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Application of solid-phase extraction and micellar electrokinetic capillary chromatography to the study of hydrolytic and photolytic degradation of phenoxy acid and phenylurea herbicides☆

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Abstract

A degradation study of two phenoxy acid [(2,4-dichlorophenoxy) propanoic acid and (2,4,5-trichlorophenoxy) acetic acid] and two phenylurea (diuron and monolinuron) herbicides, spiked at 50 ppb in water, was performed. Some samples were subjected to neutral and basic hydrolysis; other samples were subjected to photolysis using either sunlight or a xenon arc lamp. After degradation, the water samples were preconcentrated using solid-phase extraction (SPE) with Carbopack B columns and analysed by a micellar electrokinetic capillary chromatography (MECC) system with UV detection at 210 nm. Phenoxyacetic acids were not degraded neither by hydrolysis nor by sunlight photolysis, but they were photodegraded when they were exposed to a xenon arc lamp, with half-lives around 300 min. Phenylurea herbicides were hydrolysed at the two-tested pH, with half-lives varying from 25 to 290 days. The main hydrolysis products were the corresponding chloroanilines. Diuron and monolinuron were also degraded when they were exposed to sunlight and xenon arc lamp. The main photodegradation pathway for diuron corresponded to dehalogenation, while for monolinuron dealkylation and hydroxylation were also postulated. The toxicity of the studied herbicides and their degradation products was evaluated by means of Microtox tests. The obtained results indicated that the toxicity of the degraded samples was higher than the toxicity of the herbicides.

Keywords: Microtox; Toxicity; Photodegradation; Pesticides; Phenoxy acids; Phenylureas

1. Introduction

Phenylurea and phenoxy acid pesticides are commonly used in Europe as selective pre- and post-emergence herbicides. The study of mixtures of these compounds is of interest because they appear generally together in well-known commercial formulations [1]. When released to the environment, herbicides are subjected to various biotic and abiotic processes such as photolysis, oxidation, hydrolysis and biodegradation leading to different transformation products with environmental behaviours and toxicity different from those of the parent compounds [2]. Data on the environmental fate of pesticides are required in order to obtain information on their degradation pathway in natural conditions and on the toxicity of their transformation products [3]. Hydrolysis and photolysis are the main abiotic degradation processes in aqueous media [4]. Chemical hydrolysis at pH values that are normally found in the environment (pH values 5–9) is a minor process in surface waters, but it can be an important degradation way in groundwater, where photodegradation practically does not exist. In spite of the numerous photodegradation studies of different pesticides [5–10] little information is available on the photolysis under typical environmental conditions [11]. Generally, high herbicide concentrations (0.2–1 ppm) are necessary to identify the maximum number of degradation products. But the addition of high percentages of organic solvents to increase the pesticide solubility can change the pesticide behaviours with respect to those in the natural aqueous environment. Our purpose was to acquire information about the kinetics of degradation of herbicides at low concentrations, with the minimum percentage of organic solvents. Working with low concentrations and complex samples implies the use

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of sensitive and resolutive analytical techniques. The main analytical techniques used in degradation studies are GC and HPLC. There are few references about the application of capillary electrophoresis to degradation studies of pesticides [12,13] probably due to its low sensitivity. In previous works, we demonstrated the capacity of micellar electrokinetic capillary chromatography (MECC) to separate neutral and ionic herbicides in a rapid and single way. Furthermore, we developed a preconcentration system based on the use of Carbopack cartridges that was able to extract simultaneously acidic and neutral herbicides with good recoveries and low detection limits (<0.1 ppb) [14,15]. So, another objective of our study was to evaluate the capacity of the solid-phase extraction (SPE)–MECC system previously developed to analyse two phenoxy acid [(2,4-dichlorophenoxy) propanoic acid (2,4-DP) and 2,4,5-trichlorophenoxy) acetic acid (2,4,5-T)], two phenylurea (diuron and monolinuron) herbicides, and their most common degradation products (2,4-dichlorophenol, 2,4,5-trichlorophenol, 4-chloroaniline and 3,4-dichloroaniline). Herbicides and their degradation products are suspect or confirmed mutagens and oncogens [16]. In some cases the transformation products present a higher toxicity than that of the parent herbicide [17,18]. Among the different methods developed for toxicity evaluation, Microtox has been internationally adopted as a rapid screening test [19]. Microtox has demonstrated its sensitivity to a range of organic and inorganic pollutants [20] and it is a frequent tool for the toxicity evaluation of pesticides in aqueous systems [2,21–23]. The last objective of the present work was to evaluate the influence of herbicide degradation on the toxicity by means of the Microtox test.

2. Experimental

2.1. Chemicals

The standards of herbicides (2,4-DP, 2,4,5-T, monolinuron and diuron) and their main transformation products (2,4-dichlorophenol, 2,4,5-trichlorophenol, 4-chloroaniline, 3,4-dichloroaniline, fenuron and monuron) were purchased from Riedel-de Häen (Seelze-Hannover, Germany). Structures are showed in Fig. 1. All these compounds were used as they were received. Stock solutions of 50 ppm were prepared in methanol. Work solutions (50 ppb) were prepared both in Milli-Q and potable water. The percentage of methanol in the samples was 0.1%. All other chemicals were obtained from Merck (Darmstadt, Germany).

The MECC buffer was prepared from sodium dihydrogenphosphate and disodium hydrogenphosphate solutions containing sodium dodecyl sulphate (SDS) so that, after the addition of the organic modifier (4% butanol), the concentration was 0.02 M for phosphate and 0.05 M for SDS. The pH was adjusted to 7.

All the solutions were filtered through a 0.45-μm membrane filter prior to use.

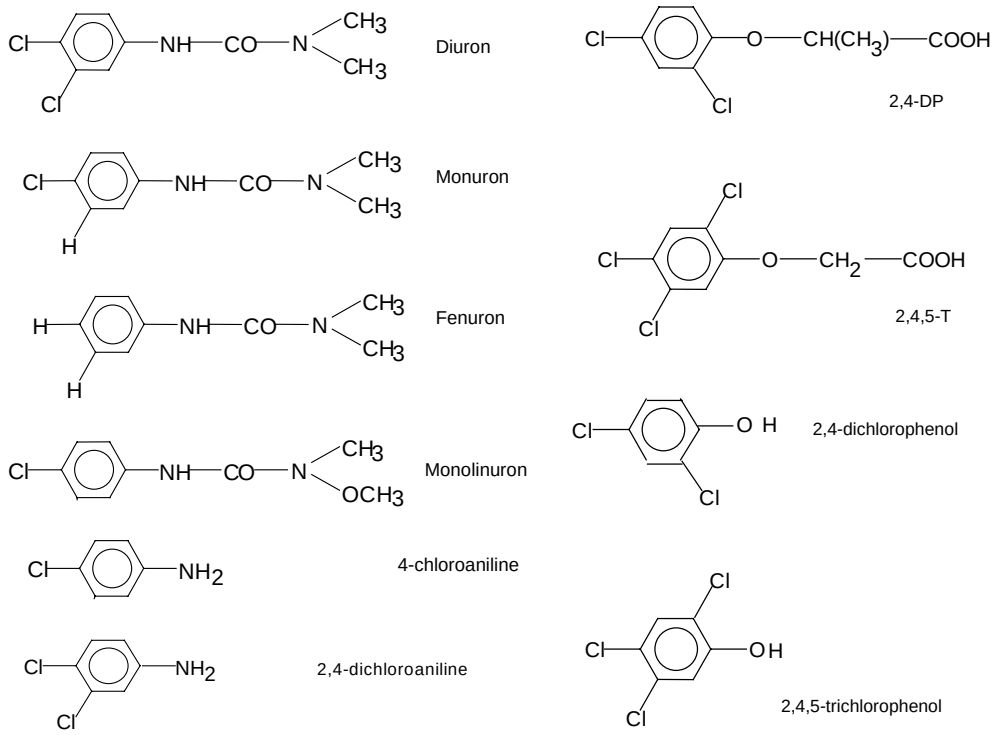

Fig. 1. Structures of herbicides (2,4-DP, 2,4,5-T, monolinuron and diuron) and their main transformation products (2,4-dichlorophenol, 2,4,5-trichlorophenol, 4-chloroaniline, 3,4-dichloroaniline, fenuron and monuron).

Cartridges with 250 mg of Carbopack B from Shandon were used for concentration experiments.

2.2. Capillary electrophoresis system

CE analyses were performed with an integrated system ISCO (Lincoln, NE, USA) model 3850, equipped with a fused-silica capillary column (600 mm × 0.05 mm i.d.) and an on-column UV detector at a placed position of 40 cm from the anode. The sample was introduced into the system by vacuum injection (0.5 psi; 1 psi = 6894.76 Pa) for an injection time of 20 s. The separation runs were done at ambient temperature and a constant voltage of 25 kV. UV detection at 210 nm was used.

2.3. SPE procedure

The SPE cartridges were conditioned with 5 ml of methylene chloride–water (80:20), then 2 ml of methanol and, finally 5 ml of hydrochloric acid (pH 2).

The passage of the samples (volume 200 ml) through the cartridges was carried out at a flow-rate of 20 ml/min by means of a vacuum pump. Once the retention step has been completed, the cartridges were cleaned with 7 ml of distilled water, and were dried by centrifugation at 2000 rpm (5 min) and under a nitrogen stream (1 min). The compounds retained were eluted with 2 ml of a mixture of methylene chloride–methanol (60:40) and potassium hydroxide 0.016 M. The obtained solution was evaporated to dryness under a nitrogen stream at 35 °C. The dry residue was dissolved in 0.1 ml of a 0.05 M sodium dodecyl sulphate solution.

2.4. Photodegradation experiments

Aqueous solutions of 2,4-DP, 2,4,5-T, monolinuron and diuron, prepared at 50 ppb both in Milli-Q and potable water, were placed in quartz reservoirs and were irradiated under simulated sunlight in a Suntest apparatus from Heraus (Hanau, Germany) equipped with a xenon arc lamp. The lamp power was fit to 550 W/m^2. Other experiments were carried out using natural sunlight irradiation, with Pyrex vessels placed capped on a terrace roof from our school in Barcelona during May and June. During this time, there was a variable climatology with sunny and cloudy days, and a mean temperature of 25 °C. At different periods of time, water samples were removed from reactors and stored at 4 °C.

2.5. Hydrolysis experiments

Aqueous solutions of 2,4-DP, 2,4,5-T, monolinuron and diuron, prepared at 50 ppb both in Milli-Q and potable water, were adjusted at pH 7 and 9. Samples were hold up in darkness to prevent photolysis during 6 months. Water samples were removed monthly from the reactor and stored at 4 °C.

2.6. Calculation of half-life

The calculation of half-life [24] was performed assuming the rate of the reaction to be first-order in herbicide concentration, by means of the kinetic 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 velocity constant. The fitting of the experimental data was satisfactory for all the samples.

When the concentration is reduced to 50% of its initial value, half-life ($t_{1/2}$) can be determined by:

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

2.7. Toxicity evaluation

The influence of degradation on the toxicity was determined with the Microtox test, using a Microtox apparatus from Microbics Corporation (Carlsbad, CA, USA). This test consist of determining the concentration in toxic compound that inhibits 50% (EC_{50}) of the natural luminescence of marine bacterium *Vibrio fischeri*. The emission is measured after exposure times of 5, 15 and 30 min at 15 °C.

Toxicity evaluation was carried out with aqueous solutions of the four herbicides before and after the degradation (photolysis and hydrolysis) experiments. Three concentrations (11.25, 22.5 and 45% of the 50 ppb aqueous solutions) were used for each sample. In some cases, mixtures of two compounds were also analysed.

3. Results

3.1. Characteristics of the MECC method

The MECC method developed in our laboratory for the analysis of different phenoxyacid and phenylurea compounds [15], was applied to the separation of the four herbicides (diuron, monolinuron, 2,4-DP and 2,4,5-T) and their main transformation products (2,4-dichloroaniline, 4-chloroaniline, 2,4-dichlorophenol and 2,4,5-trichlorophenol). A good separation of the eight compounds was achieved in a short analysis time (about 15 min) (see Fig. 2). Linear calibration graphs were found between peak areas and analyte concentration in the whole range studied (5–70 ppm). The detection limits of the method, calculated for a signal-to-noise ratio of two, were between 1 and 1.5 ppm for the different compounds. The determination of lower concentrations required a preconcentration step. Carbopack cartridges demonstrated their capacity to extract simultaneously the ionic and the neutral herbicides, and their main metabolites (anilines and chlorophenols) with recoveries

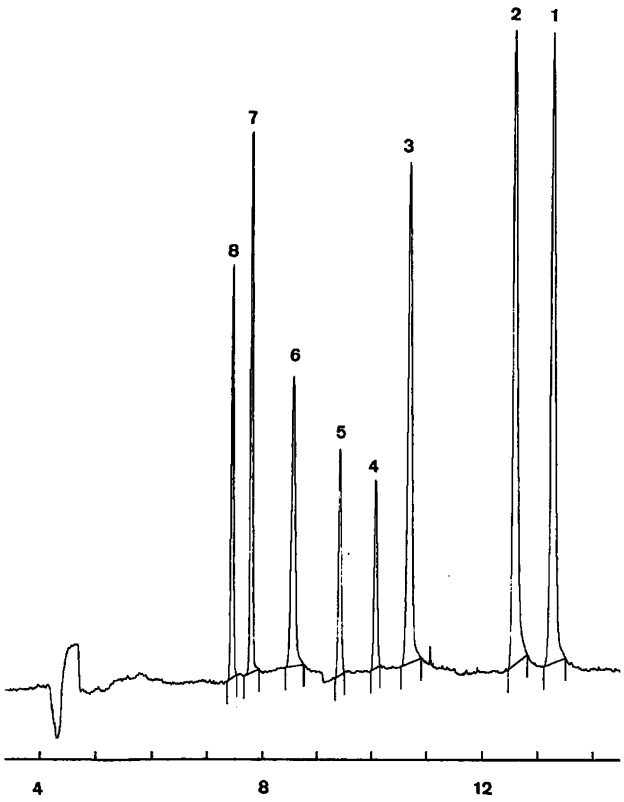

Fig. 2. Electropherogram of a 10 ppm standard solution of (1) diuron; (2) 3,4-dichloroaniline; (3) monolinuron; (4) 3,4-dichlorophenol; (5) 4-chlorophenol; (6) 4-chloroaniline; (7) 2,4,5-T; (8) 2,4-DP.

higher than 90% (see Table 1). In that case, the detection limits lowered to values between 2.0 and 5.0 ppb.

3.2. Photodegradation studies

Kinetic constants were calculated from the experimental data using Eqs. (1) and (2) for first-order kinetics. The obtained values for photodegradation studies of phenoxyacid and phenylurea herbicides are summarised in Table 2. Since experimental results for natural and distilled water herbicide

Table 1
Recoveries obtained for the studied compounds by means of Carbopack cartridges

Compound	Recovery (%)	
	Experiment 1	Experiment 2
2,4-DP	96	92
2,4,5-T	97	92
Diuron	98	95
Monolinuron	98	93
2,4-Dichlorophenol	96	93
2,4,5-Trichlorophenol	95	92
4-Chloroaniline	96	92
3,4-Dichloroaniline	97	94

Experiment 1: sample volume 200 ml, initial concentration 1.6 ppb. Experiment 2: sample volume 1000 ml, initial concentration 0.4 ppb. Other conditions as in Section 2.

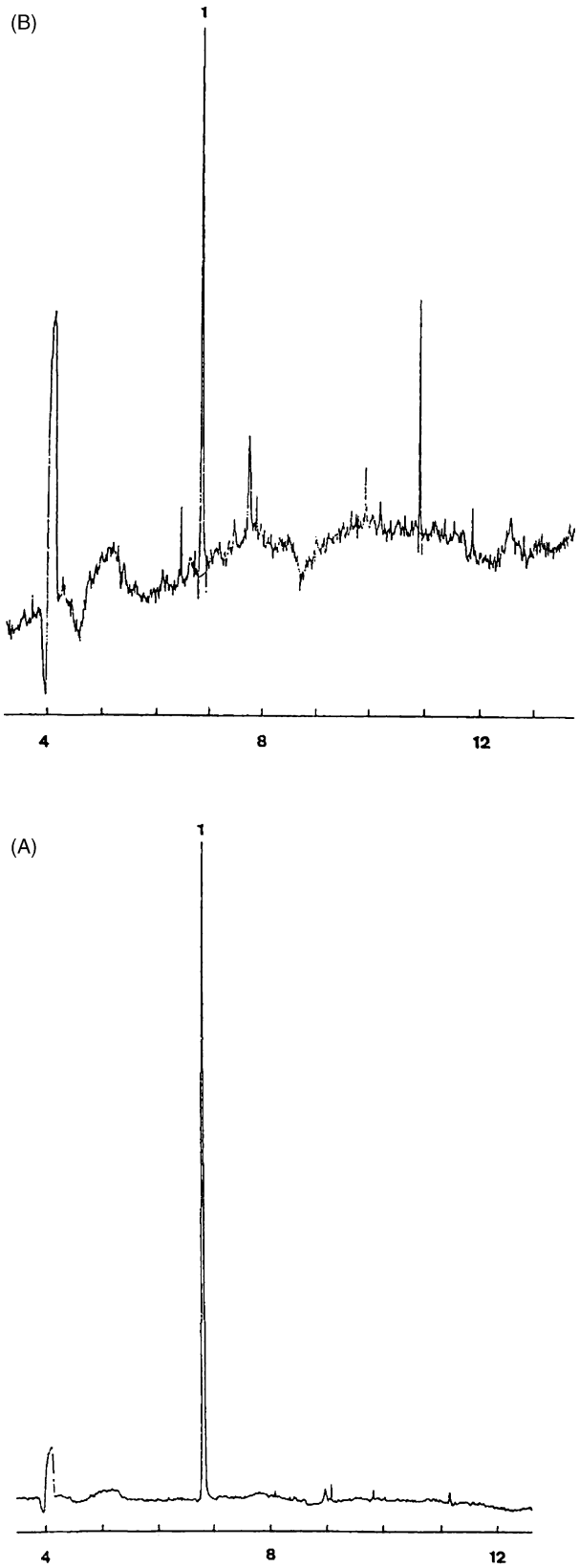

Fig. 3. Electropherogram of the photolysis of 2,4-DP (1) after irradiation times of (A) $t = 0$ and (B) $t = 12$ h, with the xenon arc lamp.

Table 2
Velocity constant (k) and half-life ($t_{1/2}$) for photodegradation studies under natural and simulated (SUNTEST) sunlight

Compound	SUNTEST		Natural	
	k (min^{-1})	$t_{1/2}$ (min)	k (per day)	$t_{1/2}$ (day)
2,4-DP	2.4×10^{-3}	284	n.d.	n.d.
2,4,5-T	2.1×10^{-3}	333	n.d.	n.d.
Diuron	3.0×10^{-3}	231	7.4×10^{-3}[a]	93[a]
Monolinuron	1.9×10^{-3}	359	5.2×10^{-3}[a]	133[a]

n.d.: no degradation was observed.
[a] Calculated by means of the modified first-order Eq. (3).

Table 3
Degradation percentage of diuron and monolinuron under natural sunlight

Photolysis time (weeks)	Diuron (%)	Monolinuron (%)
1	n.d.	n.d.
2	n.d.	n.d.
4	6	4
6	17	15
8	25	18

n.d.: no degradation was observed.

solutions showed no differences in any case, data for natural water samples are not presented in Table 2.

3.2.1. Natural sunligth

Most pesticides show UV-Vis absorption bands at relatively short UV wavelengths. Since sunligth reaching the Earth's surface contains only a small amount of short wavelength UV radiation, the direct photodegradation of pesticides by sunligth is expected to be, in general, only of limited importance [11].

In fact, no degradation was observed in the solutions of 2,4-DP and 2,4,5-T exposed to natural sunlight during May and June in Barcelona (Spain). Other studies about the sunlight photolysis of different chlorophenoxyacetic herbicides indicate that these compounds may be subject to direct photodegradation in water, with half-lives depending on the meteorological and geographical conditions. In this way, Zertal et al. [2] evaluate a half-life of 45 days for (2-methyl-4-chlorophenoxy) acetic acid (MCPA) exposed outdoors during April and May in Clermond-Ferrand (France), while Crosby and Wong [25] obtained a half-life of 15 days for 2,4,5-T exposed to the summer sunlight in California (USA).

Diuron and monolinuron exposed to natural sunlight showed persistence about the 75% and the 85% after 2 months, with no significant differences between the samples prepared in natural and distilled water. Results in Table 3 indicate that photodegradation starts during the fourth weak of exposition, and that from this moment it is a slow process. That behaviour, characteristic of surface waters, can be described by means of a modified first-order equation [26]:

$$\ln C - \ln C_0 = k(t - t_0) \quad (3)$$

where t_0 is the time of the initial phase (between the initial time and the time when degradation begins). Half-lives calculated by using the modified equation were 93 and 133 days for diuron and monolinuron, respectively.

3.2.2. Artificial photodegradation

When 2,4-DP and 2,4,5-T were irradiated in the Suntest apparatus, they were photodegraded, with half-lives of approximately five hours for both compounds (see Table 2). These values are into the large published range for

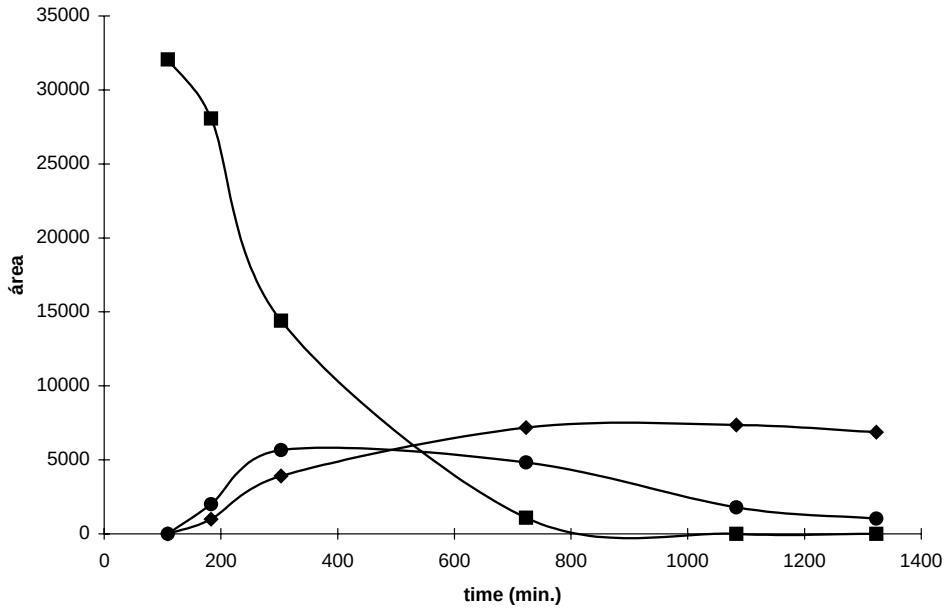

Fig. 4. Kinetics of diuron (■) disappearance and formation of photodegradation products monuron (●) and fenuron (◆) in a solution irradiated with the xenon arc lamp.

phenoxyacetic acids, which fluctuate between 10 min and 15 days depending on the experimental conditions [2,4]. In the case of phenylurea samples half-lives of 4 and 6 h, much shorter than those under sunlight conditions, have been found for diuron and monolinuron, respectively (Table 2).

3.2.3. Photodegradation products

The main compounds initially formed in the photodegradation of chlorophenoxyacetic herbicides are their corresponding chlorophenols [2,27–29]. So, in the present work, we expected the presence of 2,4-dichlorophenol and 2,4,5-trichlorophenol in the degraded samples. Different transformation compounds were observed when the photodegraded samples were analysed by MECC (Fig. 3). The comparison of their migration times with those of 2,4-dichlorophenol and 2,4,5-trichlorophenol standards showed that chlorophenols were not the photodegradation products. The MECC system does not allow the identification of the obtained compounds, but different studies proposed that the initially formed chlorophenols do not accumulate, and they are photolysed in a second stage into different hydroxy, hydroquinone and benzoquinone derivatives [27,28].

Diuron and monolinuron seems to follow different degradation pathways. When a solution of diuron after 5 and 20 h of irradiation was analysed by the SPE–MECC system, we observed the sequential dechlorination of diuron and the apparition of monuron and fenuron, identified by comparison of standards migration times, as the main degradation products. Previous photodegradation studies showed that the loss of halogen groups from the phenyl ring is one of the main degradation pathways of di-halogenated phenylureas such as diuron [5,6,9]. Kinetics represented in Fig. 4 show that until an exposition time of 4 h the main compound is diuron, the original herbicide. After 8 h, diuron, monuron and fenuron coexist at similar concentrations, while the main photoproduct after 13 h of irradiation is fenuron. On the other hand, when a solution of monolinuron after 12 h of irradiation was analysed by the SPE–MECC system, we observed the apparition of some degradation products with lower migration times than monolinuron (Fig. 5). The MECC system does not allow the identification of the obtained compounds, but Durand et al. [6] postulate a degradation pathway for linuron, a dichlorinated phenylurea very similar to monolinuron, that includes the formation of dechlorinated, demethylated and hydroxylated derivatives. So, a tentative degradation pathway for monolinuron is shown in Fig. 6.

3.3. Hydrolysis studies

Kinetic constants were calculated from the experimental data using Eqs. (1) and (2) for first-order kinetics. The obtained values for hydrolysis studies of phenoxyacid and phenylurea herbicides are summarised in Table 4.

No degradation was observed in 6 months for 2,4-DP and 2,4,5-T at any of the studied pH. Such results confirm the

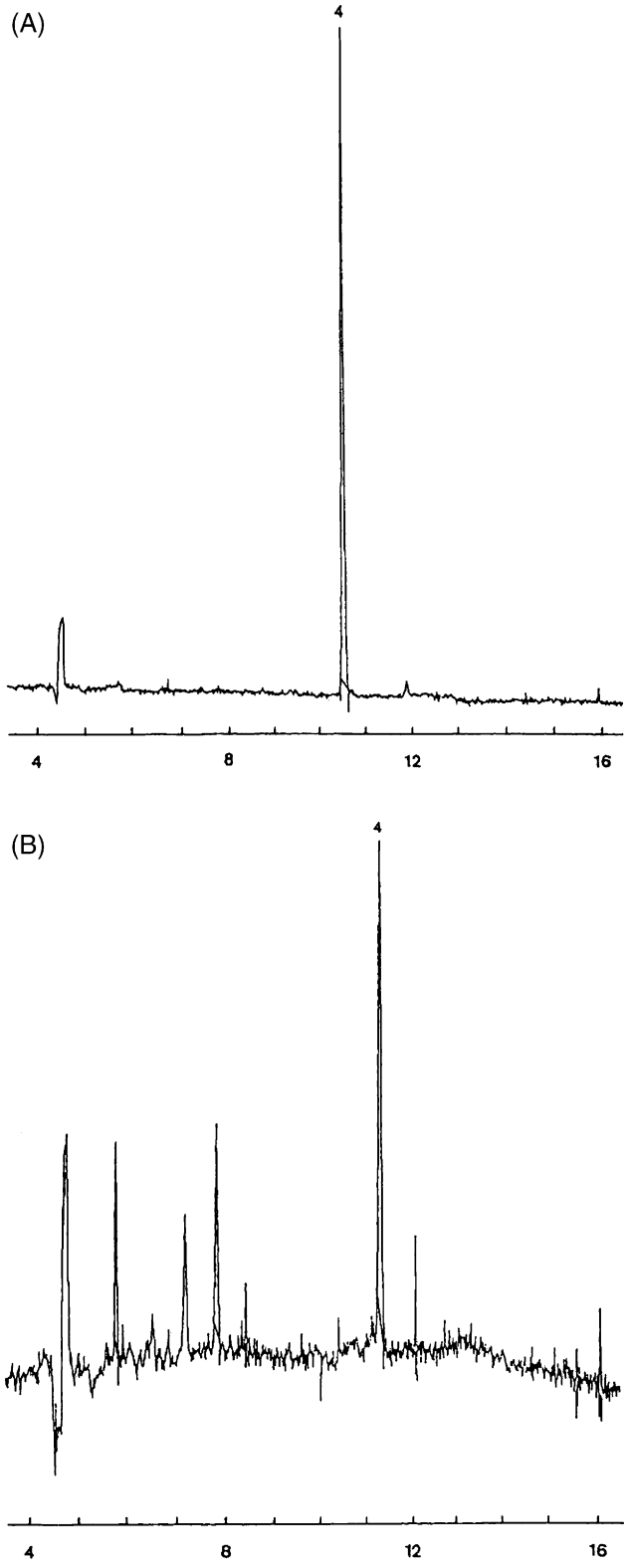

Fig. 5. Electropherogram of the photolysis of monolinuron (4) after irradiation times of (A) $t = 0$ and (B) $t = 12$ h, with the xenon arc lamp.

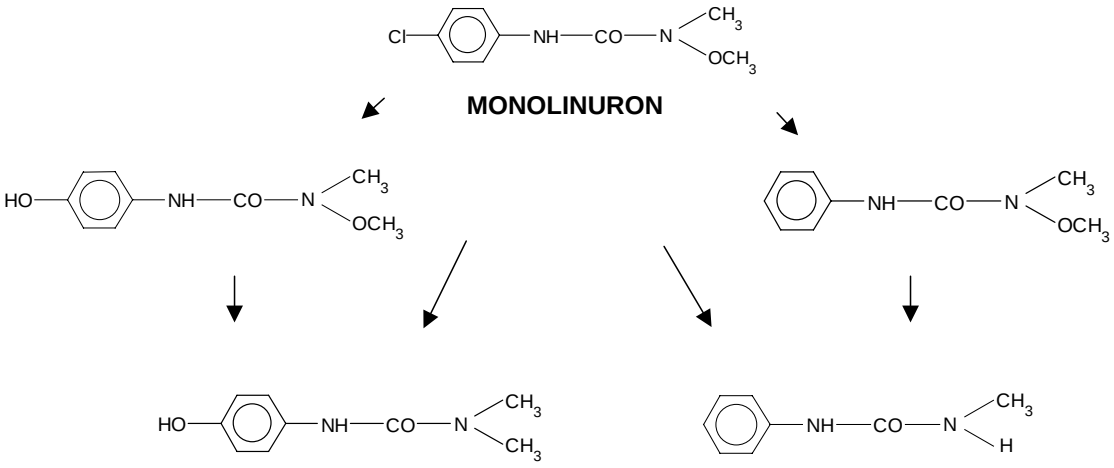

Fig. 6. Tentative degradation pathway of monolinuron.

Table 4
Velocity constant (k) and half-life ($t_{1/2}$) for hydrolisis studies at pH 7 and 9

Compound	pH 7		pH 9	
	k (per day)	$t_{1/2}$ (day)	k (per day)	$t_{1/2}$ (day)
2,4-DP	n.d.	n.d.	n.d.	n.d.
2,4,5-T	n.d.	n.d.	n.d.	n.d.
Diuron	2.4×10^{-3}	290	4.5×10^{-3}	155
Monolinuron	0.016	43	0.03	25

n.d.: no degradation was observed.

resistance to chemical hydrolysis of the functional groups of phenoxy acid compounds [4].

The phenylurea herbicides, diuron and monolinuron, were hydrolysed at both studied pH, the degradation rate increasing with the pH. In all cases, a single derivative with an aromatic ring was obtained. The hydrolysis products, by injection of pure compounds, were identified as the corresponding chloroanilines [30]. Fig. 7 shows the SPE–MECC electropherogram for a sample of 50 ppb of diuron and monolinuron after 6 months at pH 9, where the presence of chloroanilines can be clearly observed.

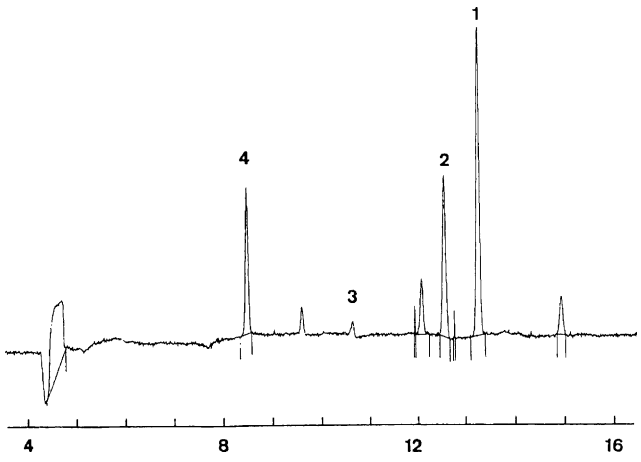

Fig. 7. Electropherogram of a sample of diuron (1) and monolinuron (3) hydrolysed 6 months at pH 9. Degradation products: 3,4-dichloroaniline (2) and 4-chloroaniline (4).

3.4. Evaluation of toxicity

Toxicity evaluation was carried out with aqueous solutions of the four herbicides before and after the degradation (photolysis and hydrolysis) experiments (see Table 5). Samples 1–6 were aqueous solutions of herbicides prepared at 50 ppb in Milli-Q water. Samples 7–10 (initial concentration 50 ppb in Milli-Q water) were irradiated with the xenon lamp at different times to obtain quantitative degradations (>95%). Sample 11 (initial concentration 50 ppb in Milli-Q water) was adjusted at pH 7 and was hold up in darkness during 6 months. The percentage of hydrolysed herbicide in sample 11 was 91% for monolinuron and 42% for diuron.

The toxicity of the different samples was evaluated by the Microtox test. The EC_{50} after 15 min exposure was determined for each sample (Table 5). No inhibition was detected in the bioluminiscence of the non-degraded samples (1–6), probably due to the low concentrations tested. Other authors [2,31] reported already the low toxicity of some phenoxyacid and phenylurea herbicides, with EC_{50} over 100 ppm. No differences were observed between the single compounds (samples 1–4) and their binary mixtures (samples 5 and 6). So, at the low concentrations tested in the present work, the additive effect on the toxicity of the mixtures already described [32] was not observed. The degraded samples (7–11) present higher toxicities than the parent compounds. The toxicity increase is more evident for the photodegradated phenoxyacids (samples 9 and 10) and the hydrolised phenylureas (sample 11). This fact can be due, for the photodegraded 2,4-DP and 2,4,5-T, to the formation of quinonic compounds that are highly toxic to *V. Fischeri* [2]. In the case of sample 11, the formation of chloroanilines, which had been described as highly toxic compounds with potential mutagenic and oncogenic activities [32], is probably the responsible of its toxicity.

Table 5
EC_{50} values (at 15 min of exposition) for the different herbicide samples

Sample	Herbicide	Degradation	Time	Percentage[a]	EC_{50} (ppb)
1	Monolinuron				n.o.
2	Diuron				n.o.
3	2,4-DP				n.o.
4	2,4,5-T				n.o.
5	Monolinuron + diuron				n.o.
6	2,4-DP + 2,4,5-T				n.o.
7	Monolinuron	Photolysis	26 h	95	79.6
8	Diuron	Photolysis	18 h	100	91.3
9	2,4-DP	Photolysis	28 h	99	14.1
10	2,4,5-T	Photolysis	28 h	98	18.9
11	Monolinuron + diuron	Hydrolysis	6 months	91 + 42	7.4

n.o.: EC value was not possible to obtain.
[a] Percentage of degraded sample.

From the results obtained, it can be concluded that the developed SPE–MECC method yields to a good separation of herbicides and their degradation products in low analysis time (15 min) and with LODs around 2–5 ppb.

Phenoxyacid herbicides only degrade by artificial photolysis. The degradation products obtained were not the corresponding chlorophenols. They probably are quinone derivatives, with higher toxicity than the phenoxyacid herbicides.

Phenylurea herbicides are degraded in all the studied conditions. Our degradation rate constant measurements suggest that hydrolysis is a major route of environmental degradation of monolinuron, while photolysis is a major route of environmental degradation of diuron. Monolinuron and diuron follow different photodegradation pathways. Diuron is sequentialy dechlorinated, while monolinuron probably has dechlorination, demethylation and hydroxylation reactions. Photodegradation products of phenylurea herbicides seem to have slightly high toxicity than the parent compounds. Chloroanilines are the main hydrolytic products of diuron and monolinuron, giving the highest toxicity of all the studied samples.

Acknowledgements

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