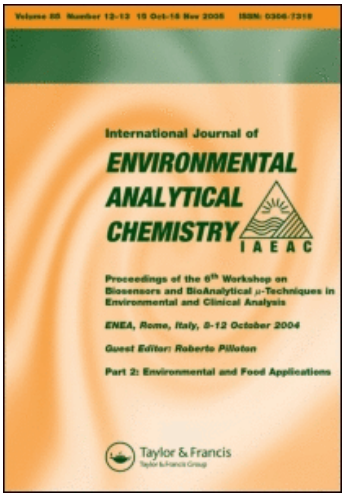

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Parrilla, P. , Vidal, J. L. Martinez , Galera, M. Martinez and Frenich, A. Garrido(1996) 'Degradation of Fenamiphos and Folpet in Water', International Journal of Environmental Analytical Chemistry, 63: 2, 137 — 145
To link to this Article: DOI: 10.1080/03067319608026259
URL: http://dx.doi.org/10.1080/03067319608026259

Intern. J. Environ. Anal. Chem., Vol. 63, pp. 137–145
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DEGRADATION OF FENAMIPHOS AND FOLPET IN WATER

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(Received, 20 November 1994; in final form, 1 July 1995)

The degradation of the pesticides fenamiphos and folpet was examined in distilled water and water from *Albufera de Adra*, a lake which is located along the west coast of Almería (Spain). pH value, ultraviolet (UV) light and activity of microorganisms affected the persistence of both fenamiphos and folpet in the *Albufera de Adra* water. The results showed a faster degradation in that water than in distilled water. Fenamiphos was more stable than folpet.

KEY WORDS: Fenamiphos, folpet, pesticides, degradation, liquid chromatography, diode-array, first-derivative signal.

INTRODUCTION

The widespread occurrence of pesticides has stimulated research about the nature, behaviour, and fate of these compounds and their degradation products in the environment. Most pesticides are semivolatile organic compounds[1] and may occur in all environmental compartments, not only in the upper layer of agricultural crop. Pesticides applied to agricultural crops, forest or recreational areas may be transported by wind and water into drainage canals, rivers, lakes and oceans and they may also be applied directly to water to control aquatic pests. In order to understand, predict and assess the environmental behaviour of pesticides, it is necessary to know their distribution and degradation rates in the different compartments. The biodegradation of pesticides may occur in natural (non-sterile) waters, which contain nutrients for the growth of microorganisms, but the main activity seems to be located in biofilms at the interface water/sediment. With the exception of hydrolysis and abiotic reduction, all abiotic degradation processes are initiated by solar radiation. They may be classified, in a broad sense, as photochemical processes[2,3]. In general, pesticides in aqueous systems can undergo chemical, photochemical and biological processes. These degradation pathways depend on the presence of light, temperature, alkali, ionic or enzymatic activities[4–14].

Fenamiphos, [O-ethyl, O-(3-methyl, 4-methylthiophenyl) N-isopropyl phosphoroamidate], is a systemic nematicide, active against ecto- and endo-parasitic, free-living, cyst-forming and root-knot nematodes; it is recommended for overall application with or without soil incorporation. Fenamiphos is oxidised in soils, both microbiologically and chemically, to fenamiphos sulphoxide and then to fenamiphos sulphone[15]. Both compounds have nematicidal activitity[16] and they are toxic to man[17]; these oxidation products are more polar and have a higher mobility in soil than the parent compounds. On the other hand, organophosphorus pesticides are considered to be a

relatively safe group of pesticide chemicals. However, certain individual members of the group are potent cholinesterase inhibitors[18], and their role as potential environmental hazards can not be overlooked.

Folpet [N-(trichloromethylthio)phthalimide] is a fungicide effective against a wide range of fungal pathogens, particularly *Botrytis, Monilia, Alternaria, Fusarium* and *Helminthosporium*. Fenamiphos and folpet are widely used in Almería (Spain) and can enter waters for percolation and runoff from agricultural lands. To our knowledge, no studies about the degradation rate of folpet in water have yet been reported. Barceló *et al.*[19] studied the photodegradation of fenamiphos in water containing 2–4% methanol using irradiation very close to natural sunlight and identifying fenamiphos sulphoxide as the main transformation product.

The *Albufera de Adra* is a lake located in Almería (Spain) with a total area of 42 ha. It is in an area where there are many greenhouses with a high production of vegetables and with a great usage of pesticides.

In a previous paper we studied the optimization of the separation, isolation and determination of nine pesticides by a new sequential procedure for the automated location of the mobile phase composition optimum, using column liquid chromatography (LC) and a diode array detector (DAD)[20]; the proposed method was extended to the determination of twenty one pesticides in water samples[21]. However, it was difficult to avoid the overlapping of peaks when analysing complex mixtures, and folpet and fenamiphos were found to co-elute. We therefore proposed a method to analyse binary mixtures of fenamiphos and folpet[22] with overlapping chromatographic peaks, using the first derivative of the chromatographic detector signal in the time domain. The method is easy to handle and time-saving.

The object of this paper is to study the degradation of fenamiphos and folpet in water from *Albufera de Adra* by LC techniques and to compare it with the persistence of these pesticides in distilled water, studying the influence of pH, light (ultraviolet; $\lambda = 360$ nm) and microorganisms on the degradation process.

EXPERIMENTAL

Instrumentation

The Waters (Milford, Mass., U.S.A.) LC system includes a 600E pump, a Rheodyne six-port injection valve with 20 µl loop and a Model 990 DAD. The detector was interfaced with an Olivetti PCS-386 personal computer using Waters 991 software. A Waters plotter was used for graphical representation of the chromatographic data. An IBM 486-DX microcomputer, provided with a Grams 386 software package from Galactic[23] was used for data treatment. A convert programme was written in Basic with the object of transferring the files obtained with the Waters 991 software to an ASCII XY format, which allows the manipulation of these files with the Grams 386 software.

LC separations were carried out on a Hypersil Shandon Green 150 × 4.0 mm I.D. (5 µm particle size) C_{18} column.

Chemicals and solvents

HPLC-grade solvents were used. Mobile phases were degassed with helium before use. Distilled water was obtained from a Millipore water purification Milli-Q system. The

pesticide standards (99% purity) were obtained from Riedel-de-Haën (Seelze, Germany). Solid standards were dissolved in acetonitrile (AcN) and stored at 4°C in the dark, where they were found to be stable for several months. All solvents and samples were filtered through a 0.5 μm PTFE membrane filters (Millipore) before injection in the column. Concentrated hydrochloric acid or sodium hydroxide addition was used to adjust the pH to study the hydrolysis rate in the water samples.

Methods development

The *Albufera de Adra* water samples were collected in 2.5 l dark bottles with PTFE tape. The water temperature was approx. 25°C. For each study, 10 ml of tested water were put into a 15 ml borosilicate glass vial lined with a PTFE cap. The vials were spiked with 0.1 ml of a 200 mg/l pesticide solution (in AcN) for an initial concentration of 2 mg/l in the testing water.

Photolysis and hydrolysis degradation were observed with distilled and *Albufera de Adra* water that were sterilized at 121°C and 1.03 atm for 15 min. In order to obtain stable and reproducible results in the photodegradation studies a suntest apparatus from atom (Uvatom-70; 50 Hz) was used. The wavelength studied was 360 nm.

0.01 M solutions of HCl and NaOH were used to adjust the pH to study the hydrolysis rate. The pH values studied were 6.0 and 8.5, which covers the range of pH values in *Albufera de Adra* water.

The effect of biological activity was examined with water collected and stored in a dark bottle. At different periods of time, an aliquot of the solution was analysed by LC/DAD.

LC/DAD operating conditions

The solvent programming was as follows. Initial: 56% water, 27% AcN, 17% MeOH; 7 min in isocratic mode: 56% water, 27% AcN, 17% MeOH; linear gradient during 20 min until: 5% water, 90% AcN, 5% MeOH. An additional 10 min of gradient programme was enough to return the system to the intial conditions. Flow rate: 1 ml/min; column at ambient temperature; wavelength: 210 and 224 nm.

RESULTS AND DISCUSSION

We applied the method referred to above[22] to determine the concentrations of fenamiphos and folpet and their degradation in water. Relevant chromatograms are shown in Figure 1. The overlapping peaks are seen to be resolved and it is possible to determine fenamiphos by measuring the analytical signal obtained in the first maximum ($^1D_{max}$) and to determine folpet by measuring the analytical signal obtained in the last minimum ($^1D_{min}$) because, at these points, the mutual contributions of the two peaks are negligible (Figure 1B). Good linearity was obtained for both substances in the ranges studied (0.5–6 μg/ml). The regression coefficients were higher than 0.999 and 0.997 for fenamiphos and folpet, respectively.

The hydrolytic and photolytic degradation of fenamiphos and folpet under acidic and alkaline conditions was tested in sterile distilled water. Figure 2A shows that fenamiphos remains stable under acidic or alkaline conditions in the dark. However, photolytic degradation takes place at pH 6.0 and 8.5, the half-life being lower at the latter pH.

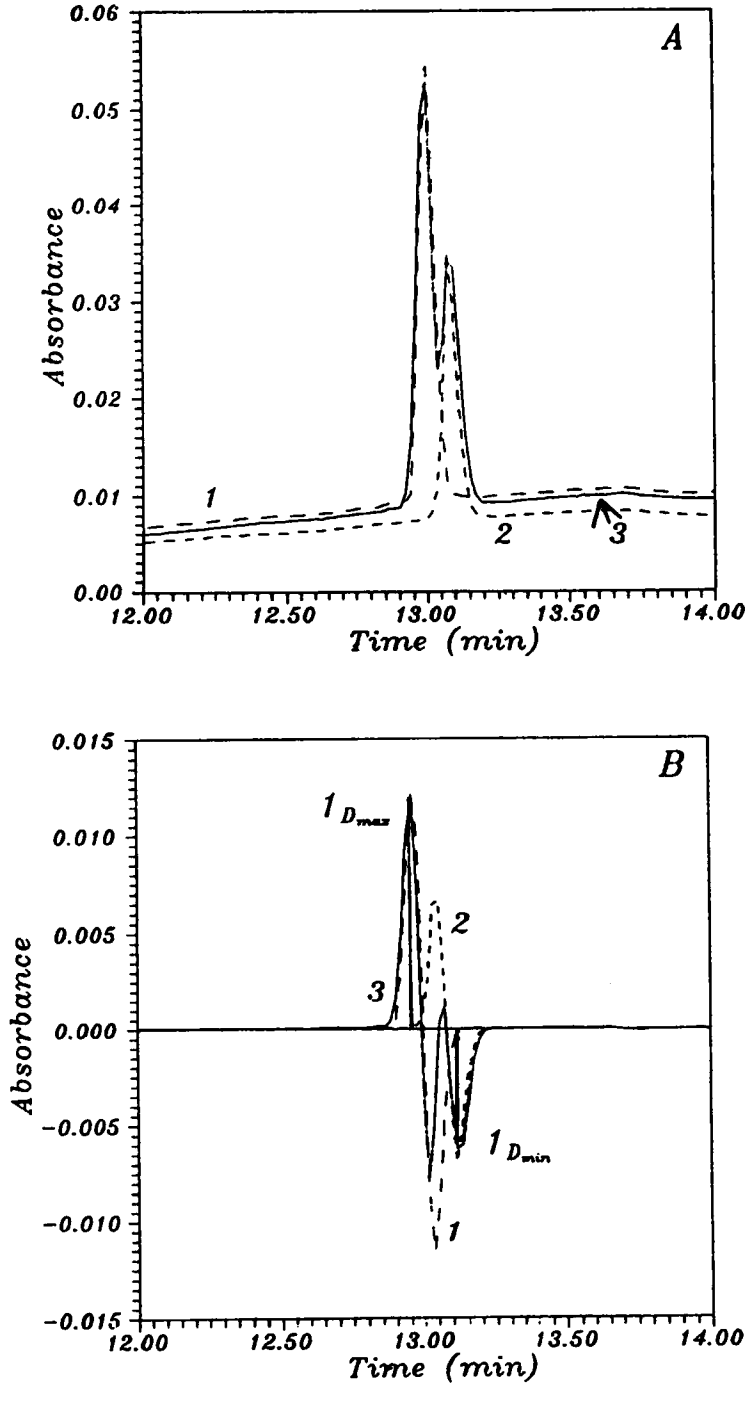

Figure 1 A: LC of fenamiphos, folpet and a mixture of both obtained by injection of 20 µl of a pesticide standard solution (4 µg ml^{-1} of fenamiphos and 2 µg ml^{-1} of folpet). B: First derivative of the chromatogram corresponding to fenamiphos, folpet and a mixture of both.

Fenamiphos was then tested in sterile and non-sterile *Albufera de Adra* water, to study the role of biological compared with hydrolytical or photolytical degradation. The chemical composition of a water sample from *Albufera de Adra* is given in Table 1. Figures 2B and 2C show that fenamiphos is stable in acidic medium and in the dark in both sterile and non-sterile *Albufera de Adra* water, but at pH 8.5 degradation occurs. The half-life is shorter in the light and in non-sterile water; this would indicate that fenamiphos is susceptible to photolytic and bilogical degradation.

By comparing the results obtained from sterile distilled water and from sterile *Albufera de Adra* water (Figures 2A and 2B) one can conclude that salinity decreases the half-life. However, when compared with biologically active water, this effect will probably be rather small, as has also been stated by other authors[6].

Folpet is quickly degraded in sterile distilled water in acidic or alkaline conditions (Figure 3A). Increasing the pH from 6.0 to 8.5 reduced the half-life under both dark and light conditions.

Under acidic conditions in the dark, the degradation of folpet in sterile and non-sterile-system was significantly different (Figures 3B and 3C). Biological degradation was favoured over hydrolytic degradation, whereas under acidic conditions in the samples exposed to light, photolytical degradation occurs in both sterile and non-sterile system to a similar extent. In both dark and light conditions, alkaline hydrolysis was the most competitive pathway for folpet degradation in *Albufera de Adra* water.

Table 1 Composition of a water sample from *Albufera de Adra* collected in May 1994.

Parameter	*Value**
Oxygen Dissolved	7.50
D.B.O.	25.00
D.Q.O.	60.00
PO_4^{3-}	0.17
NO_3^-	7.00
NO_2^-	0.07
NH_3	0.04
F^-	0.84
Solid in suspension	4.30
Na^+	940.00
K^+	60.00
Ca^{2+}	120.00
CO_3^{2-}	48.00
HCO_3^-	580.00
SiO_2	9.00
Mg^{2+}	375.00
Cl^-	1750.00
SO_4^{2-}	700.00
Conductivity	6.20 (ml mhos/cm)
pH	8.50
Chlorophylls	18.85 (mg/m^3)
Total Coliforms	1000 (colonies/100 ml)
Fecal Coliforms	70.00 (colonies/100 ml)

*In μg/ml unless otherwise indicated.

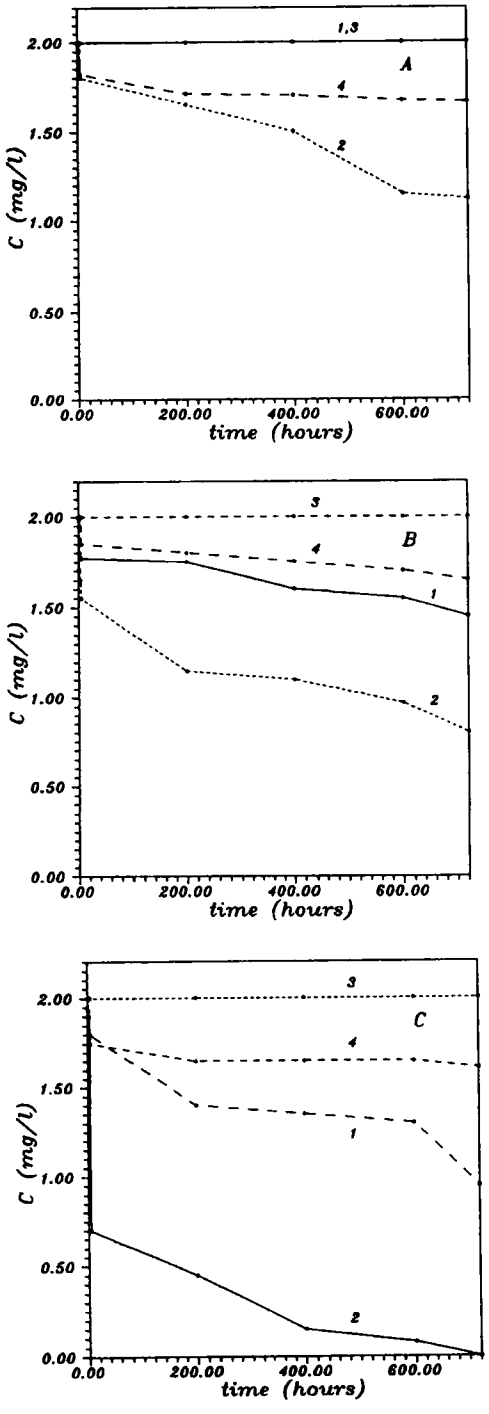

Figure 2 Degradation of fenamiphos at different pH levels after UV irradiation or dark conditions as a function of time. (A) Sterile distilled water; 1, pH 8.5 dark; 2, pH 8.5 light; 3, pH 6 dark and 4, pH 6 light. (B) Idem for sterile water of *Albufera de Adra*. (C) Idem for non-sterile water de *Albufera of Adra*.

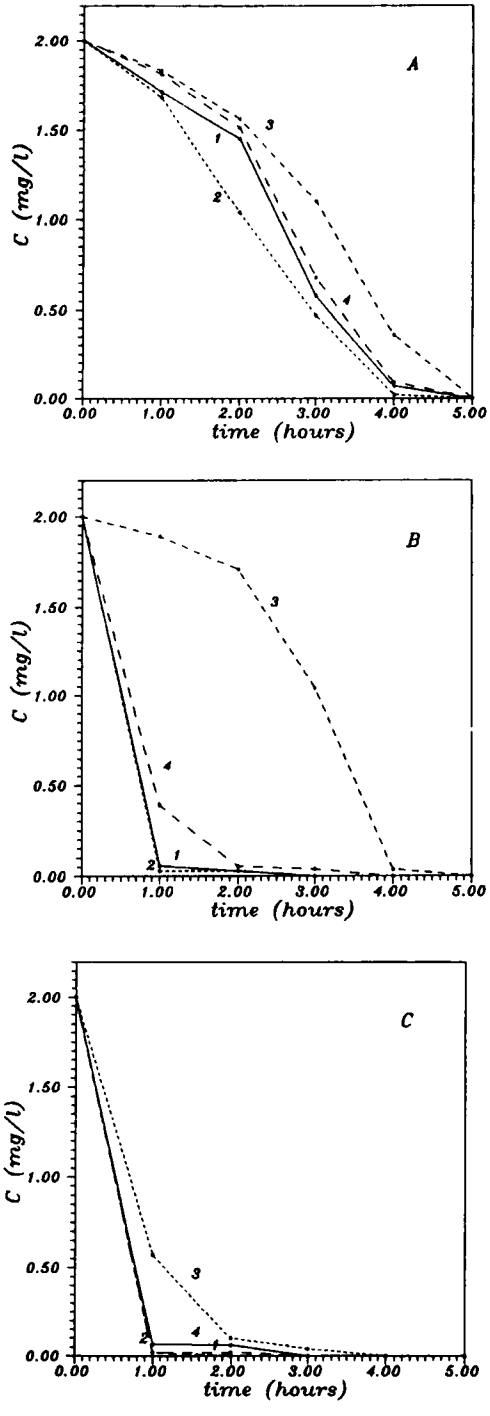

Figure 3 Degradation of folpet at different pH levels after UV irradiation or dark conditions as a function of time. (A) Sterile distilled water; 1, pH 8.5 dark; 2, pH 8.5 light; 3, pH 6 dark and 4, pH 6 light. (B) Idem for sterile water of *Albufera de Adra*. (C) Idem for non-sterile water of *Albufera de Adra*.

The data obtained at different period of times from distilled and *Albufera de Adra* water spiked with both pesticides, were used to study their degradation according to the first-order rate equation[24]:

$$C_t = C_o \cdot e^{-kt}$$

where C_t is the concentration at time t, C_o the initial concentration, and k the rate constant. The rate constant was taken as the slope of the line obtained by a linear least-squares analysis of the data. As the concentrations were reduced to 50% of the initial amounts, half-lifes ($t_{1/2}$) could be determined from the equation for each experiment. The equations obtained in those cases where regression coefficients were higher than 0.9 are shown in Tables 2 and 3. The behaviour of both pesticides in non-sterile distilled water is similar to that observed in sterile distilled water.

The degradation of fenamiphos occurs according to first-order kinetic in light conditions, its half-life being $t_{1/2} \geq 148.5$ h in all cases. Folpet is degraded quickly in both distilled and *Albufera de Adra* water, with $t_{1/2} < 1$ h.

CONCLUSIONS

The degradation of fenamiphos does not take place at pH 6.0 and dark conditions. The salinity of the water sample and the presence of microorganisms is not important for its degradation at pH 6.0 and light conditions, but both, the salinity and microorganisms, increase the rate of degradation at pH 8.5 and light conditions.

Folpet experiences a fast degradation under all experimental conditions tested, and is in general increased by the salinity of the water. Microorganisms increase the degradation in water at pH 6.0, both in dark and light conditions.

Table 2 Fenamiphos degradation at various pH values; effect of UV light, biological and photolytic activity in the degradation rate.

	pH 6			*pH 8.5*		
	Equation	*r*	$t_{1/2}$ *(hours)*	*Equation*	*r*	$t_{1/2}$ *(hours)*
			Albufera de Adra Water (sterile)			
Dark	Stable during 1 month	–	> 720.0	–	–	–
Light	$\log C_t = 0.28–8.99.10^{-5}t$	0.9603	3347.2	$\log C_t = 0.22–4.41.10^{-4}t$	0.9660	682.6
			Albufera de Adra Water (non-sterile)			
Dark	Stable during 1 month	–	> 720.0	$\log C_t = 0.28–1.57.10^{-4}t$	0.9753	1911.4
Light	$\log C_t = 0.27–3.51.10^{-4}t$	0.9658	858.8	$\log C_t = 0.06–2.03.10^{-3}t$	0.9768	148.5
			Distilled Water (steril)			
Dark	Stable during 1 month	–	> 720.0	Stable during 1 month	–	> 720.0
Light	$\log C_t = 0.27–8.38.10^{-5}t$	0.9042	3592.3	$\log C_t = 0.28–3.32.10^{-4}t$	0.9893	906.9
			Distilled Water (non-sterile)			
Dark	Stable during 1 month	–	> 720.0	Stable during 1 month	–	> 720.0
Light	$\log C_t = 0.30–8.65.10^{-5}t$	0.9714	3479.1	$\log C_t = 0.30–3.57.10^{-4}t$	0.9922	844.1

Table 3 Folpet degradation at various pH values; effect of UV light, biological and photolytic activity in the degradation rate.

	pH 6			*pH 8.5*		
	Equation	*r*	$t_{1/2}$ *(hours)*	*Equation*	*r*	$t_{1/2}$ *(hours)*
			Albufera of Adra Water (sterile)			
Dark	$\log C_t = -0.0224-0.3867t$	0.9503	0.8	$\log C_t = 0.0827-0.8980t$	0.9219	0.7
Light	$\log C_t = 0.2044-0.6022t$	0.9699	0.5	–	–	–
			Albufera of Adra Water (non-sterile)			
Dark	$\log C_t = 0.3006-0.5987t$	0.9956	0.5	–	–	–
Light	–	–	–	$\log C_t = 0.0159-1.2455t$	0.9296	0.2
			Distilled Water (sterile)			
Dark	–	–	–	–	–	–
Light	–	–	–	$\log C_t = 0.3678-0.2090t$	0.9614	0.7
			Distilled Water (non-sterile)			
Dark	$\log C_t = 0.3388-0.2952t$	0.9787	1.0	$\log C_t = 0.2035-0.5936t$	0.9618	0.5
Light	–	–	–	–	–	–

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