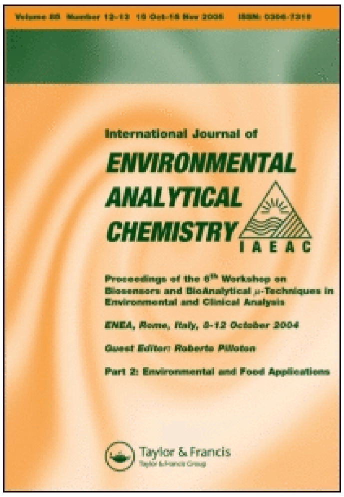

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Photodegradation of Selected Organophosphorus Insecticides Under Sunlight in Different Natural Waters and Soils

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PHOTODEGRADATION OF SELECTED ORGANOPHOSPHORUS INSECTICIDES UNDER SUNLIGHT IN DIFFERENT NATURAL WATERS AND SOILS

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In this work photodegradation of four organophosphorus insecticides (ethyl-parathion, methyl-parathion, fenitrothion, fenthion) in different natural waters and soils was studied under sunlight. The origin of the waters was from the region of Ioannina (underground, lake, and river water) and from Preveza (sea water) in Northern-West Greece. The soils used had different percentages of organic matter (0.9–3.5%) and their characterization were SCL, CL, and SL respectively.

The photodegradation kinetics of these insecticides were followed by GC-FTD. The identification of the photodegradation by-products was made by using GC-MS. The half-lives of the organophosphorus insecticides vary from 0.4 to 35.4 days in natural waters and from 3.4 to 21.3 days in soils. The humic substances and the other components of these environmental matrices seem to influence the degradation kinetics.

The use of GC-MS allowed the identification of some important photodegradation by-products such as: fenthion sulfone, fenthion sulfoxide, fenoxon, 4-methylthio-3,5-dimethyl phenol, *O*,*O*,*O*-triethyl phosphorothioate, paraoxon, 4-nitrophenol, aminoparathion.

Keywords: Photodegradation; Organophosphorus insecticides; Fenitrothion; Fenthion; Parathion

INTRODUCTION

Organophosphorus insecticides are widely used for different types of cultivation, e.g. rice [1,2], as an alternative to organochlorine pesticides for pest control owing to their relatively rapid decomposition and low accumulation in biological food chains [3]. These compounds are extremely toxic, acting on acetylocholinesterase activity [4]. Residue levels of them have been reported in environmental surfaces [5–8].

The fate of organophosphorus pesticides in the aquatic environment has led to numerous investigations in the recent years. In this regard it has been reported that degradation is influenced by hydrolysis, particularly at pH > 7 [9], by microbial degradation [10–13] and by photolysis [14].

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In natural waters, photochemical reactions are affected by changes in sunlight intensity and wavelength associated with season and time of day, amount of dissolved and particulate substances and presence of photosensitizers. A number of studies showed differences in the photolysis rate of analytes between natural and distilled water resulting from particulate and dissolved substances in natural waters which influence photolysis of analytes through attenuation of sunlight, secondary photoreactions and chemical or physical interactions [15].

The photolysis of pesticides on soils is poorly understood [16], what is somewhat surprising, because soil surfaces receive a large fraction of surface-applied pesticides and photolysis rates can proceed at a significant rate in relation to other transformation pathways [17,18].

In soils photochemical reactions are significant only at the surface [19]. On dry, sunlight-exposed surfaces, photolysis may dominate other transformation pathways that are favored under conditions found in the bulk soil [17]. Direct photolysis rates are substantially slower for soil-sorbed pesticides in comparison to rates in distilled water, presumably due to light attenuation by the soil [20,21]. Indirect photochemical processes may also affect the fate of surface-applied agrochemicals. A variety of oxidants are formed on the sunlight-exposed soil surface that can potentially transform xenobiotics [22].

The objectives of the present study were the determination of: (i) the degradation kinetics of the four selected organophosphorus insecticides in different natural waters and soils under environmental conditions, (ii) the effect of the water and soil constitution (organic matter) on the reaction rate, and (iii) the transformation products formed by photolysis.

EXPERIMENTAL

Chemicals

The tested compounds in this study – ethyl parathion, methyl parathion, fenitrothion and fenthion – were residue analysis grade and purchased from Riedel-de Haen (Seelze, Germany) and used without further purification. The physicochemical properties of these insecticides are shown in Table I. Pesticide grade hexane, acetone was purchased from Pestiscan (Labscan Ltd, Dublin, Ireland). Other chemicals were of reagent grade from various suppliers. The sodium sulfate used for drying organic extracts, and the disposable pipets, were heated to 500°C for 24 h before use. All glassware were rinsed with pesticide grade solvents before use. Organic free water for photochemical experiments was prepared with a Milli-Q system from Millipore-Waters Co. (Mississauga, ON, USA). Empore extraction disks were manufactured by 3M and distributed by Varian

TABLE I Physico-chemical properties of the selected insecticides

Insecticide	*Molecular weight*	*Solubility in water* (mg/L)	*Vapor pressure* (MPa) [23]	Log K_{ow} [24,25]	*Soil sorption* (Log K_{oc}) [26]
Ethyl parathion	291.3	24	5	3.8	3.7
Methyl parathion	263.2	50	1.3	2.9	3.7
Fenitrothion	277.2	30	18	3.4	3.3
Fenthion	278.3	55	4	4.1	3.2

(Harbor City, CA). The SPE Empore Disks used were 47 mm in diameter and 0.5 mm thick. Each disk contained about 500 mg of C_{18} bonded silica (92 ± 2%) and 10 ± 2% PTFE. The particle characteristics were: 8 μm particle size; 60 Å pore size; and irregular shape.

Water and Soil Sampling

Natural waters used in experiments were from Epirus area as ground water of Ioannina, Pamvotis lake, Louros river and Ionian sea. The natural water samples were obtained from the top meter of water bodies and refrigerated at 4°C prior to use. Their physicochemical characteristics are given in Table II.

The soils used in the experiments spring from the regions of Preveza, Orestiada and Livanates (Greece) and were collected from fields with no previous history of persistent pesticide use. The soils selected for this study correspond to intensively cultivated areas in Greece. Field-moist soils were passed through a 2 mm sieve to remove stones and large plant fragments and homogenized. Textural classes of soil samples were characterized as sandy clay loam (SCL), clay loam (CL) and sandy loam (SL). Their physiochemical characteristics are shown in Table III.

Photolytic Experiments in Water

Aqueous solutions of the selected insecticides were prepared to be irradiated under natural sunlight at 5 mg/L. Outdoor experiments were carried out in pyrex glass reservoirs placed capped in Ioannina area (University Campus, roof terrace of the Department of Chemistry) during the period May–July 1998. Water samples with no previous treatment of filtration or sterilization, were spiked with each pesticide by adding the standard pesticide in methanol using reaction reservoirs of 1000 mL before starting the

TABLE II Characteristics of selected environmental waters

Origin of water samples	*pH*	*Conductivity* (μs/cm)	*Total suspended matter* (mg/L)	[a]*DOM* (mg/L)	*Salinity* (%)
Distilled	5.89	1.1	1	[b]b.d.l	[c]n.d
Underground	7.22	313	15	0.03	[c]n.d
Pamvotis lake	8.45	310	342	12.75	0.55
Louros river	7.62	329	115	10.21	1.8
Ionian sea	7.45	52.800	240	1.32	37.5

[a]Dissolved organic matter; [b]Below detection limit; [c]Not determined.

TABLE III Characteristics of selected soils

Sampling site	*Soil texture*	*pH*	*Soil separate* (%)			*O.M*[a] (%)	*CaCO₃* (%)	*Conductivity* (m mhos)
			Sand	*Silt*	*Clay*			
Preveza	SCL[b]	7.0	43.7	24.0	33.3	0.90	0.63	0.51
Orestiada	CL[b]	7.5	22.7	46.0	35.3	1.94	4.92	0.30
Livanates	SL[b]	7.1	61.7	25.6	12.7	3.52	2.87	8.53

[a]Organic matter content; [b]SCL = Sandy clay loam, CL = Clay loam, SL = Sandy loam.

photolytic experiments. The mixtures were homogenized by magnetic stirring and were exposed outdoors after an equilibration period of 12 h. The pesticide concentrations in water varied and were below of their solubility in water but enough for carrying out the kinetic studies performed by gas chromatography (GC) with flame thermionic detector (FTD). A dark control experiment was also conducted by exposing dark pyrex glass reservoirs filled with the same pesticide solutions and covered with aluminum foil in the same environmental conditions.

Incident solar radiation was measured with a radiometer (Eppley Lab. Inc., Newport, Rhode Island, USA) that measured radiation (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 respectively as 187, 606, and 309 W/m^2 during May; 270, 729, and 335 W/m^2 during June; and 247, 743, and 409 W/m^2 during July. The average total daily shortwave radiation for this period was 674 W/m^2, with 10 h the mean sunshine duration from sunrise to sunset. The mean daily air temperature was 22°C, and maximum and minimum air temperatures were 37.2 and 7.8°C respectively, during this period. The mean daily cloudiness was 3.4 (measured in octals).

Photolytic Experiments in Soil Sorbed Phase

Soil TLC plates ($20 \times 20\,cm^2$, 1 mm thickness) were prepared with fine soil particles passed through a 2 mm sieve. The soils were homogenized and equilibrated with a half of its weight of aqueous solutions of each insecticide previously spiked with methanol standard solutions in order to achieve initial concentrations at the range of 5–20 μg/g, which are close to usual field dosage. The content of methanol in aqueous solutions did not exceed 10%. Then the plates were dried and exposed to natural sunlight for 15 days during July 1998. A dark control experiment was also conducted by covering analogous soil TLC plates with aluminum foil.

Extraction and Analysis

Water samples of 5 mL, 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 with FTD. At the end of experimental period, the final remaining water volume (about 900 mL) was extracted by means of solid phase extraction as follows: C18 Empore extraction disks were conditioned with 10 mL of acetone for 2 h and 5 mL of methanol modifier was added to the residue to allow better extraction [27]. The disks were placed in the conventional filtration apparatus and washed with 5 mL of solvent mixture, dichloromethane : ethyl acetate (1:1, v/v) with the vacuum on and with 3 mL of methanol for 3 min, with the vacuum off. The disks were not allowed to become dry [28] and the samples were allowed to percolate through the disks with a flow rate of 50 mL/min, under vacuum. The compounds trapped in the disks were collected by using 2 × 5 mL of solvent mixture dichloromethane : ethyl acetate (1:1, v/v) as eluting system. The fractions were evaporated to 0.5 mL in a gentle stream of nitrogen. This extract residue was displayed into 1 mL of isooctane and evaporated to a final volume of 1 mL prior GC-MS analysis.

A $2 \times 20\,cm^2$ zone of the soil TLC plates was scraped off and extracted twice with 10 mL acetone using a vortex. After the first extraction the samples were placed for 10 min in a sonication bath. The mixtures were centrifuged at 4000 rpm for 10 min to separate the supernatant from the soil residue. The volume of the combined supernatants was fixed at 5 mL and was analyzed by GC with FTD.

Chromatographic Conditions

The analysis of the organophosphorus insecticides was performed using a Shimadzu 14A gas chromatograph equipped with FTD and a Shimadzu AOC-20i autoinjector (1.5 μL injections). A DB-1 capillary column, 30 m × 0.32 mm i.d. and contained 5% methylsilicone (J&W Scientific, Folsom, CA) was used. The temperature program was: 150°C for 2 min, from 150 to 120°C with a rate of 5°C/min, at 210°C for 10 min, 210 to 270°C with a rate of 10°C/min, and at 270°C for 3 min. Helium was used as the carrier and nitrogen as the make-up gases. The detector gases were hydrogen and air, and the ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire. The temperatures were set at 220°C for the injector and 250°C for the detector.

For the identification of by-products a GC-MSD, QP 5000 Shimadzu equipped with DB-1 capillary column, 30 m × 0.32 mm i.d. contained 5% methylsilicone (J&W Scientific, Folsom, CA) was used at the following chromatographic conditions: injector temperature 220°C, column program of temperature, 55°C for 2 min, from 55 to 210°C with a rate of 5°C/min, at 210°C for 20 min, from 210 to 270°C with a rate of 20°C/min and at 270°C for 4 min. Helium was used as the carrier gas at 14 psi. The interface was kept at 270°C. The MSD was operated in electron impact mode with an ionization potential of 70 eV and the spectra obtained in full scan mode.

RESULTS AND DISCUSSION

Photodegradation in Water

The photodegradation rates of all studied insecticides in different natural waters followed a first order degradation curve, $C_t = C_0 \exp(-kt)$ where C_t is the concentration of an insecticide at time t, C_0 is the insecticide initial concentration and k is the rate constant. The half-life time ($T_{1/2}$) corresponds to a period of time at which the pesticide concentration is equal to half of the initial concentration given by the equation $T_{1/2} = \ln 2/k$. The photodegradation rate constants (k) were calculated by subtracting the exponents of the different degradation curves representing the apparent degradation and the degradation owed to hydrolysis, volatilization and adsorption (blank experiment). In this way the considered k constants and $T_{1/2}$ refer to the real photochemical reaction excluding the contribution of other factors (Table IV).

TABLE IV Half-lives $T_{1/2}$ (days) and photolysis constants k_{phot} (days^{-1}) of studied insecticides in natural waters

Insecticides	*Lake water*		*River water*		*Marine water*		*Ground water*		*Distilled water*	
	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})
Ethyl parathion	17.8	3.89	23.7	2.92	18.9	3.66	21.6	3.21	19.6	3.54
Methyl parathion	25.6	2.71	24.6	2.82	27.3	2.54	27.5	2.52	35.4	1.96
Fenitrothion	0.5	135.1	0.4	154.3	0.4	179.1	0.5	149.4	0.4	170.4
Fenthion	1.6	42.3	1.5	46.3	0.8	91.8	0.7	96.6	1.4	47.8

Figures 1–5 show the degradation curves of the selected insecticides in four various natural waters and distilled water.

Half-lives of the four tested insecticides range from less than one day (e.g., fenitrothion in all type of waters) to 35.4 days (methyl parathion in distilled water). The degradation of fenitrothion and fenthion reaches 100% before the end of 64 days, in natural waters. In most cases shorter half-lives were observed in river, lake, or sea water compared to distilled water, in which degradation proceeds via direct photolysis.

In natural waters the species that can absorb light, except for insecticides is dissolved organic matter (DOM) and inorganic compounds which play an important role on the photochemistry of insecticides [29]. The complexity of photodegradation rates of all the investigated insecticides can attribute to both optical filter effect (quenching) of organic matter and sensitization effect of humic and other substances of natural waters. In the first case, the organic matter can act as one of the important sunlight-absorbing components of the aquatic environment [30]. Particulate matter such as sediment particles

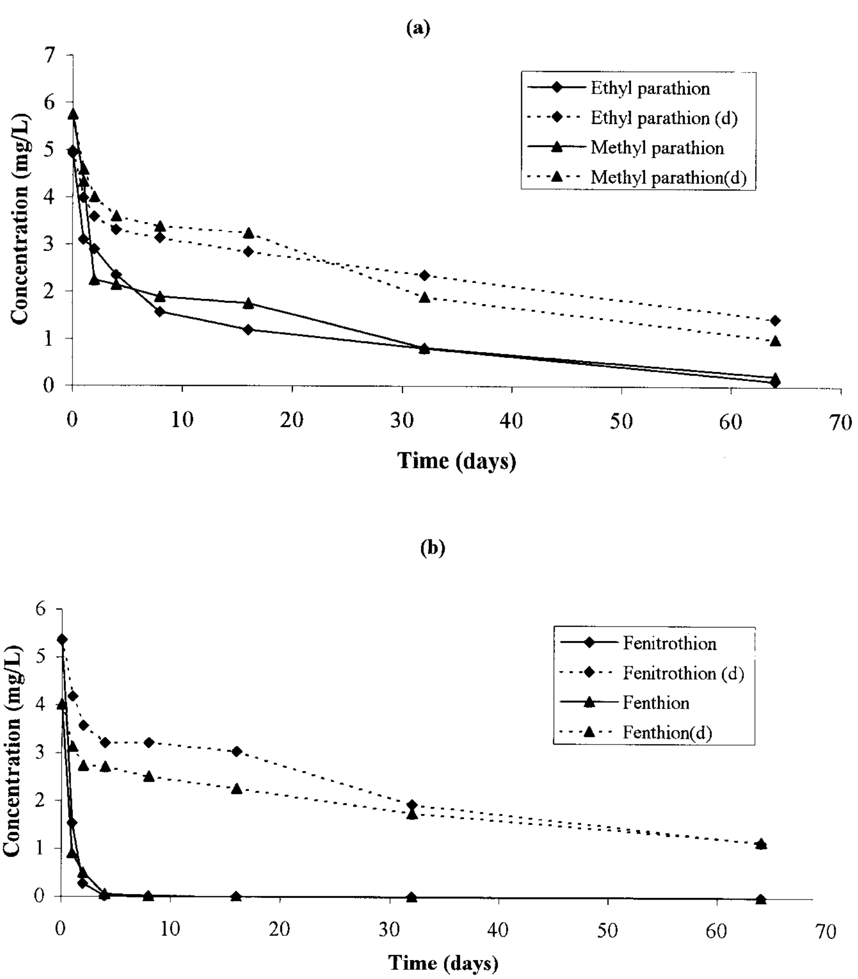

FIGURE 1 Photodegradation of (a) ethyl parathion and methyl parathion, (b) fenitrothion and fenthion in distilled water under environmental conditions, (d) = blanc experiment.

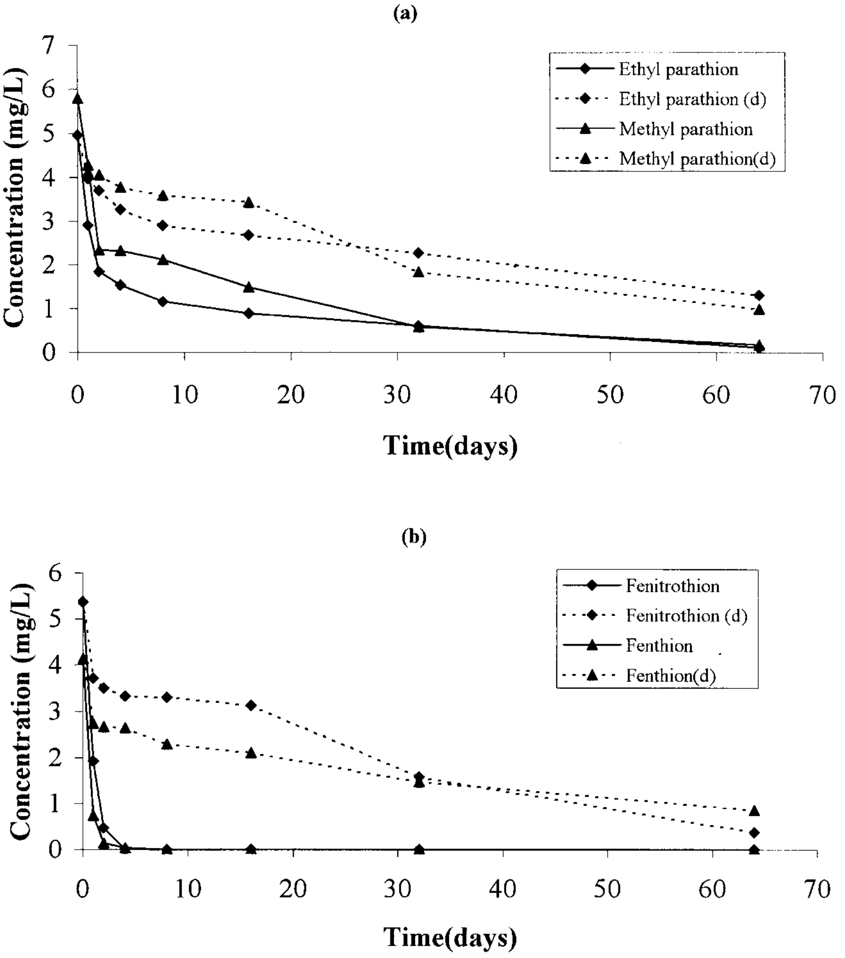

FIGURE 2 Photodegradation of (a) ethyl parathion and methyl parathion, (b) fenitrothion and fenthion in underground water under environmental conditions, (d) = blanc experiment.

and microorganisms suspended in a water column may scatter incident light, greatly reducing penetration of light beneath the surface. In the second case it is suggested that a sensitization effect of humic substances depend on the binding affinity of insecticides to the radical source of the humic material [31]. The resulting excited states of the DOM and reactive transients that were produced from DOM could participate in energy transfer, electron transfer and free radical reaction, which affect the degradation rate of insecticides. In addition inorganic species such as nitrate, nitrite and carbonate radicals can enhance the photodegradation rate of organophosphorus insecticides in natural waters [31].

This complex behavior of constituents of natural waters (acting simultaneously as optical filters and sensitizers) is clearly being reflected by the contradictable results of the photodegradation rate constants of the insecticides (Table IV) since increment of DOM concentration in natural waters (Table II) does not always result in an increment (sensitization effect) or decrement (optical filter) of degradation rates.

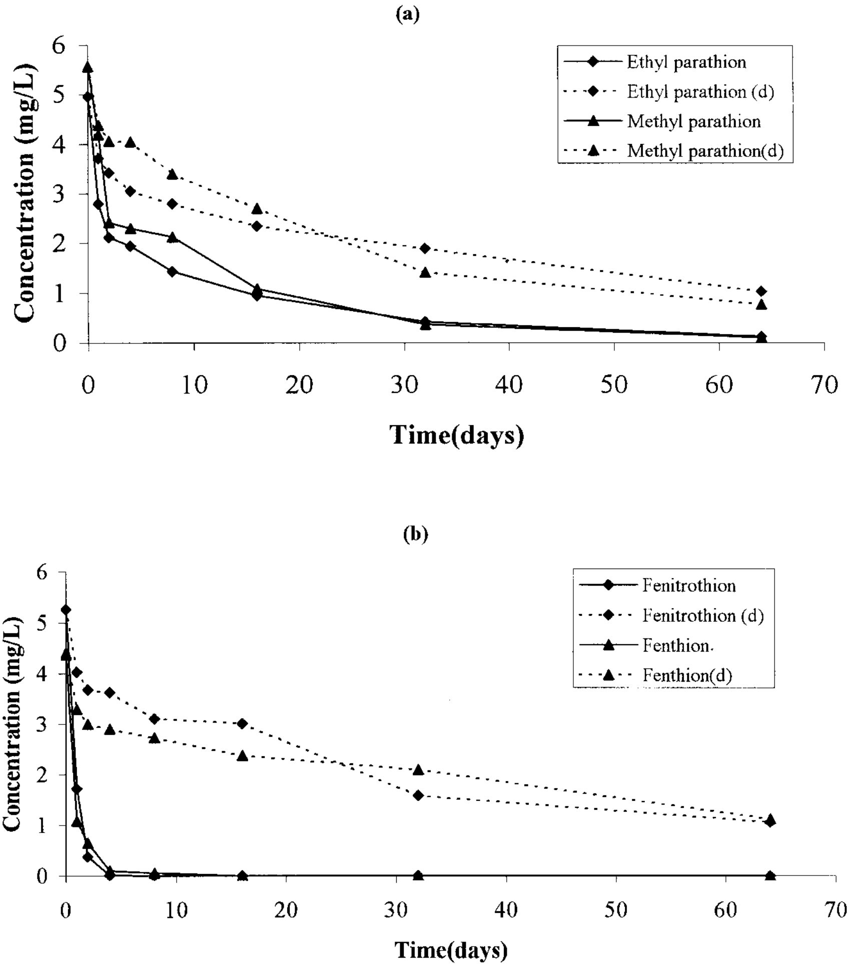

FIGURE 3 Photodegradation of (a) ethyl parathion and methyl parathion, (b) fenitrothion and fenthion in river water under environmental conditions, (d) = blanc experiment.

Methyl parathion resulted to be more stable than ethyl parathion under sunlight, as it is shown by the photodegradation rate constants (k_{phot}) (Table IV). In this case the different behavior under sunlight arose from the different quantum yields values, of these two insecticides. In fact, the measurable quantum yield (quantum efficiency) values with polychromatic [32] and monochromatic irradiation [14,33] show that ethyl parathion is amenable to photodegradation more efficiently than methyl parathion.

The rapid degradation of fenitrothion and fenthion in all type of waters is attributed to high quantum yields (quantum efficiency) of these pesticides (one magnitude greater than methyl and ethyl parathion) [32]. Thus their degradation rates are of the same order in natural waters, compared to distilled, due to their direct photolysis.

An increase in the pH generally leads to a greater degradation rate, but the limits pH ranged in our experiment (5.9 for distilled water to 8.5 for lake water) do not seem to influence strongly the degradation rate [34–37].

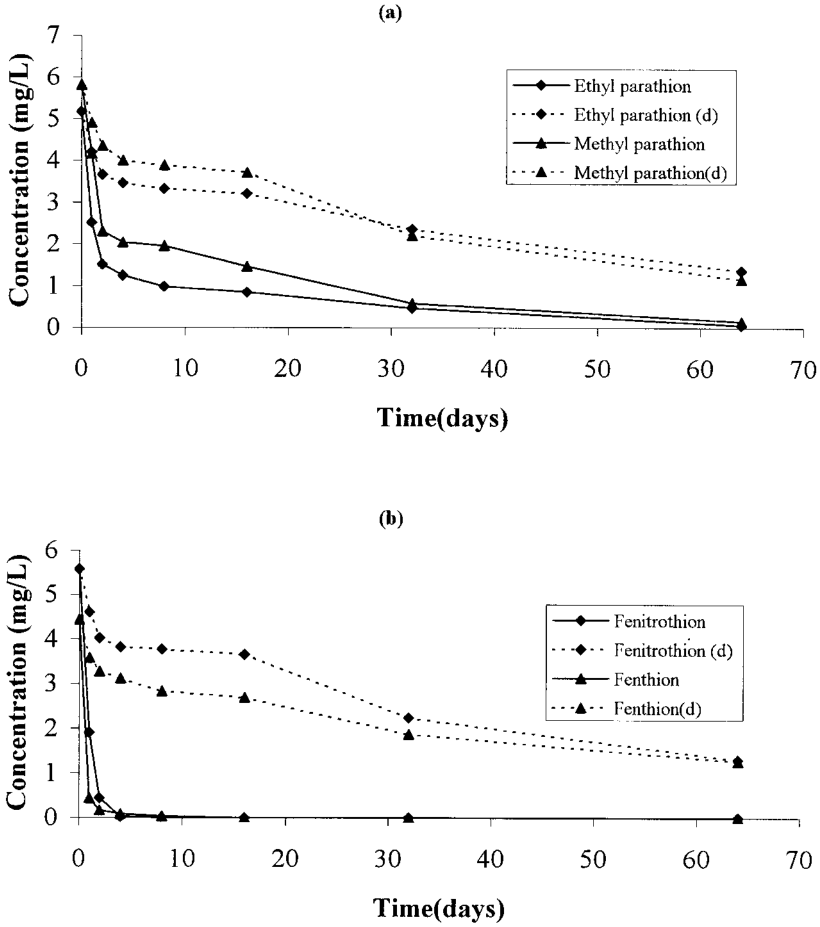

FIGURE 4 Photodegradation of (a) ethyl parathion and methyl parathion, (b) fenitrothion and fenthion in lake water under environmental conditions, (d) = blanc experiment.

The addition of the methyl group (fenitrothion, fenthion) or the replacement of NO_2 by SMe (fenthion) seems to modify the behavior of the molecule under photolysis: fenitrothion and fenthion are more sensitive to photodegradation. This may be due to the fact that an organophosphorus compound with alkyl group attached to the aromatic ring tend to have higher quantum yields, because such a group may supply a photosensitive position for photoreaction to occur, than another with an electron withdrawing group as NO_2 [33]. Degradation of fenitrothion and parathion (both methyl and ethyl parathion) whose main structural difference is the presence of a methyl group in *ortho* position of the aromatic ring, indicates that this is a photosensitive position for photoreactions to occur. It has been reported that the oxidation of the methyl group attached to the aromatic ring is the predominant photoreaction for fenitrothion [38].

Photodegradation By-products

The use of GC-MS allowed the determination of some potential transformation products of the tested compounds, in water, by using an identification program by NIST

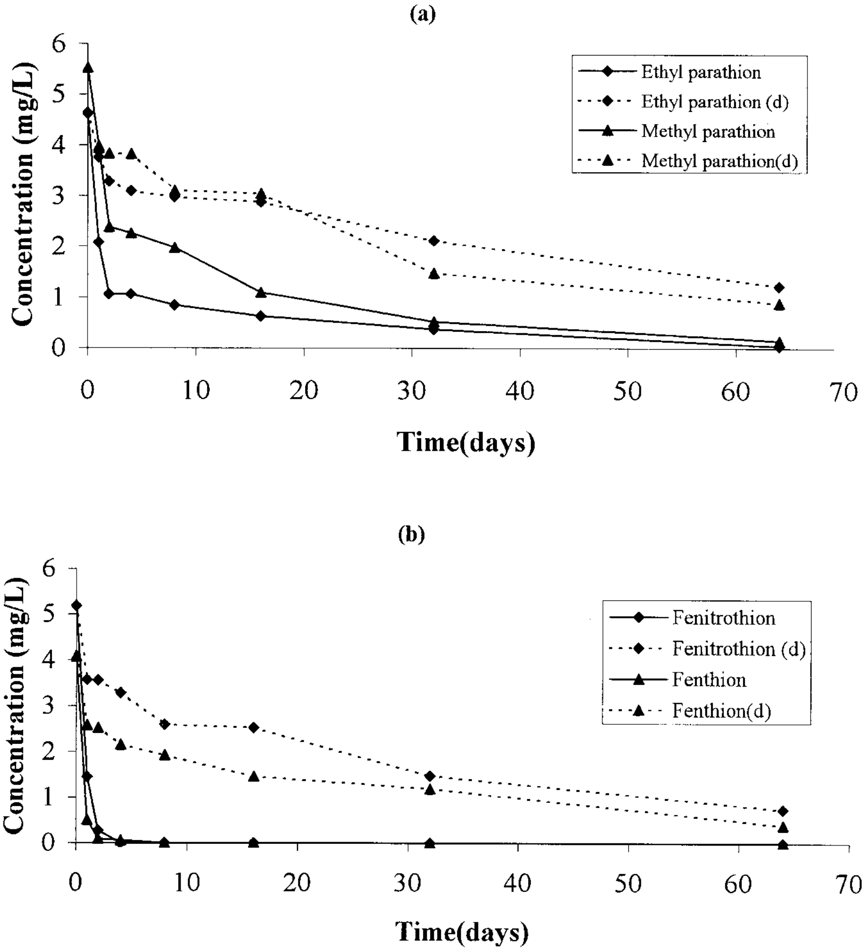

FIGURE 5 Photodegradation of (a) ethyl parathion and methyl parathion, (b) fenitrothion and fenthion in sea water under environmental conditions, (d) = blanc experiment.

library. The compounds are shown on Table V with their characteristic fragment ions and the tentative photodegradation schemes depicted in Figs 6–9. The oxon analogs (such as paraoxon, fenoxon) of organophosphorus insecticides were found to be the primary products during the photodegradation process which is in agreement with other studies [39]. The main difference between them and the parent compounds is only the substitution of sulfur by oxygen in the P=S bond. These oxo metabolites are of concern because they are the activated forms of the organophosphorus pesticides, with a considerably stronger inhibition of cholinesterase activity than that exhibited by the parent compounds [40]. In the case of fenthion the oxidative process led to the production of fenthion sulfoxide and fenthion sulfone as well as the fenoxon analogs also (compounds (h), (i), (f), and (g) respectively in Table V or in Fig. 9).

In all cases the formation of the respective phenols of each insecticide (4-nitrophenol for methyl and ethyl parathion, 3-methyl-4-nitrophenol for fenitrothion and 3-methyl-4-methylthio phenol for fenthion) was observed as a consequence of splitting of the

TABLE V Gas chromatography-mass spectrometry identification of insecticides' by-products

Insecticide	*By-product*	*Spectral data (m/z) ions*
Ethyl parathion	(a) *O*,*O*,*O*-triethyl phosphothioate	198(M$^+$), 170, 154, 142, 138, 126, 111, 110, 109, 97.
	(b) Diethyl dithiophosphate	186(M$^+$), 158, 153, 142, 137, 125, 121, 109, 97.
	(c) 1-ethoxy-4-nitro benzene	167(M$^+$), 139, 123, 109, 93, 81.
	(d) 4-nitrophenol	139(M$^+$), 123, 109, 93, 81.
	(e) paraoxon	275(M$^+$), 247, 149, 139, 127, 109, 99, 81.
	(f) aminoparathion	261(M$^+$), 233, 205, 153, 136, 125, 124, 109, 108, 97.
	(g) *O*,*O*-diethyl, *O*-phenyl phosphorothioate	246(M$^+$), 218, 190, 141, 125, 110, 109, 105, 104, 97, 94.
Methyl parathion	(a) *O*,*O*,*O*-trimethyl phosphorothioate	156(M$^+$), 126, 125, 109, 93.
	(b) *O*,*O*,*S*-trimethyl phosphorothioate	156(M$^+$), 126, 125, 110, 109, 95, 80, 79.
	(c) 4-nitrophenol	139(M$^+$), 123, 109, 93, 81.
	(d) methyl paraoxon	247(M$^+$), 230, 200, 139, 109, 96, 79.
	(e) amino methyl parathion	233(M$^+$), 125, 124, 109, 108.
Fenitrothion	(a) 3-methyl-4-nitrophenol	153(M$^+$), 136, 108, 77.
	(b) *O*,*O*,*S*-trimethyl phosphorothioate	156(M$^+$), 126, 125, 110, 109, 95, 80, 79.
	(c) 4-methoxy-6-methyl nitrobenzene	167(M$^+$), 150, 137, 122, 106, 91, 77.
	(d) *O*,*O*-dimethyl *O*-3-methylphenyl phosphorothioate	232(M$^+$), 200, 125, 109, 105, 77.
	(e) *O*,*O*-dimethyl *O*-4-methoxyphenyl phosphorothioate	248(M$^+$), 139, 125, 109, 93, 77.
	(f) *S*-methyl fenitrothion	277(M$^+$), 260, 136, 125, 79.
	(g) methyl parathion	263(M$^+$), 125, 109, 93, 79.
Fenthion	(a) 4-methoxy-2-methyl-1-methylthio benzene	168(M$^+$), 153, 138, 109, 91, 77.
	(b) 4-methylthio-3,5-dimethyl phenol	168(M$^+$), 153, 109, 91, 77.
	(c) *O*,*O*-dimethyl *O*-3-methylphenyl phosphorothioate	232(M$^+$), 200, 125, 109, 105, 77.
	(d) 3-methyl-4-methylthio phenol	154(M$^+$), 139, 107, 95, 77.
	(e) fenoxon	262(M$^+$), 247, 153, 135, 121, 110, 109, 91.
	(f) fenoxon sulfoxide	278(M$^+$), 263, 127, 109, 93, 79.
	(g) fenoxon sulfone	294(M$^+$), 215, 121, 109, 104, 79.
	(h) fenthion sulfoxide	294(M$^+$), 279, 278, 169, 153, 138, 137, 125, 109, 93.
	(i) fenthion sulfone	310(M$^+$), 231, 137, 136, 125, 121, 109, 105, 93.

phosphorus–phenoxy bond. The formation of some other aromatic intermediates listed in Table V (such as 4-methoxy-6-methyl nitrobenzene, 1-ethoxy-4-nitro benzene and 4-methoxy-2-methyl-1-methylthio benzene) which imply the transfer of alkyl (methyl, ethyl) or alkoxy (methoxy, ethoxy) groups illustrate the complexicity of the photodegradation in natural waters.

The *S*-methyl isomers of organophosphorus pesticides (e.g. *S*-methyl isomer of fenitrothion) which also exhibit a very different biological activity than their *O*-alkyl precursors [40] are produced by thermally induced isomerization, thus taking place during synthesis and storage and by photolysis [41]. Another side reaction observed on the photolysis of fenitrothion and parathion is the loss of the nitro group to give denitrofenitrothion and denitroparathion respectively. A reduction metabolite such

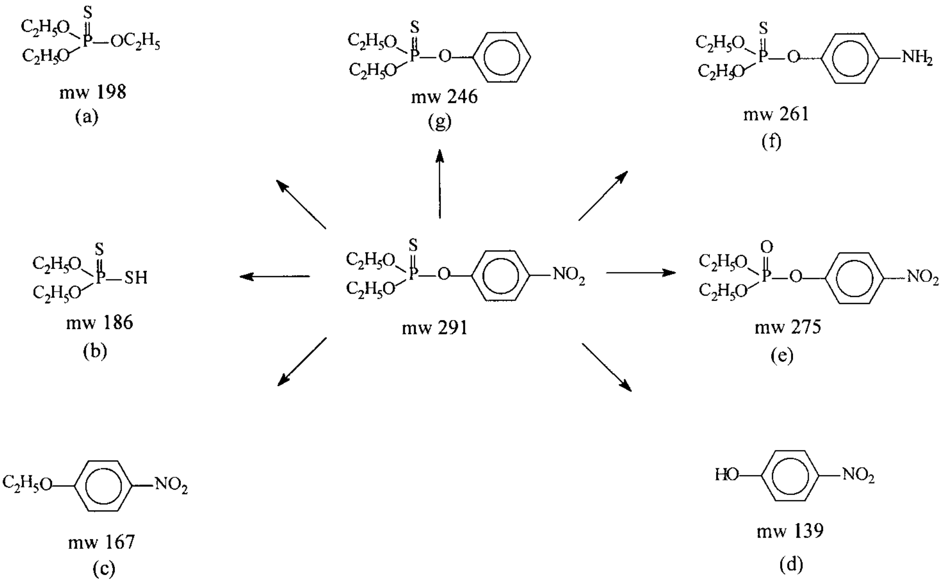

FIGURE 6 Photodegradation products of ethyl parathion in natural waters.

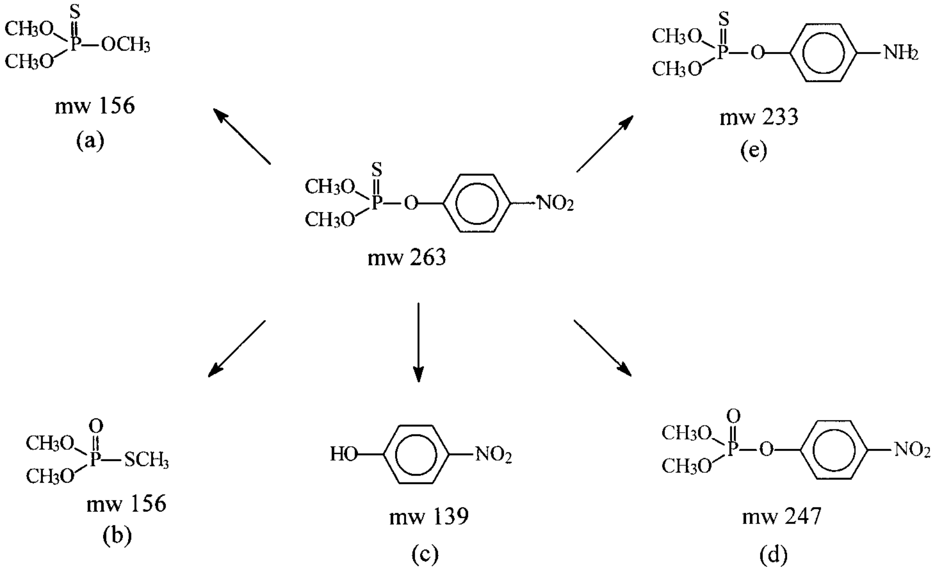

FIGURE 7 Photodegradation products of methyl parathion in natural waters.

as aminoparathion (methyl, ethyl) was identified as a by-product in the photodegradation process of methyl and ethyl parathion in natural waters.

Finally the different alkyl phosphorothioate esters (*O*,*O*,*O*-triethyl phosphorothioate, diethyl dithiophosphate, *O*,*O*,*O*-trimethyl phosphorothioate, *O*,*O*,*S*-trimethyl phosphorothioate) were identified as photodegradation by-products, which is in agreement with other studies [42].

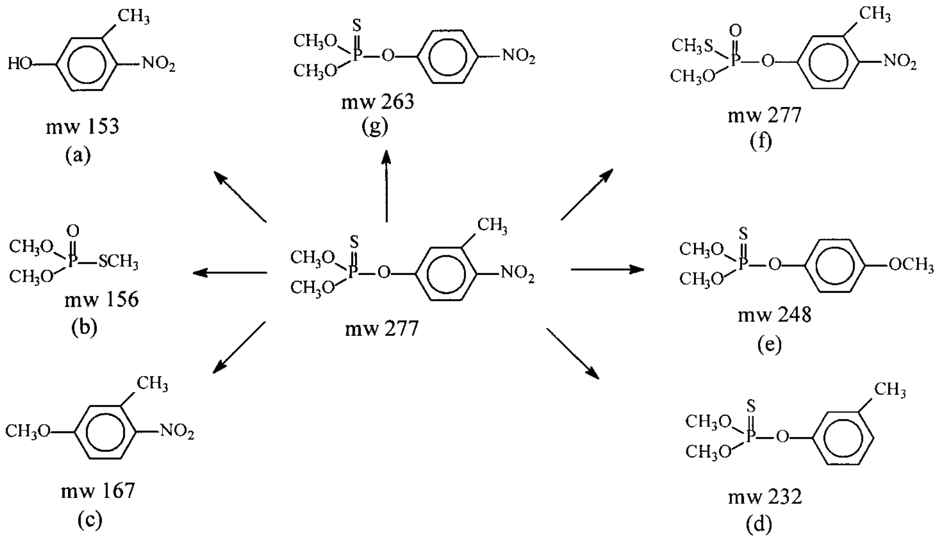

FIGURE 8 Photodegradation products of fenitrothion in natural waters.

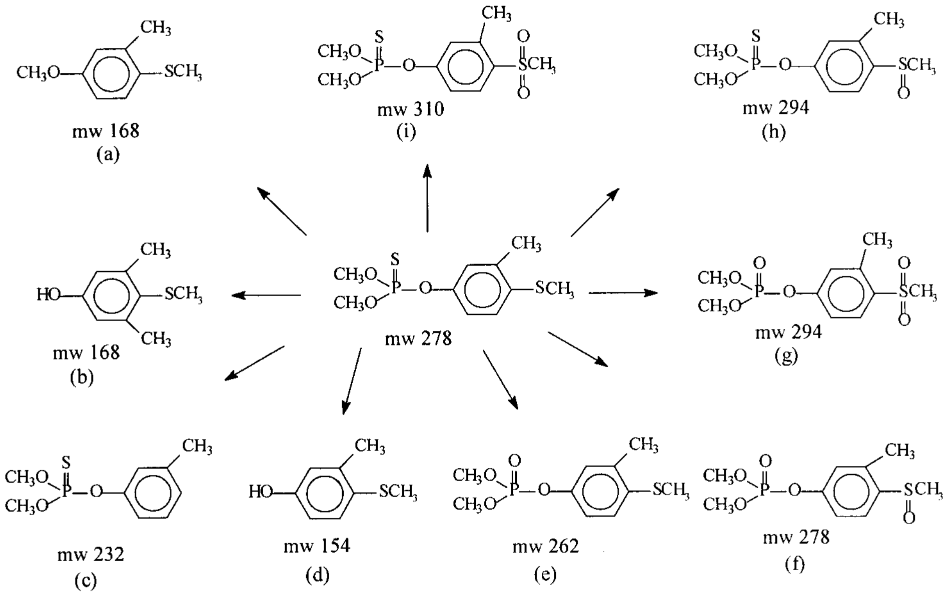

FIGURE 9 Photodegradation products of fenthion in natural waters.

From Figs 6–9 we conclude that photodegradation of organophosphorus pesticides in natural waters involves different photolytic routes, such as, oxidation (ethyl parathion to ethyl paraoxon, methyl parathion to methyl paraoxon and fenthion to fenthoxon), hydrolysis (fenitrothion to 3-methyl-4-nitrophenol, fenthion to 3-methyl-4-methylthio phenol and parathion to 4-nitrophenol), isomerization (fenitrothion to *S*-methyl isomer of fenitrothion), reduction (parathion to aminoparathion) etc.

Photodegradation in Soil

The photodegradation of the studied insecticides on different soils follows a first-order kinetics and their half-lives were calculated by the formula $T_{1/2} = \ln 2/k$, where k is the first order rate constant. The half-lives of insecticides disappearance varied (Table VI) and the lowest was observed for fenthion. A comparison between degradation rates of insecticides on soil surfaces under natural sunlight and darkness (Figs 10–13) indicates that, sunlight has a significant effect on the degradation of these compounds, although none of them degraded totally in 15 days.

A competitive sunlight absorption by soil chromophores [43], variable sorption of insecticides on organic and inorganic soil colloids and competing other transformation processes complicate the predicting of photolysis rates at the soil surfaces. Other authors [22,43,44] indicated that soil humic substances are capable of acting as sensitizers for the production of reactive intermediates such as singlet oxygen, hydroxy radicals, superoxide ion and peroxy radicals. Such reactive species can potentially diffuse to depths approaching 1 mm depending on moisture depth, soil porosity and thermal gradients on the sunlight-exposed soil interface.

TABLE VI Half-lives $T_{1/2}$ (days) and photolysis constants k_{phot} (days^{-1}) of studied insecticides on soil surfaces

Insecticides	*SCL*		*CL*		*SL*	
	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})	$T_{1/2}$	k_{phot} (10^{-2})
Ethyl parathion	21.3	3.25	15.6	4.45	20.8	3.33
Methyl parathion	11.2	6.18	5.6	12.39	9.1	7.58
Fenitrothion	9.0	7.68	7.0	9.93	5.2	13.38
Fenthion	3.4	20.34	3.8	18.06	4.2	16.63

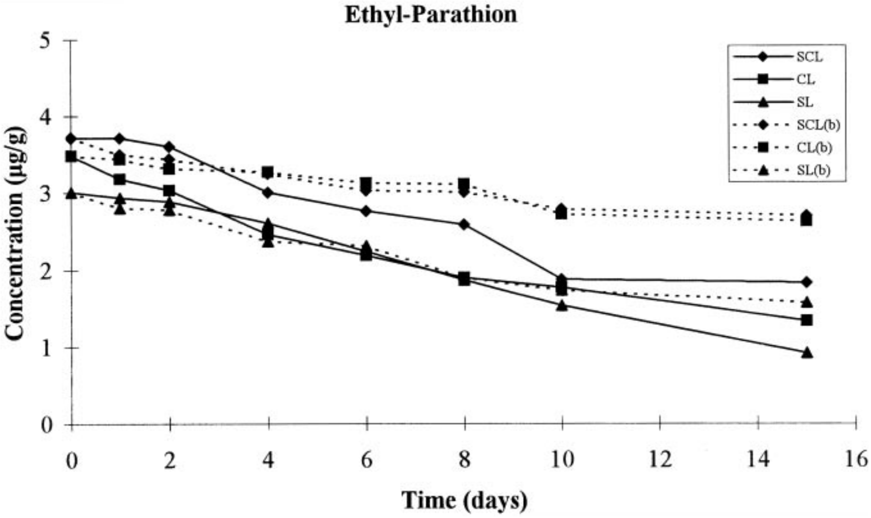

FIGURE 10 Photodegradation of ethyl parathion, in soil surfaces under environmental conditions, (b) = blanc experiment.

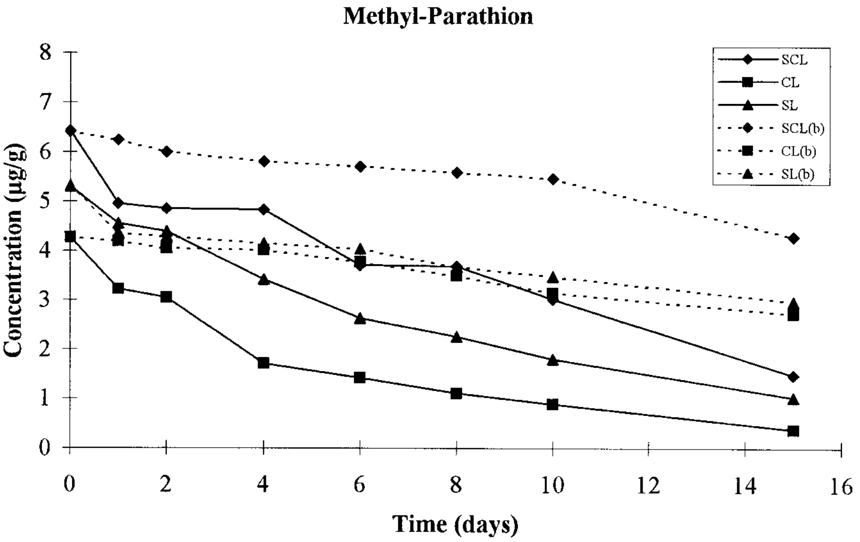

FIGURE 11 Photodegradation of methyl parathion, in soil surfaces under environmental conditions, (b) = blanc experiment.

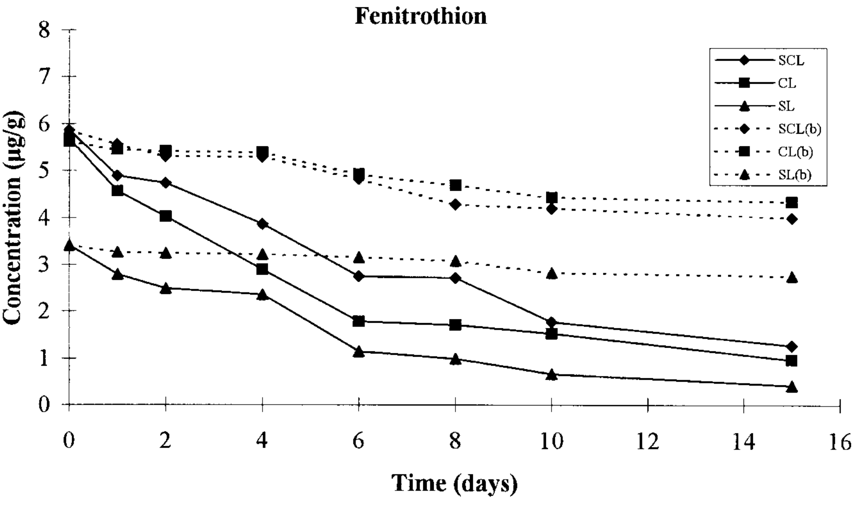

FIGURE 12 Photodegradation of fenitrothion, in soil surfaces under environmental conditions, (b) = blanc experiment.

The increase of organic matter of the selected soils was not found to sensitize the degradation rates of the organophosphorus insecticides with the exception of fenitrothion whose degradation rate increases with the organic matter content increment. The differences in behavior for the rest of insecticides (Table VI) could be attributed to organic matter quenching effect (acting as an inner filter) [43], protecting the pesticide adsorbed from photochemical degradation. The rate of losses in dark controls was significantly slower.

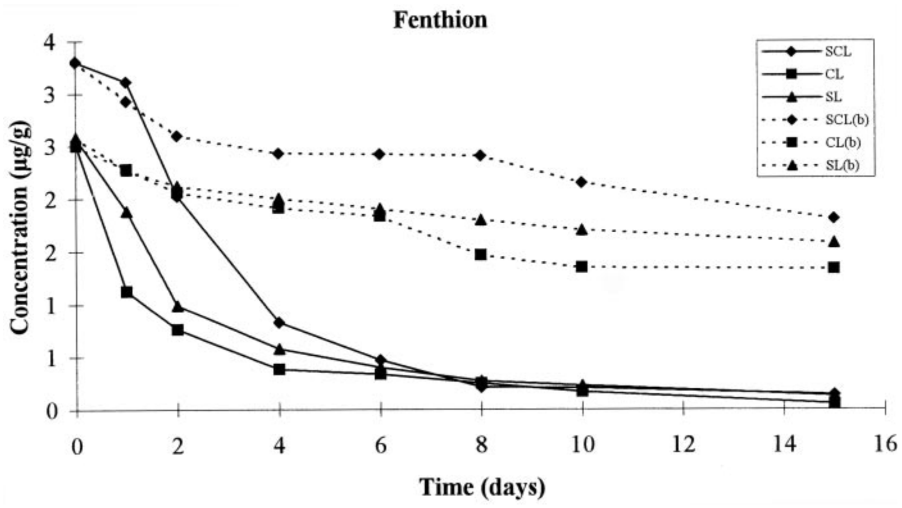

FIGURE 13 Photodegradation of fenthion, in soil surfaces under environmental conditions, (b) = blanc experiment.

Although we did not analyze for by-products, the transformation of these compounds on soil surfaces follows the photooxidation pathway as it has demonstrated by Gohre and Miller [45]. The same authors indicate that singlet oxygen is the likely reactant on irradiated soils [46].

The observed decomposition of insecticides in the covered soil samples shows that other processes also occurred under the experimental conditions used. However, the difference between the amounts decomposed in the illuminated and the covered soil samples can be considered to be the result of photodegradation.

CONCLUSIONS

The photochemical behavior of the organophosphorus insecticides – ethyl parathion, methyl parathion, fenitrothion, and fenthion – in natural waters and soils under environmental conditions has been investigated.

The photodegradation kinetics of organophosphorus insecticides followed a first order reaction curve both in natural waters and soil surfaces. The results indicated that some compounds exhibited longer half-life than others although they had very similar structures. The half-lives varied from 0.4 to 35.4 days in natural waters and from 3.4 to 21.3 days on soil surfaces depending on molecular structures that play an important part in determining insecticides' behavior with respect to adsorption on particulates or absorption of light.

The photodegradation kinetics of the selected insecticides in different natural waters and soils show a strong dependence on the composition of the water or soil sample and especially on the organic matter, which provides either a sensitization or an optical filter effect. The organic matter concentration and the type of functional groups and aromaticity present in organic matter influence the photoprocess differently.

The GC-MS analysis showed the formation of several transformation by-products such as 4-nitrophenol, paraoxon, aminoparathion, 3-methyl-4-nitrophenol, fenthion sulfone, fenthion sulfoxide, fenoxon indicating different photolytic routes of organophosphorus insecticides in natural surfaces.

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