



ELSEVIER

Journal of Chromatography A, 823 (1998) 81–90

JOURNAL OF
CHROMATOGRAPHY A

Photodegradation and stability of chlorothalonil in water studied by solid-phase disk extraction, followed by gas chromatographic techniques

Gustavo A. Peñuela, Damià Barceló*

Department of Environmental Chemistry, CID-CSIC, c/Jordi Girona 18–26, 08034 Barcelona, Spain

Abstract

Photodegradation of chlorothalonil was studied in deionized and ground water with sunlight and Suntest apparatus, with and without $\text{FeCl}_3/\text{H}_2\text{O}_2$ and $\text{TiO}_2/\text{H}_2\text{O}_2$. After irradiation of the water samples spiked at 28–100 $\mu\text{g}/\text{l}$ of chlorothalonil, the water solutions were preconcentrated using solid-phase disk extraction with C_{18} and analyzed by gas chromatography–electron capture and gas chromatography–mass spectrometric detection. The degradation products identified by GC–MS were: trichloro-1,3-dicyanobenzene, dichloro-1,3-dicyanobenzene and chloro-1,3-dicyanobenzene. The degradation kinetics followed a first order reaction and the R.S.D. of rate constants, for $n=3$, varied from 2 to 14%. Halfives varied between 0.7 and 101 h. The stability of chlorothalonil on C_{18} Empore disks was also investigated at 20°C, 4°C and –20°C for periods of up to 3 months. Chlorothalonil was not degraded on C_{18} Empore disks. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Photodegradation; Stability studies; Kinetic studies; Environmental analysis; Chlorothalonil; Pesticides; Organochlorine compounds

1. Introduction

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is a nonsystemic foliar fungicide used to protect a large number of agricultural crops, especially vegetables and fruits, and registered under several trade names, Bravo, Daconil 2787, Bombardier, Clortosip and Vislor [1]. Chlorothalonil is an organochlorine pesticide, stable to UV light in aqueous media and in the crystalline state. It degrades mainly through dechlorination and partly through a substitution reaction [2].

Contamination of waters by xenobiotic compounds such as pesticides presents a serious environmental problem because of their potential toxicity and widespread use. Thus, their removal from the aquatic

environment has become a very important task, and so different methods are used (carbon adsorption, ozonization, microbial degradation, photodegradation, etc). Hydrolysis, photolysis, aquatic metabolism and field dissipation can also contribute to decomposition [3]. Photolysis, using natural sunlight or xenon arc lamps is effective in removing the pesticides [4–6]. However, photolysis may be slow, and for this reason, the photodegradation of xenobiotic compounds is assisted by inorganic semi-conductors such as TiO_2 [7,8] or photosensitized by iron(III) [9,10]. H_2O_2 accelerates the degradation of organic pollutants [11], and so we have used $\text{TiO}_2/\text{H}_2\text{O}_2$ and $\text{FeCl}_3/\text{H}_2\text{O}_2$ with excellent results in the photodegradation of alachlor, chlorpyrifos and endosulfan [12–14]. In this study we selected chlorothalonil, an important fungicide, that has been detected in waters from the Mediterranean [15] and in Brazil [16].

*Corresponding author.

Concentrations of chlorothalonil <100 µg/l were used in order to reflect more closely what happens in the real environment. An additional enrichment step is required before the irradiated solution could be analyzed; solid-phase extraction (SPE) of irradiated solutions was combined with gas chromatography (GC).

C₁₈ SPE disks were found to be adequate to preconcentrate pesticides from water samples [5,6,12–14]; the SPE disks permit concentration of the analytes and it can be used to follow the degradation of pesticides at environmental concentration (µg/l) levels. Multiresidue analytical methods identify and quantify all pesticides but it is difficult because some decompose in water, so extraction from water is necessary.

The stability of pesticides in SPE disks has been previously studied by our group [17,18]. By studying the stability, we could demonstrate whether water samples could be replaced by SPE disks in environmental monitoring, making storage and transportation easier.

We used ethyl acetate for the elution of C₁₈ disks because chlorothalonil is very stable in this solvent. In very dilute solutions of a large number of solvents chlorothalonil was completely degraded in a few minutes [19].

The objectives of this work were (1) to compare the degradation kinetics of chlorothalonil in water by using photolysis with sunlight, photolysis with Suntest apparatus, photocatalysed degradation with TiO₂ and FeCl₃, (2) to identify the degradation products formed and (3) to study the stability of chlorothalonil on C₁₈ disks.

2. Experimental

2.1. Chemicals

Chlorothalonil (99%) was from Chem Service (Tower Lane, USA), iron(III) chloride 6-hydrate (98–102%) was from Panreac (Barcelona, Spain) and titanium dioxide P25 from Degussa (Japan). Ethyl acetate was obtained from Panreac and methanol and acetone were purchased from Merck (Darmstadt, Germany). Hydrogen peroxide (30% solution) was from Foret (Barcelona). Organic-free water (pH

8.0) was prepared with a Milli-Q system from Millipore–Waters. Ground water (pH 7.67, 344 mg/l of sulphates, 360 mg/l of chlorides, 68 mg/l of nitrates, 260 mg/l of Ca, 78 mg/l of Mg, 1.6 mg/l of TOC, conductivity 2050 µS/cm) was used in some of the experiments. Empore 3M, extraction disks C₁₈ were from J.T. Baker (Deventer, Netherlands). DB-5 column (5% of methylphenyl siloxane) was from J&W Scientific, and HP-5MS (5% of methylphenyl siloxane) was from Hewlett-Packard.

2.2. Chromatographic conditions

The kinetics of photodegradation, study of stability, and monitoring were determined using a Hewlett-Packard 5890 gas chromatograph equipped with an electron-capture detection (ECD) system. A DB-5 column (30 m×0.23 mm I.D.) was programmed from 60 to 300°C at 6°C/min; 60°C was held for 1 min and 300°C was held for 5 min. Injector and detector temperatures were held at 270°C and 310°C, respectively. Helium was used as the carrier gas at a flow-rate of 2.8 ml/min and was used as the make-up gas at 70.0 ml/min. Injection mode was splitless and injection volume was 1.0 µl.

2.3. Mass spectrometric analysis

A Fisons MD 800 mass spectrometer coupled to a Fisons GC 8000 apparatus was used for GC–MS in the electron impact (EI) mode. EI spectra was obtained at 70 eV, in full scan mode from *m/z* 50 to 500. A HP-5MS column (30 m×0.25 mm I.D.) was programmed from 60 to 300°C at 6°C/min; 60°C was held for 1 min and 300°C was held for 5 min. Injector and detector temperatures were 270°C, ion source temperature 280°C. Helium was used as the carrier gas with a pressure of column head of 12 p.s.i. (1 p.s.i.=6894.76 Pa). Injection mode was splitless and injection volume was 1.0 µl.

2.4. Photolysis experiments

Irradiations were carried out using a Suntest apparatus from Heraeus (Hanau, Germany) equipped with a xenon arc lamp, as reported previously [6]. Others experiments were carried out using natural sunlight irradiation, with capped quartz reservoirs

placed on a terrace roof at our institute in Barcelona, during August 1997. Water samples, spiked with chlorothalonil in ethyl acetate, were placed in quartz reservoirs of 500 or 1000 ml. Chlorothalonil concentrations in water were 28 and 100 $\mu\text{g}/\text{l}$ for the kinetic studies and identification of degradation products, respectively. At different periods of time, water samples were removed from reactor and stored at 4°C. The preconcentrated volume of water was 25–250 ml.

2.5. Photocatalysis experiments

These experiments were carried out in the presence of photosensitizers, such as Fe_2O_3 and TiO_2 . Irradiations were carried out using a Suntest apparatus and natural sunlight irradiation. Water samples, spiked with chlorothalonil by adding the standard pesticide in ethyl acetate, were placed in 500- or 1000-ml quartz reservoirs. The concentrations of chlorothalonil used were same as in photolysis studies. After different periods of time, water samples were removed from the reactor and stored in a refrigerator. The preconcentrated volume of water on C_{18} disks was 25–250 ml.

Experiments with FeCl_3 or TiO_2 were carried out at concentrations of 15 mg/l (as Fe^{3+}) and 10 mg/l (as TiO_2), respectively. In all experiments, H_2O_2 at 0.05% (v/v) was also added. The experiments began with the addition of either TiO_2 or FeCl_3 to the water, after which the mixture was homogenized for 15 min by careful agitation. The chlorothalonil standard solution was then added, followed by agitation and finally the H_2O_2 was added.

2.6. Recovery on C_{18} Empore disks

The recovery of chlorothalonil was investigated at two concentrations; 31 $\mu\text{g}/\text{l}$, which was similar to the concentration in the photodegradation experiments and 15 $\mu\text{g}/\text{l}$ which was half the concentration in the photodegradation experiments. The volume used in preconcentration on C_{18} Empore disks varied between 25 and 500 ml.

2.7. Stability on C_{18} Empore disks

The stability of chlorothalonil was carried out at

three temperatures, -20°C , 4°C and 20°C , during 3 months and in triplicate. The volume used in preconcentration on C_{18} disks was 50 ml. After the preconcentration of chlorothalonil, using the method described in Section 2.8, the disks were dried for 30 min to prevent water from causing hydrolysis of chlorothalonil on the silica surface. The Empore disks containing the preconcentrated chlorothalonil were wrapped in aluminum foil and stored in special boxes at different temperatures. Three of the thirty disks were analyzed immediately (time 0) and nine were stored at three different temperatures. Before analysis, the disks stored at -20°C and 4°C were left at laboratory temperature for 15 min before extraction.

2.8. Sample preparation

The water sample removed from reactor was preconcentrated as detailed in [5,6]. The C_{18} Empore disk was placed on a sintered glass filter funnel apparatus attached to a vacuum source. A 10-ml volume of ethyl acetate was added to the filter funnel and the disk was dried for 2 min. Subsequently, 10 ml of acetone were added and the disk was dried for 5 min. Then 15 ml of methanol were added and after almost all the methanol was drawn through the disk, 10+10 ml of deionized water was added. A 25–250 ml volume of water sample was added when the deionized water was almost drawn through the disk. After the water sample had passed through, the vacuum was left on for 30 min to allow the disk to dry. The filtration system was put in a reservoir to receive the extract containing chlorothalonil and the degradation products. The extraction was done with three 20-ml portions of ethyl acetate. After addition of the first portion, the vacuum was left on for 5 min and when the second and third portions were added, the vacuum was left on for 3 min. The solvents and sample were drawn through the disk at a rate of approximately 0.5 ml/s. The reservoir with the extract was placed in a rotaevaporator system and the extract was carried to a volume between 0.1 and 1.0 ml, depending of the analysis (GC-ECD or GC-MS) and the preconcentrated water sample. The concentrated extract was analyzed by GC-ECD or GC-MS. The samples were quantified by external standard using automated injection. Calibration

graphs in GC–ECD were performed by plotting area (y) versus amount injected (x), with the calibration equation constructed at absolute amounts of chlorothalonil injected of 4, 11, 22, 66, 111, 221, 443, 664, 886 and 1107 μg . The calibration was done each day of analysis, and R^2 varied between 0.994 and 0.999.

2.9. Calculation of half-life

The calculation of half-life [20] was performed using the first-order rate equation:

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_t represents the concentration at time t ; C_0 represents the initial concentration and k is the rate constant. When the concentration is reduced to 50% of its initial amount, the half-life ($t_{1/2}$) can be determined by:

$$t_{1/2} = 0.693/k \quad (2)$$

where k is the degradation constant.

3. Results and discussion

3.1. Recovery studies

The same concentration used in the photodegradation experiments was used for the recovery studies (Table 1) and high recoveries at preconcentration volumes between 25 and 500 ml were found. A

Table 1
Recovery of chlorothalonil using C_{18} Empore disks at different water volumes, $n=3$ for each experiment

| Concentration ($\mu\text{g}/\text{l}$) | Volume (ml) | Recovery (%) | R.S.D. ^a (%) |
|--|-------------|--------------|-------------------------|
| 15.46 | 25 | 108.33 | 10.83 |
| 15.46 | 50 | 92.70 | 9.75 |
| 15.46 | 100 | 90.40 | 14.52 |
| 15.46 | 250 | 84.84 | 13.43 |
| 15.46 | 500 | 70.94 | 14.38 |
| 30.92 | 25 | 97.89 | 17.49 |
| 30.92 | 50 | 103.49 | 10.43 |
| 30.92 | 100 | 85.94 | 11.53 |
| 30.92 | 250 | 79.37 | 4.70 |
| 30.92 | 500 | 88.61 | 7.62 |

^a Relative standard deviation.

second concentration — corresponding to the half the concentration in the photodegradation experiments — was used in determining the recovery, and it better reflected the photodegradation reaction. The recoveries were high except at preconcentration volume of 500 ml (70.9%). However, the recoveries are still acceptable and are within the US Environmental Protection Agency (EPA) limits (between 70 and 120%).

3.2. Stability on C_{18} Empore disks

The different disks spiked with chlorothalonil were analyzed during a 3-month period (Table 2). When removed from storage at -20°C and 4°C the disks were kept at room temperature for 15 min before elution with ethyl acetate (3×20 ml). The same concentration as in the photodegradation experiments was used and a volume of 50 ml in the preconcentration.

Table 2 shows the data obtained from the study of the stability of chlorothalonil. At -20°C , the concentrations of chlorothalonil varied between 24.5 and 27.7 $\mu\text{g}/\text{l}$. At 4°C , the concentrations varied between 24.8 and 29.1 $\mu\text{g}/\text{l}$, and at 20°C , between 24.8 and 27.1 $\mu\text{g}/\text{l}$. These results indicate that chlorothalonil did not degrade during the storage. The R.S.D. was similar at three temperatures, 5.0–8.6% at -20°C , 5.3–9.1% at 4°C and 3.1–8.4% at 20°C . The differ-

Table 2
Mean concentrations found in the study of stability of chlorothalonil on C_{18} Empore disks^a

| Temperature ($^\circ\text{C}$) | Time (month) | Conc. ($\mu\text{g}/\text{l}$) | R.S.D. ^b (%) |
|----------------------------------|--------------|----------------------------------|-------------------------|
| -20 | 0 | 24.8 | 7.9 |
| -20 | 1 | 24.5 | 5.0 |
| -20 | 2 | 27.7 | 6.6 |
| -20 | 3 | 26.9 | 8.6 |
| 4 | 0 | 24.8 | 7.9 |
| 4 | 1 | 29.1 | 9.1 |
| 4 | 2 | 26.7 | 5.5 |
| 4 | 3 | 28.9 | 5.3 |
| 20 | 0 | 24.8 | 7.9 |
| 20 | 1 | 26.1 | 3.1 |
| 20 | 2 | 24.8 | 8.1 |
| 20 | 3 | 27.1 | 8.4 |

^a Volume of deionized water preconcentrated: 50 ml, spiked at 27.7 $\mu\text{g}/\text{l}$, $n=3$.

^b Relative standard deviation.

ence in the values is due to the reproducibility of the method. Acidification is a common practice in studies of the stability of pesticides in water; in order to preserve the compounds to be analyzed, acid is added to the water matrix immediately after sampling and kept at 4°C. The approach used in this work enabled us to study the chlorothalonil in its original matrix. The only treatment was preconcentration on C₁₈ Empore disks. Therefore, it is possible to store chlorothalonil on the disks after each photodegradation experiment, and the samples can be analyzed later. It is also possible to collect real samples, store them on the SPE disks and then transport them to the laboratory. After 1–3 months all samples from a monitoring survey can be analyzed together, thus saving time and increasing efficiency.

3.3. Photodegradation kinetic of chlorothalonil

All photodegradation reactions determined in this work were of first order. The photolysis in deionized water with sunlight showed that chlorothalonil degraded slowly (Table 3). The half-life of the photodegradation was 101 h (Table 5), but after 348 h of solar irradiation (Table 3) 6% of chlorothalonil remained. The photolysis experiment with sunlight was carried out on August, and the temperature varied between 26 and 31°C.

The photolysis of chlorothalonil in deionized water with Suntest apparatus (half-life of 36.86 h) was faster than with sunlight (half-life 101.17 h). The Suntest apparatus has a xenon lamp with an internal closed-loop monitoring device that measures the spectral output of the lamp between 300 and 800 nm, similar to solar spectral, and adjusts the current to the lamp to maintain the monitored region constant [21]. Suntest emits energy higher than solar radiation, so degradation is faster. Sunlight can be quite variable in intensity depending on the time of day and on cloud cover [22].

Any absorption of wavelengths >290 nm is an indication that the molecule will be susceptible to photodegradation. Chlorothalonil has two peaks of absorption, 313 nm (log ϵ =3.28) and 325 nm (log ϵ =3.39) in ethanol [23], so chlorothalonil decomposes through either a free radical attack or auto-oxidation process [24].

In ground water (half-life of 0.71 h), the degradation was faster than in deionized water (half-life of 36.86 h). The rate of photodegradation can be affected by dissolved and suspended matter in aqueous media [25,26]. Some ions of ground water such as nitrite and nitrate absorb light, λ_{\max} 355 (ϵ =22) and λ_{\max} (ϵ =7), respectively, and undergo homolysis to produce free radicals [21]. It seems probable that in nitrite and nitrate photolysis, the dominant process is the production of hydroxyl

Table 3

Percentage of degradation of chlorothalonil in the photolysis in deionized water and ground water, using a initial concentration of 27.7 $\mu\text{g/l}$ of chlorothalonil, each experiment $n=3$

| Deionized water | | | | Ground water | |
|-----------------|-------------------|-------------------------------|-------------------|------------------|-------------------|
| Sunlight | | Artificial light ^a | | Artificial light | |
| Time (h) | Degrad., % (S.D.) | Time (h) | Degrad., % (S.D.) | Time (h) | Degrad., % (S.D.) |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 48 | 16.43 (1.91) | 6 | 16.01 (8.20) | 0.5 | 22.41 (3.91) |
| 96 | 26.69 (2.62) | 12 | 19.34 (7.25) | 1.0 | 42.17 (4.30) |
| 144 | 32.25 (1.92) | 18 | 26.70 (9.80) | 1.5 | 65.62 (9.71) |
| 192 | 61.35 (9.61) | 24 | 30.56 (7.50) | 2.0 | 86.55 (1.60) |
| 240 | 70.15 (6.92) | 36 | 45.98 (2.93) | 2.5 | 92.95 (1.30) |
| 288 | 77.02 (11.76) | 48 | 58.73 (2.03) | 4.0 | 99.07 (0.70) |
| 324 | 81.93 (6.08) | 60 | 63.87 (2.47) | 6.0 | 99.67 (0.21) |
| 348 | 93.95 (9.79) | 72 | 74.87 (1.79) | 8.0 | 99.76 (0.14) |
| | | 84 | 80.20 (1.84) | 10.0 | 99.83 (0.07) |

^a Xenon lamp (Suntest apparatus).

Table 4

Percentage of degradation of chlorothalonil in the photocatalysis with FeCl_3 and TiO_2 in deionized water, using an initial concentration of 27.7 $\mu\text{g}/\text{l}$ of chlorothalonil, each experiment $n=3$

| FeCl_3 | | | | TiO_2 | |
|-------------------------------|-------------------|------------|-------------------|------------------|-------------------|
| Artificial light ^a | | Sunlight | | Artificial light | |
| Time (min) | Degrad., % (S.D.) | Time (min) | Degrad., % (S.D.) | Time (min) | Degrad., % (S.D.) |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | 14.17 (6.75) | 30 | 12.94 (6.62) | 20 | 14.59 (1.98) |
| 30 | 27.80 (4.08) | 60 | 19.90 (8.25) | 40 | 23.36 (11.35) |
| 45 | 38.59 (4.32) | 90 | 23.43 (3.47) | 60 | 40.12 (2.65) |
| 60 | 46.96 (1.28) | 135 | 32.13 (5.57) | 80 | 46.25 (3.99) |
| 80 | 57.31 (2.77) | 180 | 37.93 (9.39) | 100 | 51.39 (4.76) |
| 100 | 65.70 (1.76) | 225 | 43.77 (0.90) | 120 | 55.67 (3.96) |
| 120 | 68.57 (2.17) | 270 | 49.13 (2.28) | 150 | 75.82 (2.68) |
| 150 | 78.18 (1.76) | 330 | 55.47 (0.42) | 180 | 87.52 (1.62) |
| 180 | 82.87 (1.69) | 390 | 69.82 (0.86) | 210 | 91.68 (0.11) |
| | | 450 | 71.95 (1.23) | | |

^a Xenon lamp (Suntest apparatus).

radical which accelerates the organic reactions. Other ions also accelerate the photodegradation, such as calcium and magnesium which take part in complexation reactions enhancing the photolysis of organic compounds [27].

In the degradation with the Suntest apparatus in deionized water using a photocatalyzer (Tables 4 and 5), Fe^{3+} and TiO_2 , accelerated the degradation process of chlorothalonil, to half-lives of 82 and 60 min, respectively. In the homogeneous photocatalysis, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, Fe^{2+} is formed, and so Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) generates hydroxyl radical that attack organic compounds. H_2O_2 absorbs (although weakly) up to 315 nm and will also

directly generate hydroxyl radicals under light irradiation [28]. When chlorothalonil absorbs UV radiation, the primary photochemical reaction is the homolytic cleavage of the 4-Cl-C bond [23]. The monodechlorate aryl radical can react by different routes but the fastest is oxidation with hydroxyl radical. The hydroxyl radical increases the dechlorination rate of chlorothalonil, so $\text{FeCl}_3/\text{H}_2\text{O}_2$ and $\text{TiO}_2/\text{H}_2\text{O}_2$ decreased the half-life of chlorothalonil compared to photolysis without a catalyzer.

The degradation reaction rate with $\text{FeCl}_3/\text{H}_2\text{O}_2$ and sunlight (Tables 4 and 5) was slower than with $\text{FeCl}_3/\text{H}_2\text{O}_2$ and the Suntest apparatus because sunlight radiation exhibits lower energy than the

Table 5

Kinetics of the photodegradation of chlorothalonil in water^a

| Photodegradation | Reaction order | Rate constant (h^{-1}) | R.S.D. ^b | Half-life (h) |
|--|----------------|-----------------------------------|---------------------|---------------|
| Sunlight, deionized water | 1 | 0.0069 | 14.35 | 101.17 |
| Xenon lamp, deionized water | 1 | 0.0188 | 3.58 | 36.86 |
| Xenon lamp, ground water | 1 | 0.9694 | 6.97 | 0.71 |
| Xenon lamp, deionized water, FeCl_3 | 1 | 0.5044 | 2.53 | 1.37 |
| Xenon lamp, deionized water, TiO_2 | 1 | 0.6972 | 9.02 | 0.99 |
| Sunlight, deionized water, FeCl_3 | 1 | 0.1634 | 5.12 | 4.24 |

^a Number of experiments, for each degradation experiment, $n=3$.

^b Relative standard deviation.

Suntest lamp. We also found that other organochlorine pesticides such as alachlor [12], chlorpyrifos [13] and endosulfan [14] degrade very quickly with $\text{FeCl}_3/\text{H}_2\text{O}_2$ and $\text{TiO}_2/\text{H}_2\text{O}_2$.

3.4. Degradation products

Products 1, 2 and 3 (Fig. 1) which were formed by dechlorination were detected in the photodegradation

of chlorothalonil by GC–MS. These products correspond to trichloro-1,3-dicyanobenzene (1), dichloro-1,3-dicyanobenzene (2) and chloro-1,3-dicyanobenzene (3). Giumanini et al. [23,29] reported several degradation products of which we identified two compounds, trichlorocyanobenzene and dichlorocyanobenzene by comparison with the mass spectra reported by Giumanini. EI spectra of trichlorocyanobenzene (Fig. 1) exhibit parent ions at

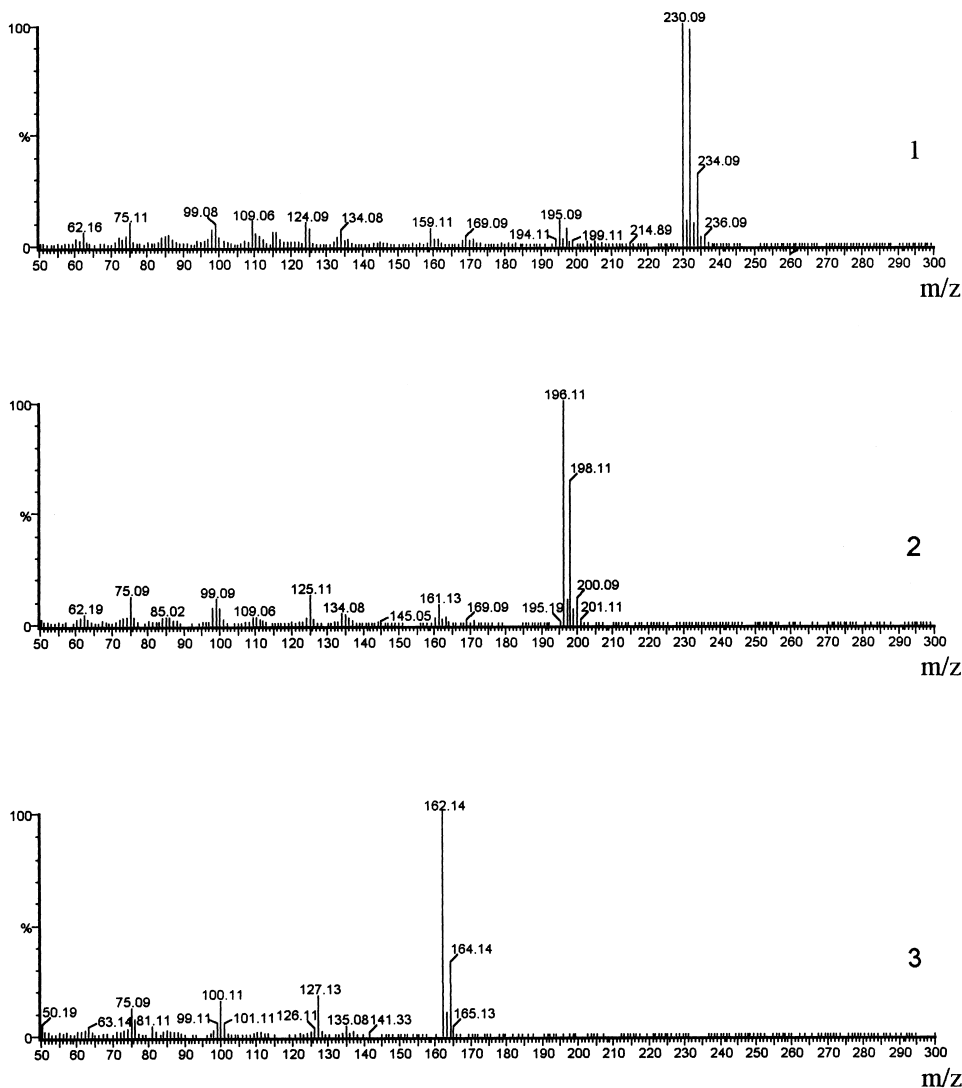


Fig. 1. Mass spectra of degradation products formed in the photolysis of chlorothalonil in ground water, using Suntest apparatus. (1) Trichloro-1,3-dicyanobenzene, (2) dichloro-1,3-dicyanobenzene and (3) chloro-1,3-dicyanobenzene.

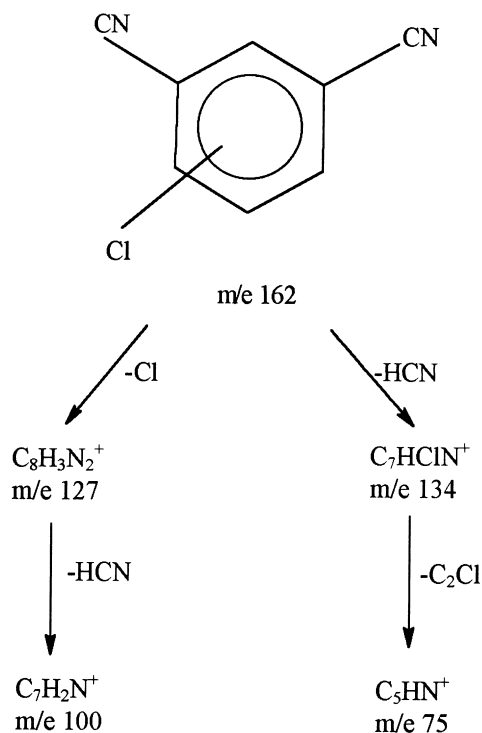


Fig. 2. Fragmentation of chloro-1,3-dicyanobenzene.

m/z 230 with the quadruplet in the correct ratio for Cl_3 . The identification of chlorocyanobenzene (3) could not be done by comparison, but it was very easy by GC–MS because its mass spectrum (Fig. 1) presents the characteristic fragmentation ions of this product (Fig. 2). Tanaka et al. [30] reported these three degradation products but they did not present the mass spectra.

Fig. 3 shows the chromatograms corresponding to the formation of degradation products. Trichlorodicyanobenzene is formed first and then dichlorodicyanobenzene and chlorodicyanobenzene are produced. In deionized water, only trichlorodicyanobenzene was detected and quantified.

Two isomers of trichlorodicyanobenzene and dichlorodicyanobenzene were detected in a few samples e.g. the sample '240 min of photocatalysis with $FeCl_3$ and Suntest' but we could not identify the isomers. Tanaka et al. identified four isomers of trichlorodicyanobenzene, two isomers of dichlorodicyanobenzene and three isomers of monochlorodicyanobenzene. In Fig. 4 we present the photodegradation pathway of chlorothalonil but the

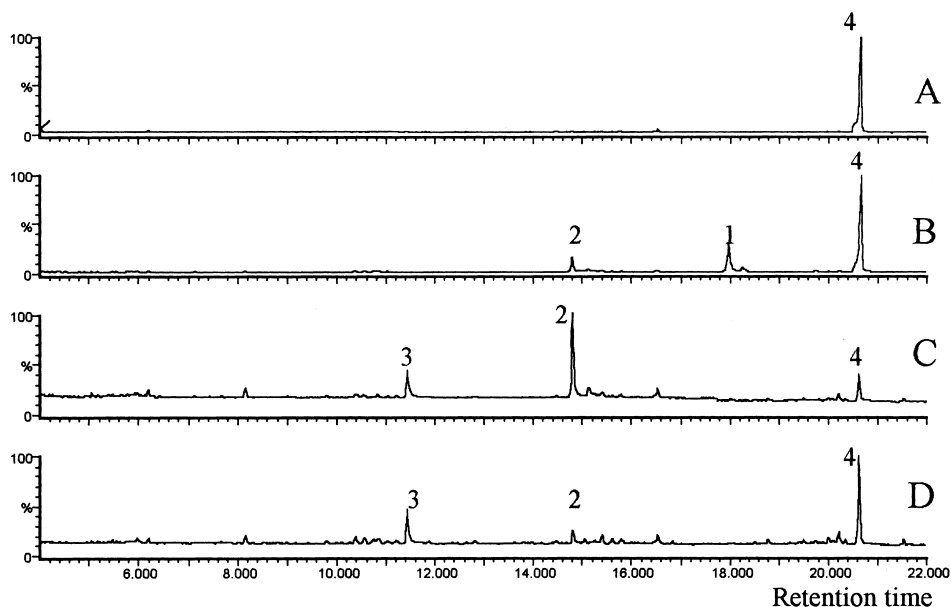


Fig. 3. Total ion chromatograms of chlorothalonil photodegradation and chlorothalonil (peak 4) in ground water, using the Suntest apparatus. Peaks: 1 = trichloro-1,3-dicyanobenzene, 2 = dichloro-1,3-dicyanobenzene and 3 = chloro-1,3-dicyanobenzene. (A) 0 h of reaction (volume of preconcentration: 100 times); (B) 3 h (volume of preconcentration: 500 times); (C) 6 h (volume of preconcentration: 1000 times); (D) 9 h (volume of preconcentration: 2500 times).

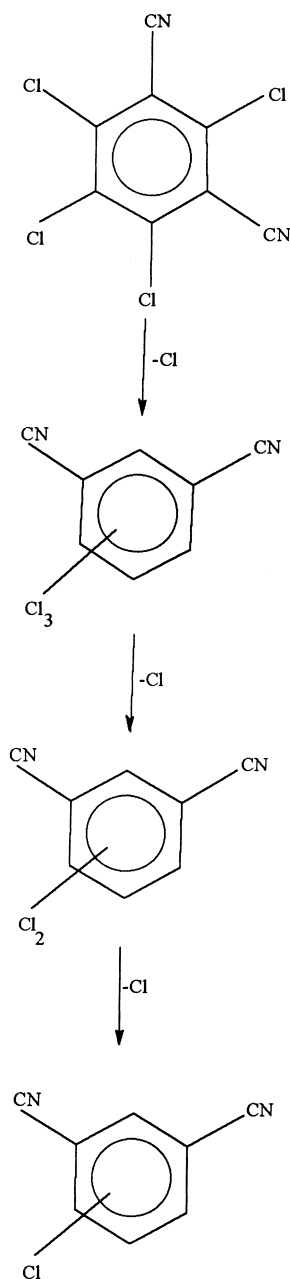


Fig. 4. Photodegradation pathway of chlorothalonil in water.

identification of the isomers could not be unequivocally made.

Relative percentages of degradation products were obtained (Table 6) assuming that recovery of each

one is similar to chlorothalonil, which can be expected because these products have a similar structure. Trichlorodicyanobenzene was most abundant and monodichlorodicyanobenzene was least abundant. We detected traces of dicyanobenzene, its mass spectrum is similar to the standard, but only in the 6- and 9-h degradation samples in ground water.

4. Conclusions

The extraction with C_{18} Empore disks in photodegradation studies is a good technique to study the degradation of chlorothalonil at low concentrations. GC-ECD can be used to evaluate the degradation kinetic of chlorothalonil, whereas GC-MS can be used to identify the metabolites formed.

Chlorothalonil was degraded slowly using natural sunlight, but with the Suntest apparatus the degradation rate was increased, and in ground water the degradation was very fast. The photodegradation of chlorothalonil using the $FeCl_3/H_2O_2$ or TiO_2/H_2O_2 systems and Suntest apparatus was very fast. The degradation rate using $FeCl_3/H_2O_2$ and sunlight was slower than using $FeCl_3/H_2O_2$ and the Suntest apparatus. Low amounts of $FeCl_3$ (15 mg/l) and TiO_2 (10 mg/l) are very effective in catalysing the destruction of chlorothalonil in waters.

We identified three degradation products of chlorothalonil, but the identity of the isomers could not be determined. Further research is needed, for instance, synthesis of the various isomers.

Chlorothalonil is stable on C_{18} Empore disks at $-20^\circ C$, $4^\circ C$ and $20^\circ C$. So SPE disks can be used for storage and transportation of water containing chlorothalonil.

Acknowledgements

G.A. Peñuela acknowledges financial support from Mutis grant from the Spanish Ministry of Foreign Affairs and also acknowledges support from the University of Antioquia, at Medellín (Colombia). This work has been supported by CICYT (AMB95-0075-C03).

Table 6

Relative percentage of degradation products (1–3) detected in the photodegradation experiments, using the Suntest apparatus

| Degradation experiments | 4 ^a (%) | 1 (%) | 2 (%) | 3 (%) |
|--|-----------------------|----------|----------|----------|
| Photolysis, deionized water, 0 h | 100 | 0 | 0 | 0 |
| Photolysis, deionized water, 24 h | 31.88 | 1.15 | N.d | N.d |
| Photolysis, deionized water, 48 h | 14.48 | 0.92 | N.d | N.d |
| Photolysis, deionized water, 72 h | 9.86 | 1.28 | N.d. | N.d. |
| Photolysis, ground water, 0 h | 100 | 0 | 0 | 0 |
| Photolysis, ground water, 3 h | 32.11 | 9.99 | 3.88 | N.d. |
| Photolysis, ground water, 6 h | 0.73 | N.d. | 2.36 | 0.70 |
| Photolysis, ground water, 9 h | 1.10 | N.d. | 0.20 | 0.40 |
| Photocatalysis, FeCl ₃ , deionized water, 0 min | 100 | 0 | 0 | 0 |
| Photocatalysis, FeCl ₃ , deionized water, 80 min | 40.53 | 5.99 | Traces | N.d. |
| Photocatalysis, FeCl ₃ , deionized water, 180 min | 21.28 | 6.39 | 0.45 | Traces |
| Photocatalysis, FeCl ₃ , deionized water, 240 min | 3.69 | 2.37 | 0.49 | 0.03 |
| Photocatalysis, TiO ₂ , deionized water, 0 min | 100 | 0 | 0 | 0 |
| Photocatalysis, TiO ₂ , deionized water, 80 min | 61.03 | 12.14 | 1.48 | N.d. |
| Photocatalysis, TiO ₂ , deionized water, 180 min | 30.25 | 7.68 | 3.54 | 0.52 |
| Photocatalysis, TiO ₂ , deionized water, 240 min | 5.78 | 3.65 | 2.57 | 0.89 |

^a Chlorothalonil (4) concentration is residual concentration.

References

- [1] C. Tomlin (Editor), *The Pesticide Manual*, Farnham, 3rd ed., 1994, pp. 201–202.
- [2] K. Sato, H. Tanaka, *Biol. Fertil. Soils* 3 (1987) 205–209.
- [3] D. Barceló, *Analyst* 116 (1991) 681–689.
- [4] G. Durand, N. De Bertrand, D. Barceló, *J. Chromatogr. A* 554 (1991) 233–250.
- [5] S. Lacorte, D. Barceló, *Environ. Sci. Technol.* 28 (1994) 1159–1163.
- [6] S. Chiron, J. Abian, M. Ferrer, F. Sanchez-Baeza, A. Messegeur, D. Barceló, *Environ. Toxicol. Chem.* 14 (1995) 1287–1298.
- [7] D. Ollis, E. Pelizzetti, N. Serpone, *Environ. Sci. Technol.* 25 (1991) 1523–1529.
- [8] C. Minero, E. Pelizzetti, P. Pichat, M. Sega, M. Vicentini, *Environ. Solar Techn.* 29 (1995) 2226–2234.
- [9] R. Zepp, F. Bruce, J. Hoigné, *Environ. Sci. Technol.* 26 (1992) 313.
- [10] Y. Sun, J. Pignatello, *J. Agric. Food Chem.* 41 (1993) 1139–1142.
- [11] N. Serpone, E. Pelizzetti (Editors), *Photocatalysis*, New York, 1989.
- [12] G. Peñuela, D. Barceló, *J. Chromatogr. A* 754 (1996) 187–195.
- [13] G. Peñuela, D. Barceló, *Toxicol. Environ. Chem.* 62 (1997) 135–147.
- [14] G. Peñuela, D. Barceló, *J. Chromatogr. A* 795 (1998) 93–104.
- [15] J.W. Readman, T.A. Albanis, D. Barceló, S. Galassi, J. Tronczynski, G.P. Gabriellides, *Mar. Pollut. Bull.* 34 (1997) 259–263.
- [16] A. Oubiña, E. Martinez, J. Gascón, D. Barceló, I.B. de Alleluia, *Int. J. Environ. Anal. Chem.*, in press.
- [17] E. Martinez, D. Barceló, *Chromatographia* 42 (1996) 71–76.
- [18] I. Ferrer, D. Barceló, *J. Chromatogr. A* 778 (1997) 161–170.
- [19] E.L. Finley, J.B. Graves, F.C. Hewitt, H.F. Morris, C.W. Harman, F.A. Iddings, P.E. Schilling, K.L. Koonce, *Bull. Environ. Contam. Toxicol.* 22 (1979) 598–602.
- [20] A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry*, American Chemical Society, Washington, DC, 1st edn., 1988, p. 49.
- [21] L.A. Bard, *Evaluation chemical photodegradation: Instrumental approach*, American Laboratory News Edition, Febrero, 1992.
- [22] R.G. Zepp, D.M. Cline, *Environ. Sci. Technol.* 11 (1977) 359–366.
- [23] A.G. Giumanini, G. Verardo, P. Strazzolini, *J. Photoch. Photob. A Chem.* 48 (1989) 129–153.
- [24] P.D. Gabriele, R.M. Iannucci, *J. Coat. Tech.* 56 (1984) 33–48.
- [25] R.G. Zepp, A.M. Braun, L. Hoigné, J.A. Leehneer, *Environ. Sci. Technol.* 21 (1987) 485–490.
- [26] O.C. Zafiriou, J. Jousot-Dubien, R.G. Zepp, R.G. Zika, *J. Am. Chem. Soc.* 18 (1984) 358–371.
- [27] R.A. Larson, E.J. Weber, *Reaction Mechanisms in Environmental Organic Chemistry*; CRC Press, Boca Raton, FL, 1994, p. 372.
- [28] B. Faust, J. Hoigné, *J. Atm. Environ.* 24A (1990) 79.
- [29] A.G. Giumanini, G. Verardo, M. Poiana, P. Strazzolini, *Annali Chimica* 85 (1985) 553–565.
- [30] K. Sato, H. Tanaka, *Biol. Fertil Soils* 3 (1987) 205–209.