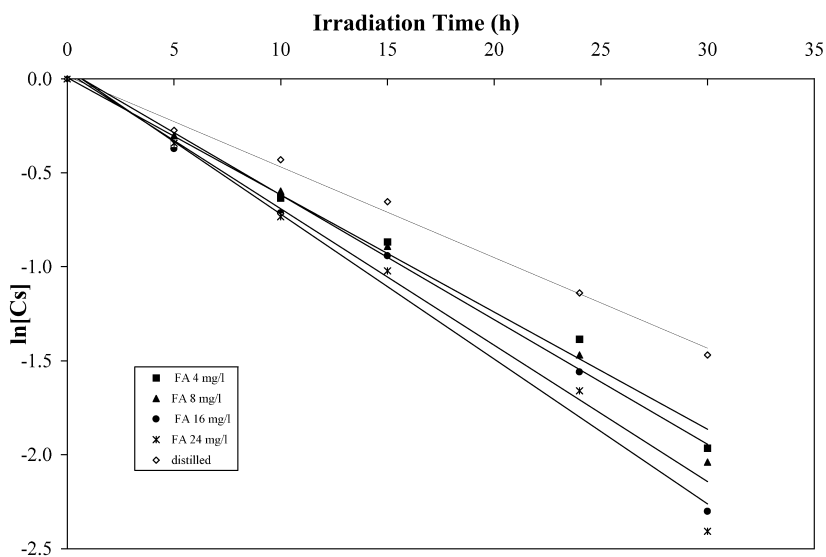


Fig. 5. Phototransformation of Sea-Nine 211 in various concentrations of fulvic acids in distilled water under simulated solar irradiation.

while the rest are considered as possible transformation intermediates since their amounts increased in the early steps of photolysis and then decreased with longer irradiation time. The mass spectra of the unlabelled peaks were not characteristic enough to enable us to propose the structure. The GC–MS characteristics of the reaction byproducts are presented in Table 3.

Mainly two routes of transformation pathways are observed during the phototransformation of Sea-Nine 211 according to the proposed reaction scheme (Fig. 8). The first pathway (a) involves cleavage of the

isothiazolone ring and subsequent oxidation of the resulting alkyl metabolites [33].

Compound 4 appearing at $R_t=20.9$ min was identified by using an identification program of NIST library with a fit value higher than 80%. It exhibited a molecular ion peak at $m/z=171$ $[M]^+$ as well as fragments at $m/z=156$ $[M-CH_3]^+$, $m/z=128$ $[M-COCH_3]^+$ and it is associated to *N-n*-octyl acetamide. The cleavage of the weakest bond of the molecule (N–S) of Sea-Nine 211 and subsequent dechlorination and hydroxylation results in *N-n*-octyl hydroxypropionamide. Further oxidation yields the

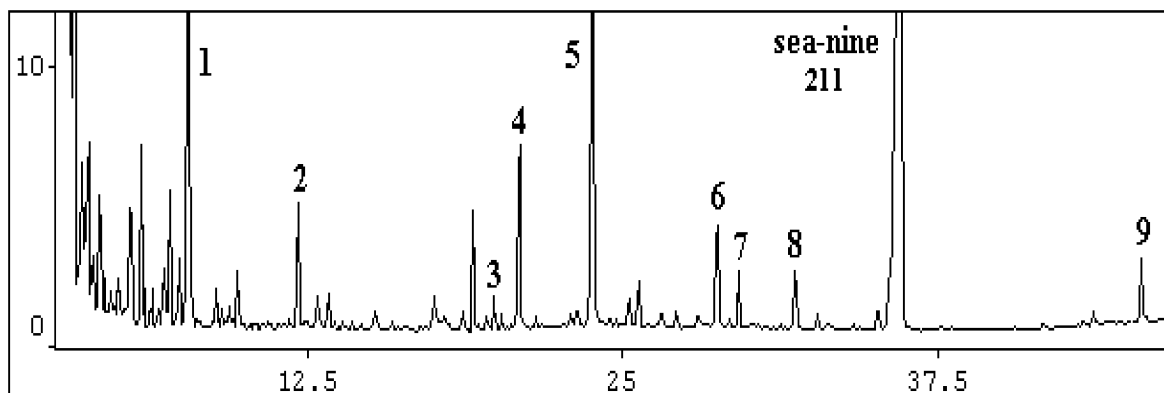


Fig. 6. Total ion chromatogram of Sea-Nine 211 phototransformation in lake water, using SPE and GC–MS analysis (outdoor experiment).

Table 3
GC–MS–EI retention times (R_t) and spectral characteristics of Sea-Nine 211 major photoproducts

No.	Compound	R_t (min)	M_r^b	Mass spectrum peaks ^c
1 ^a	<i>n</i> -Octanal	7.8	128	57(100), 69(30), 84(27), 100(6)
2	<i>n</i> -Octyl isocyanate	12.3		55(100), 99(61), 85(26), 112(17), 126(7)
3	<i>n</i> -Octyl amine	20.1	129	58(100), 72(17), 100(15), 86(6), 114(5)
4	<i>N-n</i> -Octyl acetamide	20.9	171	72(100), 86(34), 100(25), 114(20), 156(10), 128(7), 171(5)
5	<i>N-n</i> -Octyl oxamic acid	23.7	201	201(6), 156(85), 71(48), 128(23), 100(8), 114(4), 86(5)
6	Unidentified	28.8		123(100), 118(61), 152(54), 216(48), 218(15)
7	Unidentified	29.6		123(100), 118(70), 152(35), 216(33), 218(10)
8	4,5 Dichloro-3- <i>n</i> -octyl-thiazolin-2-one	31.8	281	57(100), 169(25), 246(23), 281(5)
	Sea-Nine 211	36.0	281	55(100), 169(33), 182(18), 246(11), 281(2)
9	Unidentified	45.4		55(100), 72(98), 106(88), 156(73), 94(54), 170(48)

^a Corresponding number in Figs. 6 and 7.

^b Molecular ion.

^c Relative abundance in parentheses.

formation of *N-n*-octyl malonamic acid which is then decarboxylated to give the corresponding *N-n*-octyl acetamide. The presence *N-n*-octyl hydroxypropionamide and *N-n*-octyl malonamic acid could not be identified by our study in neither sample.

The above transformation pathway was observed also during the analysis of the dark control samples in outdoor experiment indicating that this route accounts also for other processes such as hydrolysis and biodegradation [33,34]. In the case of distilled water, degradation owed to hydrolysis (dark experiment) accounted for 30% of the decline in Sea-Nine 211 concentration while in lake water dark controls analyses (hydrolysis and biodegradation) have shown a 65% contribution to the transformation of the biocide indicating that biodegradation is considerable [35].

Further oxidation of *N-n*-octyl acetamide leads to the formation of *N-n*-octyl oxamic acid (compound 5, $R_t=23.7$ min) which was identified by interpretation of the mass spectra (Fig. 7). It exhibited a

molecular ion peak at $m/z=201$ as well as fragment ions at $m/z=156$, $m/z=128$, $m/z=114$, $m/z=100$ and $m/z=86$ common to *N-n*-octyl acetamide corresponding to the oxidation of the methyl group. *N-n*-octyl oxamic acid could be then phototransformed to the corresponding *N-n*-octyl carbamic acid as indicated by Thomas [34], in the metabolic pathway of Sea-Nine 211 under aerobic conditions. *N-n*-octyl carbamic acid could not be identified in neither sample in our study. However the presence of compound 2 ($R_t=12.3$ min) identified by NIST library with a fit value higher than 80% associated to *n*-octyl isocyanate may support the formation of *N-n*-octyl carbamic acid since it reacts rapidly with water [36] in a nucleophilic addition step generating the corresponding *N-n*-octyl carbamic acid. Although unstable in water its presence may be attributed to the loss of water of *N-n*-octyl carbamic acid probably due to a thermal process prior to ionization in the GC–MS chamber.

N-n-Octyl carbamic acid decarboxylates yielding

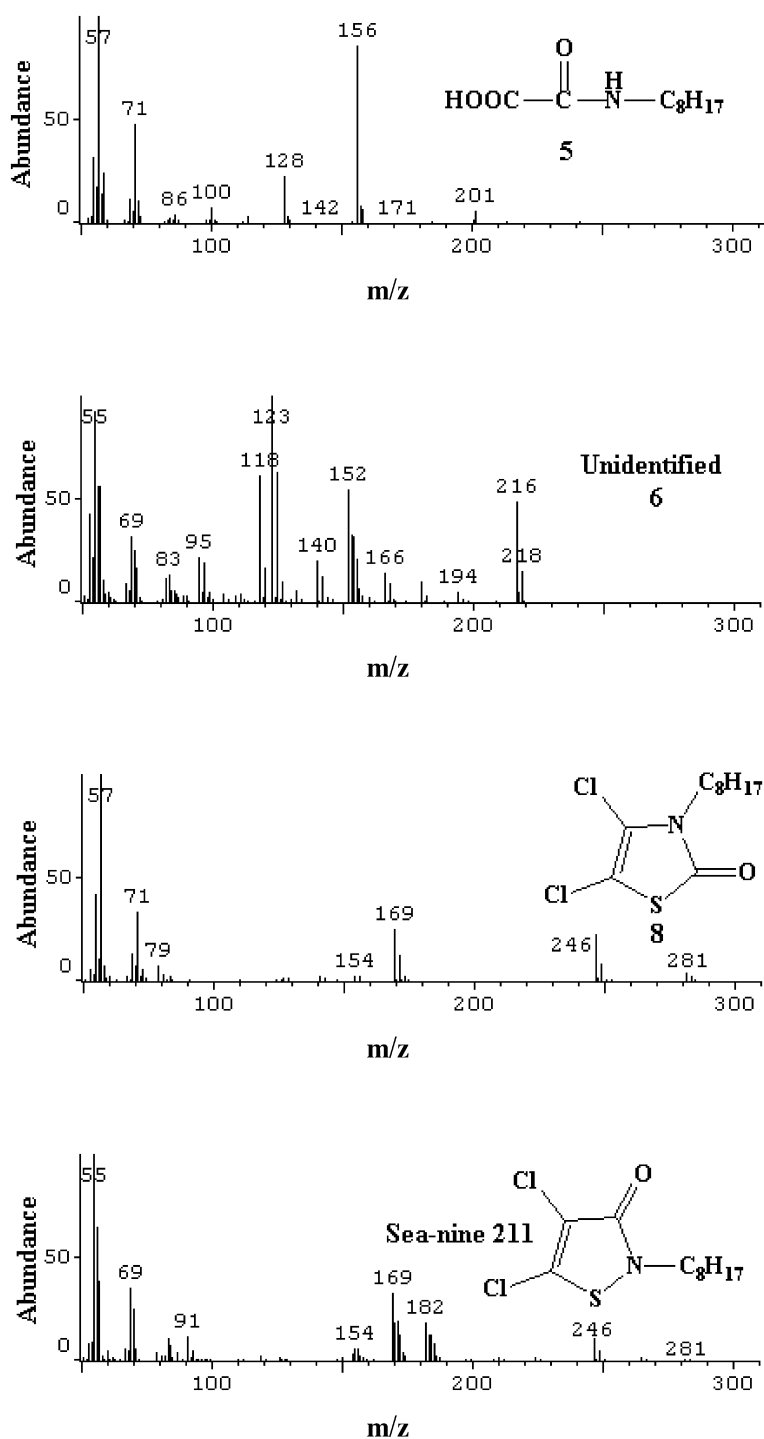


Fig. 7. Mass spectra of Sea-Nine 211 and some intermediates formed during the photolysis of Sea-Nine 211 in natural waters.

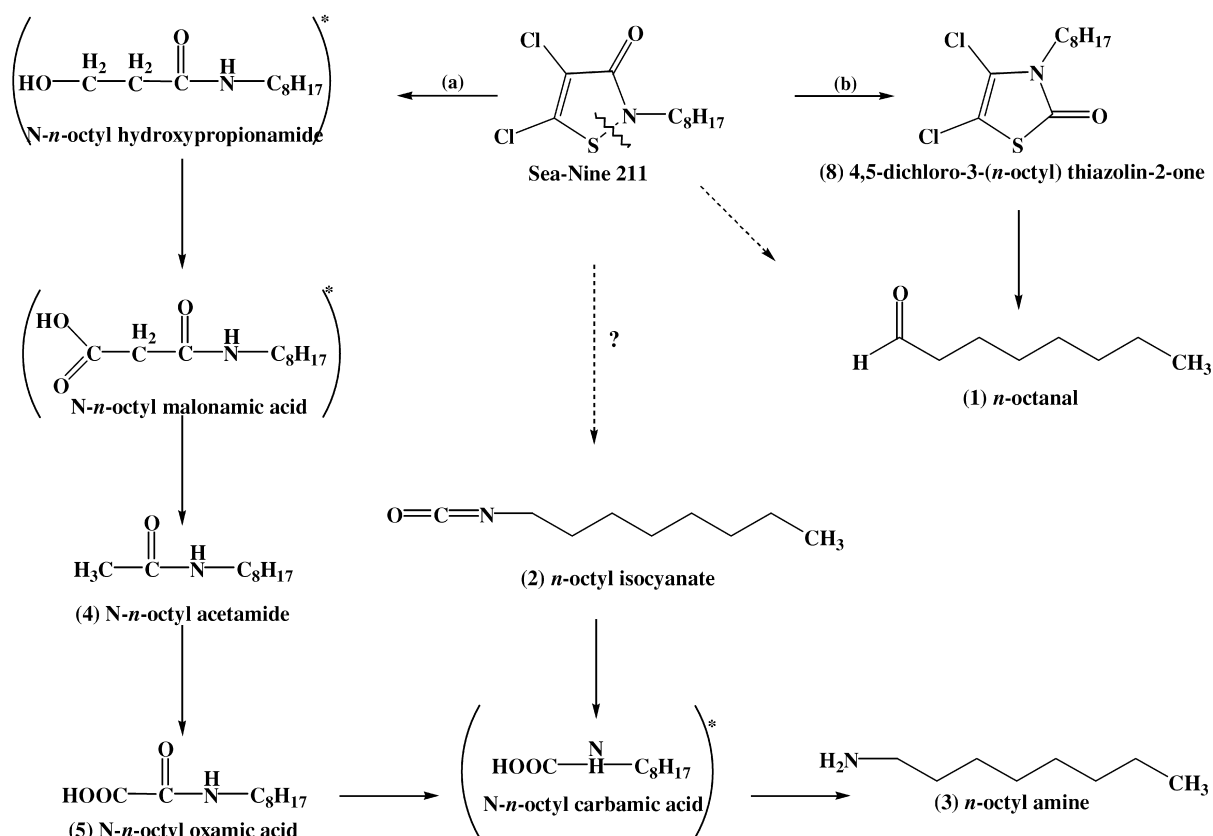


Fig. 8. Proposed phototransformation pathway of Sea-Nine 211 in aqueous solutions (*not identified by our group).

n-octyl amine (compound 3, $R_t=20.1$ min) which was identified by interpretation of the mass spectra. It exhibited a molecular ion peak at $m/z=129$ $[M]^+$ and fragments at $m/z=114$ $[M-CH_3]^+$, $m/z=100$ $[M-CH_2CH_3]^+$, $m/z=86$ $[M-CH_2CH_2CH_3]^+$ common to *N*-*n*-octyl acetamide and *N*-*n*-octyl oxamic acid.

The second pathway (b) consists on the photo-transposition of Sea-Nine 211. Photochemical inter-conversion of 1,2 into 1,3 isomers has been reported for dihetero compounds like isoxazole to oxazole, imidazole to pyrazole, as well as isothiazolone to thiazolones [37–39]. Photoexcitation of isothiazolones is suggested to result in cleavage of the N–S bond, resulting in the formation of a species that can be viewed as diradical, which can then lead to the formation of thiazolones. In the case of Sea-Nine 211 the photoisomerization of the parent molecule (Fig. 9) yields to 4,5-dichloro-3-*n*-octyl-

thiazolin-2-one (compound 8, $R_t=31.8$ min). The mass spectra of 4,5-dichloro-3-*n*-octyl-thiazolin-2-one was similar to Sea-Nine 211 (Fig. 7) and the fact that it appears at lower retention time than Sea-Nine 211 ($R_t=36.0$ min) supports the proposed structure, being less polar than the starting molecule.

Compound 1 appeared at $R_t=7.8$ min, was identified as *n*-octanal using the identification program of NIST library with a fit value more than 80%. It exhibited a molecular ion at $m/z=128$ as well as fragment ions at $m/z=100$, $m/z=84$ and $m/z=69$ arising from the N–C alkyl bond cleavage of 4,5-dichloro-3-*n*-octyl-thiazolin-2-one and the oxidation of the alkyl group.

Chromatographic data indicated the presence of three more compounds 6, 7 and 9 found at $R_t=28.8$, 29.5 and 45.4 min that could not be identified, however, were regarded as possible transformation products because they were detected in all experi-

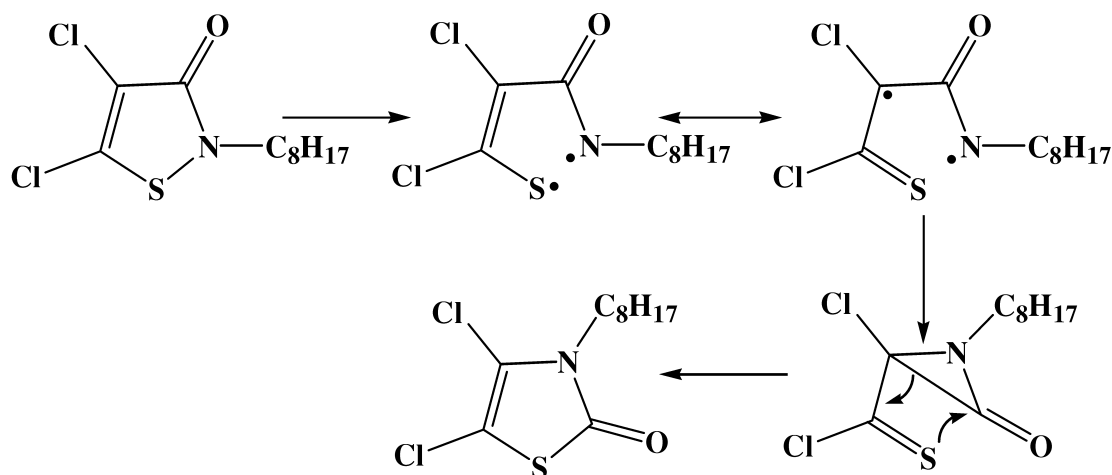


Fig. 9. Photoisomerization of Sea-Nine 211 describing the formation of 4,5 dichloro-3-*n*-octyl-thiazolin-2-one in the proposed transformation pathway of Sea-Nine 211.

ments and their concentration increased and decreased as a function of the reaction time. Compounds 6 and 7 have identical spectral characteristics and are considered as isomers. The isotopic pattern of their molecular ions at $m/z=216 [M]^+$ and $m/z=218 [M+2]^+$ (Fig. 7) with a ratio 3:1 which is highly characteristic of chlorine atoms [40] suggests the presence of chlorinated intermediates. The evolution of chloride ions (Fig. 10) that reach only 63% of

the stoichiometric value after 30 h of simulated solar irradiation in distilled water clearly demonstrates that chlorinated transient organics are present in the solution after that time.

4. Conclusions

The present work demonstrates that the biocide

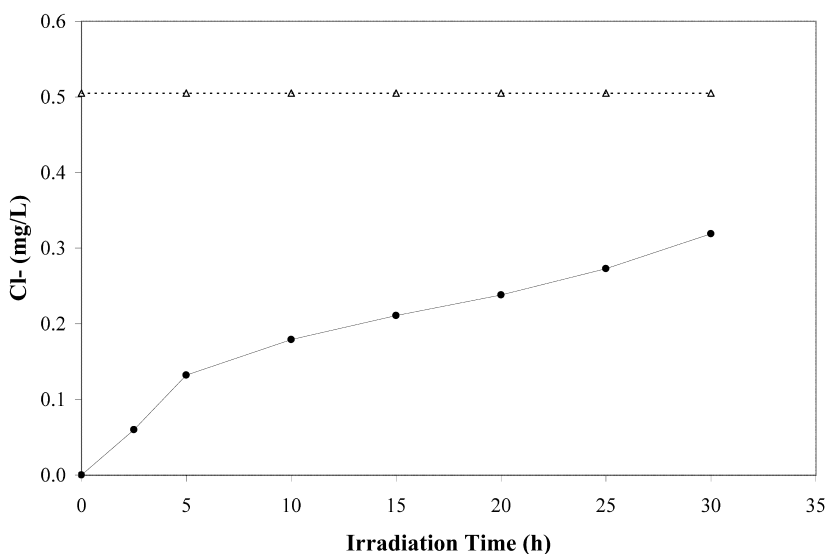


Fig. 10. Evolution of chloride ions during simulated solar irradiation of Sea-Nine 211 in distilled water (dotted line represents the stoichiometric concentration of Cl^-).

Sea-Nine 211 degrades photochemically in the aquatic environment leading to the formation of several photoproducts. The transformation rates were higher in natural waters than in distilled water showing a strong dependence on the composition of the water sample. The presence of DOM enhances the rate of the photolysis while the formation of various transformation products was followed via first-order reactions. Six photoproducts have been tentatively identified using GC–MS techniques as *n*-octanal, *n*-octyl isocyanate, *n*-octyl amine, *N*-*n*-octyl acetamide, *N*-*n*-octyl oxamic acid and 4,5-dichloro-3-*n*-octyl-thiazolin-2-one.

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