Photodegradation study of the antifouling booster biocide dichlofluanid in aqueous media by gas chromatographic techniques

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Abstract

The aquatic photochemical behavior of the biocide dichlofluanid has been studied under natural sunlight conditions as well as under artificial solar irradiation in different types of natural waters (sea, river and lake water) as well as in distilled water. In order to examine the effect of dissolved organic matter (DOM), the photodegradation of the tested biocide was investigated also in the presence of various concentrations of humic and fulvic acids. It was found that the photodegradation proceeds via first-order reaction in all cases and that the presence of various concentrations of DOM inhibits the photolysis reaction. Kinetic experiments are monitored with GC–ECD with half-lives varied between 8 and 83 h. The major photodecomposition products identified by GC–MS were dichlorofluoromethane, aniline, and DMSA. Based on this byproduct identification a possible degradation pathway is proposed for the photolysis of dichlofluanid in aqueous media. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dichlofluanid (N-dichlorofluoromethylthio-N′,N′-dimethyl–N-phenylsulfamide) is a fungicide primarily used to control spoilage of crops through fungal attack. In the last few years due to the restriction imposed by European Union regulations on the use of TBT-based antifouling paints on boats under 25 m, new formulations have been introduced in the 'small boat' market including dichlofluanid [1]. These coatings are already used and applied to the hulls of ships and boats to prevent the growth of bacteria, macroalgae, mussels and other invertebrates [2]. As a result considerable coastal concentrations of these biocides have been found in areas of high yachting activity, particularly in marinas and sportive harbors [3–6].

Pesticide contamination of waters presents a serious environmental problem because of their potential toxicity and widespread use. Therefore, information about their possible degradation mechanisms in the environment is important in order to estimate the persistence of these compounds and to identify the factors that influence their behavior.

Among the different transformation processes (biotic and abiotic), photodegradation is an important factor influencing the fate of organic micropollutants in the field [7]. Several authors have reported on organic pesticides photodecomposition under a variety of irradiation conditions and different solutions.

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Most of these works use artificial solar sources of irradiation (xenon arc lamps) or ultraviolet (UV) light combined with catalyst particles such as TiO_2 or Fe_2O_3 [8–11].

Dissolved organic matter (DOM) present in natural water plays an important role in regard to pesticide degradation. Being the primary light-absorbing species in surface water, DOM can either enhance [12,13] or inhibit the rate of photolysis [14,15].

Several analytical methods have been developed for the analysis of dichlofluanid. These studies include SPME coupled to ECD and MS [16], on-line SPE–LC–MS with (APCI) interface [2], or on-line SPE–GC technique [17,18]. In this study, the determination of the kinetic rate constants was followed by means of liquid–liquid extraction with hexane and GC–ECD analysis. For the identification of the transformation products a SPE–GC–MS technique has been selected using SDB extraction disks 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 [19,20]. SPE is generally preferred to LLE when using medium and large volume extraction because it minimizes most of the drawbacks of LLE. On the other hand 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. This powerful technique was also used for the quantification of the byproduct DMSA (N,N-dimethylaminosulfanilide). For this case and to obtain maximum sensitivity, the GC–MS instrument was operated in the selected ion monitoring (SIM) mode collecting the major ion fragments of this compound.

Although dichlofluanid has been widely used on various crops as well as additive in antifouling paints and its presence has been reported in the Mediterranean region and UK coastal cites (ranged from 0.016 to 0.6 μg/l) [5,6,21], no data have been reported about its environmental fate, to date. This is the first time that the aquatic photodegradation of dichlofluanid has been studied in environmental waters under laboratory and natural sunlight conditions.

The present study deals with the determination of (i) the degradation kinetics of dichlofluanid in differ-

ent natural waters under natural and simulated solar irradiation, (ii) the effect of dissolved organic matter on the reaction rate and (iii) the transformation products formed by photolysis.

2. Experimental section

2.1. Chemicals

Dichlofluanid (N-dichlorofluoromethylthio-N′,N′-dimethyl–N-phenylsulfamide), aniline and DMSA (N,N-dimethylaminosulfanilide) were residue analysis grade, purchased from Riedel-de Häen (Germany) and Dr. Ehrenstorfer, respectively, and used without further purification. The humic and the fulvic acid (isolated from Suwannee River) standards were purchased from Fluka and from International Humic Substances Society (IHSS), respectively. Pesticide grade n-hexane, methanol, dichloromethane and ethylacetate were purchased from Pestiscan (Labscan Ltd, Dublin, Ireland). Sodium sulfate (proanalysis) was from Merck (Darmstadt, Germany). SDB (styrenedivinylbenzene copolymer) extraction disks (47 mm) were purchased from 3 M Empore (St. Paul, USA), and a conventional filtration apparatus was purchased from Supelco (Bellefonte, USA). Concentration of Total Organic Carbon (TOC) in the water samples was measured on a total carbon analyzer (TOC-5000 Shimadzu) using the High Temperature Catalytic Oxidation method (HTCO).

2.2. Water sampling

Natural water 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 and stored at 4°C prior to use. All water samples were used without previous treatment, filtration or sterilization. The water samples were analyzed to ensure that they were free of interfering compounds. Their physicochemical characteristics are given in Table 1.

Table 1
Characteristics of selected environmental waters

Water type	pH	Conductivity (μS/cm)	TDS[a]	TOC[b] (mg/l)	Salinity (%)
Distilled	5.72	1.1	n.d.[c]	b.d.l.[d]	n.d.
Ionian sea	7.72	52.800	219	2.53	36.5
Kalamas river	7.90	318	198	5.11	1.7
Pamvotis lake	7.67	326	358	10.34	0.51

[a] Total dissolved solids.
[b] TOC = total organic carbon.
[c] n.d. = not determined.
[d] b.d.l. = below detection limit.

2.3. Chromatographic conditions

2.3.1. GC–ECD

Chromatographic analysis of dichlofluanid was performed using a Shimadzu 14A capillary gas chromatograph equipped with [63]Ni electron capture detector (ECD) at 300°C. Analytes were separated with a DB-1 column (J & W Scientific, Folsom, CA, USA), 30 m×0.32 mm I.D., contained dimethyl-polysiloxane with a phase thickness of 0.25 μm. The temperature program used for the analysis was: from 150°C (2 min) to 210°C (held – 14 min) at 5°C/min and from 210 to 270°C at 20°C/min. The injector temperature was set to 240°C. The splitless mode was used for injection with the valve opened for 60 s. Helium was used as the carrier gas at 30 ml/min and nitrogen as the make-up gas at 25 ml/min according to the optimization results of the instrument given by the manufacturer.

2.3.2. GC–MS

A GC–MS, QP 5000 Shimadzu instrument equipped with capillary column DB-5-MS, 30×0.25 mm×0.25 μm, contained 5% phenylmethyl and 95% dimethylpolysiloxane (J & W Scientific, Folsom, CA, USA) was used for the identification of the transformation products under the following chromatographic conditions: Injector temperature 250°C, oven temperature program 55°C (2 min) to 210°C (held – 20 min) at 5°C/min and to 270°C at 10°C/min. Helium was used as the carrier gas at 15 ml/min. The interface was kept at 290°C. The splitless mode was used for injection with the valve opened for 30 s. 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 quantification analysis of DMSA was performed by means of SPE with SDB extraction disks and analysis in the GC–MS instrument in the selected ion monitoring (SIM) mode. The low concentration level of DMSA detected in the tested samples made the use of the SIM mode necessary, which provide response factors up to 50 times higher than full scan mode. The ions (m/z) that were selected from the spectrum for DMSA in order to quantify the response under SIM mode were: 92 (100), 200 (41) and 108 (18). The values in parentheses give the relative abundance (%) of each peak in the spectrum.

2.4. Photolysis in natural waters

Irradiation experiments of dichlofluanid under natural sunlight in three different natural waters (sea, river and lake) as well as in distilled water, were carried out in capped Pyrex glass reservoirs in the Ioannina area (University Campus, roof terrace of the Department of Chemistry) during May 2000. Water samples (750 ml) were placed in reaction reservoirs of 1000 ml and spiked with dichlofluanid (1 mg/l) by adding the appropriate volume of standard biocide solution (2000 mg/l) in methanol. Mixtures were homogenized by magnetic stirring and were exposed outdoor without stirring. The concentration was below its solubility limit in water but of sufficient concentration to carry out the kinetic studies performed by GC with electron capture detection (ECD). A dark control experiment was also conducted by exposing amber Pyrex glass reservoirs

filled with the same solution and covered with aluminum foil in the same environmental conditions.

Incident solar radiation was measured with a radiometer (W/m^2) in the wavelength range of 285–2800 nm. The mean sunlight intensity at the beginning, middle and end of the day was estimated as 231, 651 and 278 W/m^2, respectively. The average total daily short-wave radiation for this period was 639 W/m^2, with a 10-h mean sunshine duration from sunrise to sunset. The mean daily temperature was 20°C and maximum and minimum air temperatures were 33.2 and 7.8°C, respectively.

Laboratory experiments were carried out on a 100 ml UV-reactor by exposing 50 ml of the four different aqueous solution of dichlofluanid (1 mg/l) under artificial solar irradiation. The irradiation was carried out using a Suntest CPS+ apparatus from Heraeus (Hanau, Germany), equipped with a xenon arc lamp (1500 W) and special glass filters restricting the transmission of wavelength below 290 nm. The light source was on the top of the reactor used and an average irradiation intensity of 750 W/m^2 was maintained throughout the experiments measured by an internal radiometer. The corresponding light dose for 1 h of irradiation was 2700 kJ/m^2. Chamber and black panel temperature were regulated by pressurized air cooling circuit and monitored using thermocouples supplied by the manufacturer. The temperature of samples did not exceed 25°C using tap water cooling circuit for the UV-reactor. A dark control experiment was also conducted in this series of experiments since dichlofluanid is quite sensitive in alkaline media [22] and to biodegradation.

2.4.1. Photolysis in the presence of humic and fulvic acids

In order to examine the effect of the dissolved organic matter (DOM) experiments were also carried out in the presence of various concentrations of humic (HA) and fulvic acids (FA). Irradiations were carried out using the suntest apparatus and the same reactor and initial concentration of dichlofluanid. Experiments with HA and FA were conducted at concentrations of 4, 8, 16 and 24 mg/l, respectively.

2.5. Recovery on SDB empore disks

Recovery experiments have been also conducted using SPE with SDB extraction disks. The concentrations studied for dichlofluanid were 1 mg/l and 0.5 mg/l which are the initial and the half concentration, respectively, while the recovery experiments for DMSA were carried out at a concentration of 0.08 and 0.02 mg/l, respectively. The volume used for the preconcentration on SDB disks varied between 700 and 20 ml.

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.

At specific time intervals samples of 5 ml were withdrawn from the Pyrex 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 Na_2SO_4 and finally analyzed by GC, quantified by internal standard (chlorothalonil 0.4 mg/l).

For the identification of the transformation products, 100 ml from the outdoor experiments and the left solution from the suntest experiments (20 ml) were extracted by means of solid-phase extraction as follows: SDB extraction disks were conditioned with 10 ml of acetone for 2 h. Samples of 5 ml (outdoor experiment) and 1 ml (suntest experiment) of methanol modifier was added to the residues to allow better extraction. The disks were placed in the filtration apparatus and washed with 5 ml of solvent mixture dichloromethane:ethyl acetate (1:1, v/v) under vacuum and with 5 ml of methanol for 3 min, with no vacuum applied. The disks were not allowed to become dry and the samples were allowed to percolate through the disks with a flow-rate of 5 ml/min, under vacuum. The compounds trapped in the disks were collected by using 3×10 ml of solvent mixture dichloromethane:ethyl acetate (1:1, v/v) as eluting system. The fractions were evaporated to 0.1 ml in a gentle stream of nitrogen and 3.0 μl was injected into the GC–MS instrument. Chlorothalonil was also selected as internal standard for the quantification of DMSA. Calibration standards of both compounds at the range of 0.1–1.0 mg/l for dichlofluanid and 0.005–0.08 mg/l for DMSA were linear with excellent correlation coefficients.

2.7. Calculation of half-life

In order to determine the degradation kinetics, plots of concentration against time were made. The rate constant k was calculated from the first-order equation:

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

where C_t represents the concentration at time t, and C_0 represents the initial concentration. When the concentration reduces to 50% of its initial amount the half-life can be determined by $t_{1/2} = \ln 2/k$.

The confirmation of the first-order kinetics was derived from the linearity of the plots of the natural log of the concentration ln C_{dic} against time.

The photodegradation constants 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.

3. Results and discussion

3.1. Recovery on SDB empore disks

The recoveries found for dichlofluanid were not very good, however, they were higher than the recoveries reported when using different kinds of sorbents such as C_{18} and PLRP-S cartridges ($<10\%$) [2], graphitized carbon (Envi-carb) and polymer cartridges (40%) [23]. SDB extraction disks not only overcome some limitations of the more traditionally used cartridges but seem to work better for medium polarity compounds [19]. The recoveries of dichlofluanid and DMSA were generally the better, the lower the extraction volume was, and the highest found were at the lowest extraction volume (20 ml) which corresponds to the final remaining volume in the UV-reactor after irradiation experiment (Table 2).

3.2. Kinetic of dichlofluanid

Dichlofluanid was irradiated in different types of natural waters both under natural and artificial sunlight conditions. The data were plotted as the concentration versus irradiation time. The first-order rate constants (k_{phot}) and the half-lifes ($t_{1/2}$) for natural and simulated solar irradiation are summarized in Table 3.

The photodegradation rate of dichlofluanid was lower in the natural waters than in distilled water following the order: lake water<river water<sea water<distilled water; showing a strong dependence on the constitution of the irradiated media and especially from the concentration of dissolved organic matter (Figs. 1 and 2). As the TOC concentration increases in natural waters the rate of photolysis decreases. The above result could be due to the optical filter effect (quenching) of the organic

Table 2
Recovery of dichlofluanid and DMSA using SDB extraction disks and different water volumes[a]

Concentration (mg/l)		Volume (ml)	Recovery (%)		RSD[b] (%)	
Dichl	DMSA		Dichl	DMSA	Dichl	DMSA
1	0.08	700	56.3	60.5	12.1	9.8
1	0.08	350	64.2	68.1	11.9	12.2
1	0.08	100	70.6	76.3	10.8	13.2
1	0.08	50	73.9	80.1	13.7	8.9
1	0.08	25	79.2	84.9	11.0	9.1
0.5	0.02	700	57.1	64.8	9.8	10.2
0.5	0.02	350	68.4	70.9	10.1	9.8
0.5	0.02	100	69.8	79.0	8.9	12.1
0.5	0.02	50	76.6	83.9	11.1	8.4
0.5	0.02	25	78.5	85.2	7.9	6.3

[a] Number of each experiment, $n=3$.
[b] Relative standard deviation.

Table 3
Kinetics of the photolysis of dichlofluanid in different aqueous media[a]

Photolysis	$t_{1/2}$ (h)	k_{phot} (h^{-1})	RSD[b]	R^2
Natural solar irradiation (outdoor)				
Distilled water	43	0.0163	12.41	0.914
Sea water	53	0.0132	9.76	0.977
River water	59	0.0117	13.74	0.979
Lake water	83	0.0084	12.98	0.991
Simulated solar irradiation (suntest)				
Distilled water	8	0.0817	7.79	0.975
Sea water	13	0.0518	8.04	0.993
River water	18	0.0394	10.12	0.989
Lake water	21	0.0335	6.09	0.989
Simulated solar irradiation (suntest)[c]				
Humic – 4 mg/l	18	0.0392	5.13	0.990
Humic – 8 mg/l	19	0.0360	6.81	0.987
Humic – 16 mg/l	21	0.0324	4.98	0.987
Humic – 24 mg/l	25	0.0281	9.11	0.978
Simulated solar irradiation (suntest)[c]				
Fulvic – 4 mg/l	25	0.0277	3.57	0.969
Fulvic – 8 mg/l	30	0.0233	6.01	0.995
Fulvic – 16 mg/l	36	0.0195	4.54	0.992
Fulvic – 24 mg/l	41	0.0171	7.03	0.990

[a] Number of each degradation experiment, $n = 3$.
[b] Relative standard deviation.
[c] Distilled water.

Fig. 1. Photodegradation of dichlofluanid in a) distilled and sea water; b) river and lake water under environmental conditions. (b) = blank experiment.

matter that could act as one of the most important sunlight-absorbing components of the aquatic environment [24,25]. Particulate matter such as sediment particles and microorganisms suspended in a water column may scatter incident light, greatly reducing penetration of light beneath the surface.

However, a sensitization effect can not be excluded since sunlight absorbance by the DOM and other organic chromophores as riboflavin and flavin could provide a rich variety of photochemical reactions [26]. It seems that DOM competes with dichlofluanid for UV visible light decreasing the photodegradation rate. In other words the sensitization effect is hidden by the strong filter effect.

The photolysis was faster under simulated irradiation than under natural sunlight producing first-order rate constants of 0.0817 and 0.0163 for distilled water, 0.0518 and 0.0132 for sea water, 0.0394 and 0.0117 for river, 0.0335 and 0.0084 for lake water.
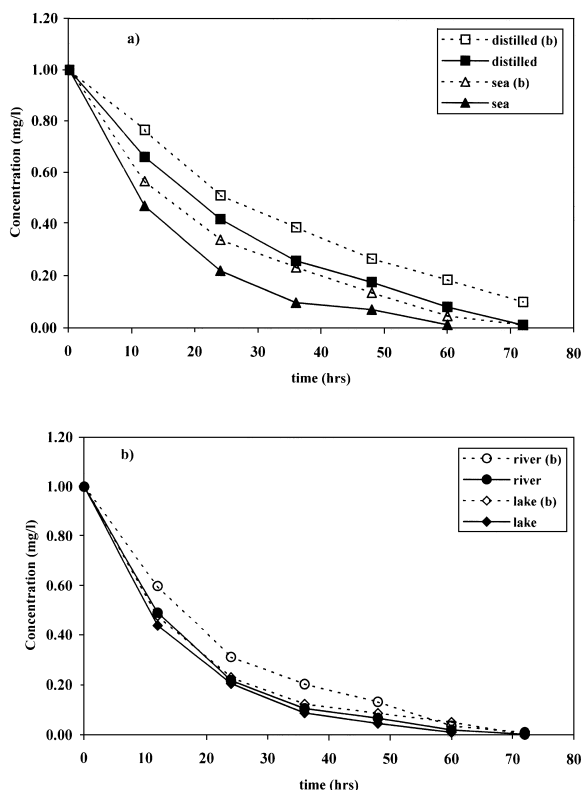
This observation seems normal when considering the sunlight intensity variation depending on the time of day and on cloud cover while the suntest apparatus keeps the intensity constant. By including the effects of diurnal cycling the reported photolysis rates of the outdoor experiments will be substantially slower, however, this will also provide more realistic environmental transformation rates.

Experiments conducted with the same initial concentration of dichlofluanid and various concentrations of DOM (HA and FA) produced also first-order degradation curves, allowing for the calculation of the rate constants. In all cases the presence of DOM slowed the rate of photolysis. For example, experiments contacted with concentrations 4, 8, 16 and 24 mg/l of HA produced rate constants of 0.0392, 0.0360, 0.0324 and 0.0281, respectively. The same tendency has been observed for the case of FA. The rate constants decreased as the concentration of FA
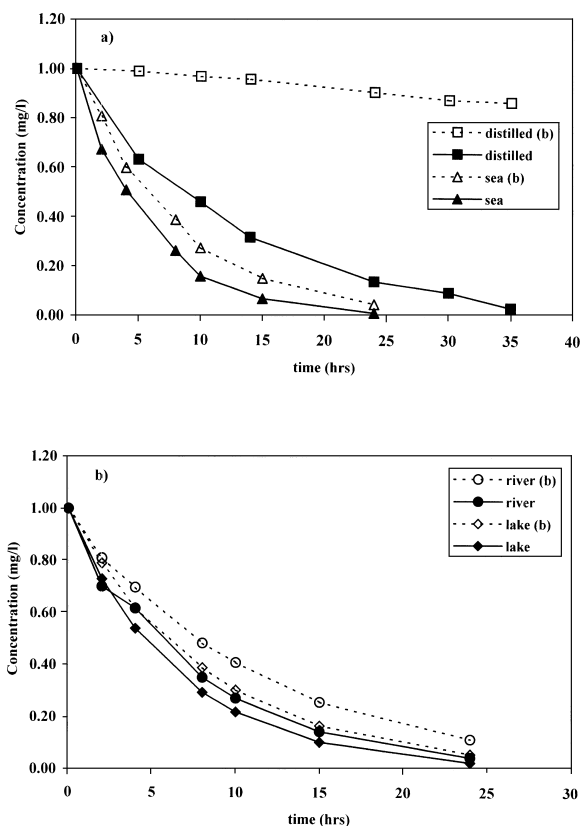
Fig. 2. Photodegradation of dichlofluanid in a) distilled and sea water; b) river and lake water under simulated solar irradiation. (b) = blank experiment.

increased: 0.0277, 0.0233, 0.0195, 0.0171 at concentration of 4, 8, 16 and 24 mg/l, respectively. The magnitude of the rate inhibition is different for each DOM sample (Table 3) by HA producing the least amount of ratio reduction. Figs. 3 and 4 display the rate data for these experiments. One can see that increasing the DOM concentration decreases the slope of the rate plots, indicating a decreasing reaction rate. The decrease in the rate of photodegradation could be due to either DOM competing with dichlofluanid for the available photons or to binding between DOM and dichlofluanid. The very low solubility of the compound in water (2 mg/l) and its high octanol/water partition coefficient (3.7), based on data from the manufacturer, Bayer AG, indicate that this biocide has a tendency to associate with particulate matter. This assumption is in agreement with the observations of Voulvounis et al. [5] who
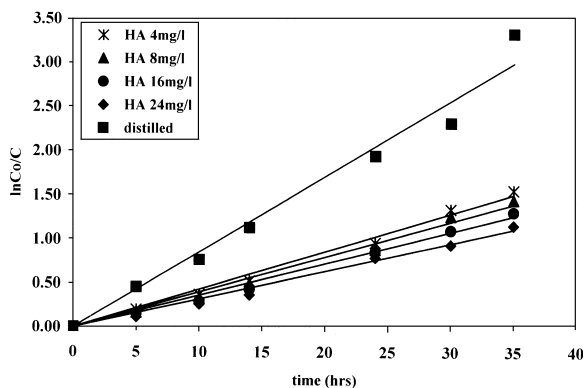

Fig. 3. Photodegradation of dichlofluanid in various concentrations of humic acids in distilled water under simulated solar irradiation.

found considerable concentrations in sediments but not in waters. The above results reveal further the dependence on the constitution of the irradiated media in the photodegradation rates.

3.3. Degradation products

The total ion chromatogram obtained by GC–MS for a SPE extract of dichlofluanid solution after 14 h of simulated irradiation in distilled water is shown in Fig. 5. Similar chromatograms were obtained also for the other experiments. From the seven peaks obtained including the parent molecule four of them were identified as possible degradation intermediates.
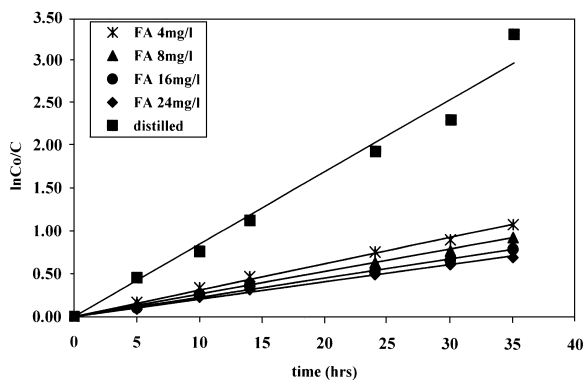

Fig. 4. Photodegradation of dichlofluanid in various concentrations of fulvic acids in distilled water under simulated solar irradiation.
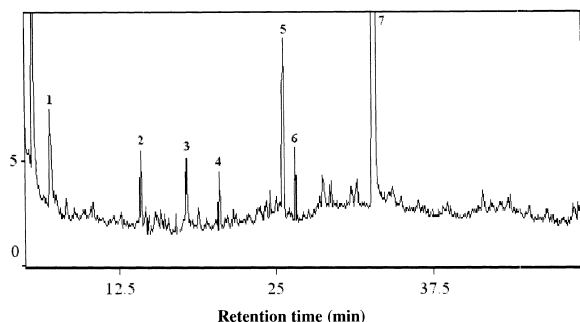
Fig. 5. Total ion chromatogram of dichlofluanid photodegradation in distilled water, using SPE and GC–MS analysis (suntest experiment).

The molecular masses of the reaction byproducts and the basic ions are summarized in Table 4.

The compounds (7 and 1) at retention times 32.7 and 7.3 min were identified as dichlofluanid and aniline, respectively. Also compound 5 at retention time 25.6 was identified as DMSA, arising from the N–S bond cleavage and the rearrangement of the *N,N*-dimethylsulfonyl group in the para position. These assignments are based on a comparison of retention times and mass spectra to standard solutions. Compound 3 appearing at retention time 17.9 was identified by using an identification program of NIST library with a fit value higher than 70%. It exhibited a molecular ion peak at $m/z = 103$ and it is associated to dichlorofluoromethane which arises from the N–S bond cleavage of dichlofluanid.

Compound 4 ($R_t = 20.5$) not included in the library was tentatively identified by interpretation of the mass spectra. It exhibited a molecular ion peak at $m/z = 225$ which corresponds to the loss of *N,N*-dimethylsulfonamyl $SO_2N(CH3)_2$ group ($m/z = 108$) from dichlofluanid and fragment ions $m/z = 124$ and 92 which are common with dichlofluanid spectra. This compound was tentatively identified as *N*-dichlorofluoromethylthio-aniline. There where also two peaks which may refer to possible degradation products. Compound 2 ($R_t = 14.9$) exhibited a base peak at $m/z = 135$ and fragment ion at $m/z = 108$ which are common with dichlofluanid spectra. Compound 6 ($R_t = 26.2$) which couldn't be identified, exhibited a base peak at 151 and fragment ions at $m/z = 123$ and 108 similar to dichlofluanid as well as fragment ion at $m/z = 96$. The mass spectra and the structures of the degradation products are shown in Fig. 6. Similar fragments (to DMSA) have been reported as a degradation product of dichlofluanid in a SPE–LC–APCI-MS system [17] during a monitoring study but the proposed structure was different. The formation of DMSA quantified by GC–MS-SIM technique using simulated solar irradiation (suntest) is shown in Fig. 7.

Based on the previous structure identification of the transformation products a possible photolytic degradation pathway is proposed for dichlofluanid in aqueous media (Fig. 8).

The environmental profiles of biocides in alternative antifoulants are poorly known until now. Laboratory studies showed that there are considerable differences in the degradation of these compounds. In all cases the alternative biocides including dichlofluanid seem to be more easily photodegra-

Table 4
Mass fragmentation pattern and retention time of dichlofluanid and its transformation products

No.	Compound	R_t (min)	M_r [a]	Mass spectrum peaks [b]
1	Aniline	7.3	93	93(100), 66(52)
2	Unidentified	14.9		135(100), 108(39)
3	Dichlorofluoromethane	17.9	103	85(100), 87(80)
4	*N*-dichlorofluoromethylthio-aniline [c]	20.5	226	225(20), 124(100), 92(56)
5	DMSA	25.6	200	200(33), 92(100), 108(14)
6	Unidentified	26.2		151(100), 96(89), 123(70)
7	Dichlofluanid	32.7	333	123(100), 92(36), 224(24), 167(29), 108(14), 200(10)

[a] Molecular ion.

[b] Relative abundance in parenthesis.

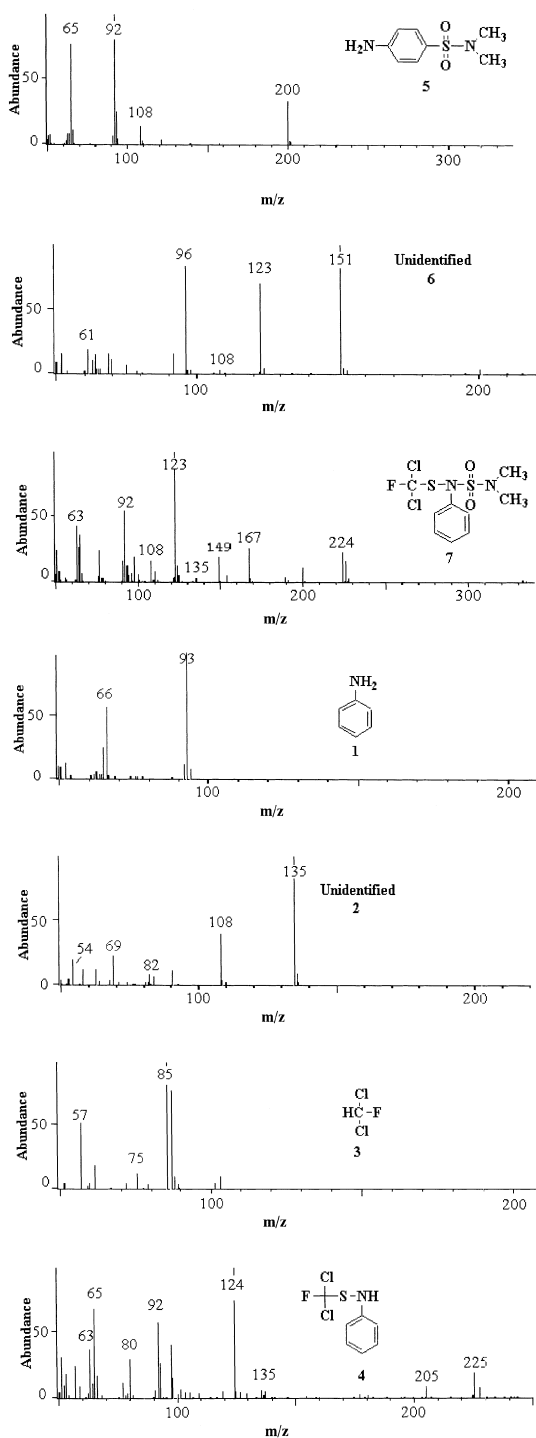[c] Tentatively identified.

Fig. 6. Mass spectra of degradation products formed in the photolysis of dichlofluanid in distilled water, using suntest apparatus.
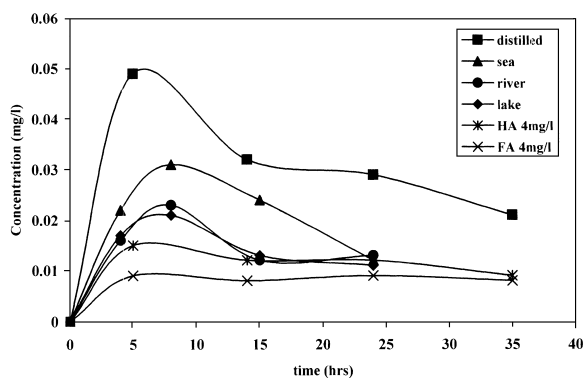

Fig. 7. Formation of DMSA in different irradiated media under simulated solar irradiation.
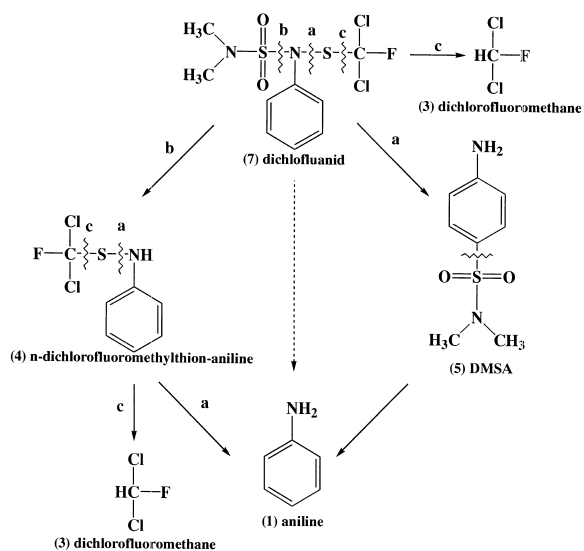

Fig. 8. Proposed photodegradation pathway of dichlofluanid in aqueous solutions. Retention time (min).

dated compared to TBT, in which photolysis was not taking place and biological degradation was the primary degradative process with half lives of 9 days in seawater [27]. Photodegradation of irgarol 1051 in seawater under artificial solar irradiation is rapid with a half-live of 107.5 min [28]. Chlorothalonil photodegradation under the same sunlight conditions in ground water, is also rapid with a half-live of 42.6 min [11]. Sea-nine 211 photodegradation experiments conducted under natural and simulated solar irradiation demonstrated half-lives of 315 and 10 h, respectively [29].

Although dichlofluanid is rapidly degraded in the aquatic environment, the formation of dichloro-fluoromethane as a photodegradation byproduct could be a disadvantage that has never been taken into consideration. Studies have shown that reactions of chlorofluorohydrocarbons in the stratosphere are a main contribution to the greenhouse effect and global warming. However, the presence of hydrogen in the molecule allows the removal of this compound by natural processes in the lower atmosphere. Its efficiency as a source gas in depleting stratospheric ozone is therefore low [30].

4. Conclusions

The photochemical behavior of dichlofluanid has been investigated. The degradation rates in natural waters were lower than in distilled water showing a strong dependence on the composition of the water sample. The presence of DOM slows the rate of the photolysis while the formation of various transformation products was followed via first-order reactions. Three of the byproducts have been identified by GC–MS techniques as the dichlorofluoromethane, aniline, and DMSA derivatives while a proposed structure is given for another transformation product.

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