Absorption of Pesticides on Plastic Films Used as Agricultural Soil Covers

C. Nerín,* A. R. Tornés, C. Domeño, and J. Cacho

Departamento Analytical Chemistry, CPS Ingenieros, Universidad de Zaragoza, 50015 Zaragoza, Spain

The absorption of some organochlorine and organophosphorus pesticides on low-density polyethylene (LDPE) films used as agricultural soil covers is studied. Four different types of LDPE films (black, normal, thermic, and extra low density) and a copolymer of ethylene and vinyl acetate (EVA) were selected to do the kinetic study. Temperature ranged from 24 to 50 °C, and contact time between plastic films and a standard solution of pesticides in aqueous phase varied between 3 and 20 days. As pesticides the following were studied: dicloran, malathion, procymidone, folpet, α- and β-endosulfan, chlorothalonil, chlorpyriphos, and methylchlorpyriphos. Kinetic equations of first order were obtained in all cases having kinetic constants from 6.5×10^{-4} to 1×10^{-4} days^{-1}. Most of the pesticides studied were completely absorbed on the plastic films after 15 days of contact time. No degradation of pesticides was observed once they were absorbed on the plastic. Both the absorption process and the capacity of absorption of each type of plastic are discussed.

Keywords: *Absorption; organochlorine pesticides; organophosphorus pesticides; agricultural soil covers; low-density polyethylene films*

INTRODUCTION

The use of plastic films in agricultural work either in greenhouses or as soil covers in crops has improved the quality and the production of different vegetables (*Plasticos en la Agricultura*, 1993). The plastic films offer great advantages to man, since they permit the intensive cultivation of poor soils as well as the growth of products out of the expected period of the year. Thus, strawberries, green vegetables, peppers, and tomatoes are able to grow in winter in areas in which metereological conditions are normally bad. The type of plastic used is mainly low-density polyethylene (LDPE); it is available in the market as film of different thicknesses and characteristics. A copolymer of ethylene and vinyl acetate (EVA) is also employed in greenhouse activities. Most of these plastic films are now recovered and recycled to avoid environmental problems, and because of the good mechanical strength and general properties of some of these recycled films (Roy, 1994), they could be used again as agricultural soil covers.

Depending on the specific applications in which the plastic films have been used, the exposure time of the film to the sun under different meteorological conditions varies from 2 months (the plastics used as agricultural soil covers) to 3 years (those used in greenhouses). Obviously, the longer the exposure time, the greater the degradation of the film (Roy, 1994). This implies that the most appropriate films to be recycled are those which are used as agricultural soil covers, which means about 2−3 months of exposure to environmental conditions.

LDPE density ranges from 0.92 to 0.94 g cm^{-3}, and it is characterized by good flexibility, low transparency, and high resistance to temperature. In fact, it only becomes soft at 80 °C. The extended use of this type of film is a consequence of its excellent properties, the absence of both odors and toxicity as well as its low cost (Brydson, 1995).

However, the plastic films used in agricultural applications as agricultural soil covers either in crops or in greenhouses are also exposed to the pesticides sprayed on the crops, including fungicides, herbicides, and all type of biocides, which can be absorbed by the polymer. If this polymer is recovered and recycled, the presence of such compounds could be a great disadvantage that would strongly affect its future usage.

From a general point of view, pesticides are considered as accumulative and toxic compounds. Their determination in different matrices such as animal fat, foodstuffs, air, and water has been extensively studied (Nerín et al., 1995; Leidy et al., 1993; Van der Hoff et al., 1991; Yeary et al., 1993; Grob et al., 1991) but only a few studies are focused on their presence in plastics (Topp et al., 1992; Desriac, 1991), even in agricultural plastics (Vuik et al., 1990).

If the plastic is to be recycled, it is important to know tto what extent the pesticides are absorbed on LDPE films to estimate the risk associated with their second usage.

The present paper deals with the absorption of some pesticides often used in the south of Spain in different crops in which plastic films are used as agricultural soil covers. Kinetic constants of the absorption process in five different types of agricultural films are calculated. The absorption process and the behavior of each pesticide in each plastic are discussed.

EXPERIMENTAL PROCEDURES

Apparatus and Reagents. A Varian (Harbor City, CA) Star 3400 CX gas chromatograph equipped with an ECD (^{63}Ni) and a Varian 8200 CX autosampler was used. A temperature programmable septum-equipped-programmable injector (SPI) was used with the following program: initial temperature, 40 °C; held for 0 min; ramped at 150 °C/min to 240 °C; and then held at 240 °C for 20 min.

The capillary column was a DB-5, 60 m × 0.25 mm × 0.25 mm film thickness supplied by Tecknokroma (Spain) with the following program: initial temperature, 60 °C for 2 min; ramped at 25 °C/min to 215 °C; and held at 215 °C for 2 min. A second ramp at 5 °C/min increased the temperature to 242 °C, which was held for 1.5 min. A third ramp at 1 °C/min increased the temperature to 255 °C, which was held for 2 min, and a fourth ramp at 25 °C/min increased the temperature to 280 °C, which was held for 3 min. The carrier gas was

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Table 1. Analytical Features

compound	detection limit splitless (ng/g)	detection limit SPI (ng/g)	reproducibility SPI (RSD, %)	linear response SPI (ng/g)
dichloran	5.0	1.0	4.6	15−1000
malathion	25.0	5.0	6.2	30−1000
procymidone	10.0	3.0	7.6	20−500
folpet	50.0	10.0	10.8	50−500
α-endosulfan	2.0	0.1	7.0	5−1000
β-endosulfan	2.0	0.1	9.6	5−1000
chlorothalonil	50.0	5.0	7.4	50−1000
chlorpyriphos	2.0	0.5	5.2	5−1000
methylchlorpyriphos	2.0	0.5	4.2	5−1000
γ-HCH (internal standard)	1.0	0.1	2.5	1−1000

hydrogen (C-50 quality) with a flow rate of 1.26 mL/min. The makeup gas was nitrogen at a rate flow of 30 mL/min.

The following certified standards of pesticides were used: γ-hexachlorocyclohexane (γ-HCH, lindane), dicloran, malathion, procymidone, folpet, α-endosulfan, β-endosulfan, chlorothalonil, chlorpyriphos, and methylclorpyriphos, all supplied by Dr. Ehrenstofer GmbH (Wesel, Germany).

The solvents used were hexane and dichloromethane (residue analysis quality) supplied by Merck (Darmstadt, Germany). Whatman 1PS paper filters (15 cm; Maidstone, U.K.) and PTFE 25 mm × 0.45 mm syringe Whatman filters were used to dry and filter the organic extracts.

The following agricultural plastic films supplied by Macresur (Almería, Spain) were used: normal LDPE film, black LDPE film, thermic LDPE film, extra-LDPE film, and EVA.

Procedure. Small pieces of each sample of LDPE or EVA of 16 × 12 cm thickness (∼3 g weight) were cut and introduced into a glass beaker containing 750 mL of an aqueous solution of 1000 ng/mL of each pesticide. This aqueous solution was prepared by adding 1 mL of an ethanolic solution of 1000 mg/mL to 1000 mL of milliQ water so that the final content of ethanol was negligible. The contact time between each plastic film and the aqueous solution varied from 3 to 20 days. The same experiment was repeated at 24, 35, and 50 °C at each contact time. Three independent replicates of each experiment were done. Once the exposure time was over, the film sample was carefully washed with distilled water and it was dried at room temperature. Each piece of plastic was then cut off and extracted with 50 mL of dichloromethane in an ultrasonic bath for 2 h (C. Nerín, A. Tornés, R. Batlle, and J. Cacho, unpublished results). It was verified that a second extraction was not necessary since the quantitative extraction was achieved under the mentioned experimental conditions. The organic extract was filtered through a Whatman 1PS paper (phase separatory paper) to eliminate the solid residues as well as to dry the extract. To the organic and clean extract was added γ-HCH as internal standard. This extract was evaporated to dryness, and then 2 mL of hexane was added. The final sample was filtered through a PTFE syringe filter of 0.2 mm pore size before being injected in the chromatographic column.

RESULTS AND DISCUSSION

Chromatographic Analysis. The linear range, detection limit, and reproducibility of the analysis of all the pesticides under study are shown in Table 1. As can be seen, detection limits are very low compared to those obtained with splitless injection. This improved sensitivity can be attributed to the use of the SPI injector since with this type of injector, the sample is directly injected into the cold capillary column. The SPI injector also avoids the degradation of thermolabile compounds as was previously demonstrated (C. Nerín et al., unpublished results). The long-term (1 month) reproducibility was calculated with a standard solution of each compound (10 independent replicates) and also shows very low RSD values, as indicated in Table 1.

Four different steps in the temperature program were necesary to get a good enough chromatographic separation. Even in this case, when a high concentration of procymidone and folpet was used, the overlapping of both compounds could not be avoided. When other capillary columns such as DB-8 or DB-170 were used, worse results were obtained.

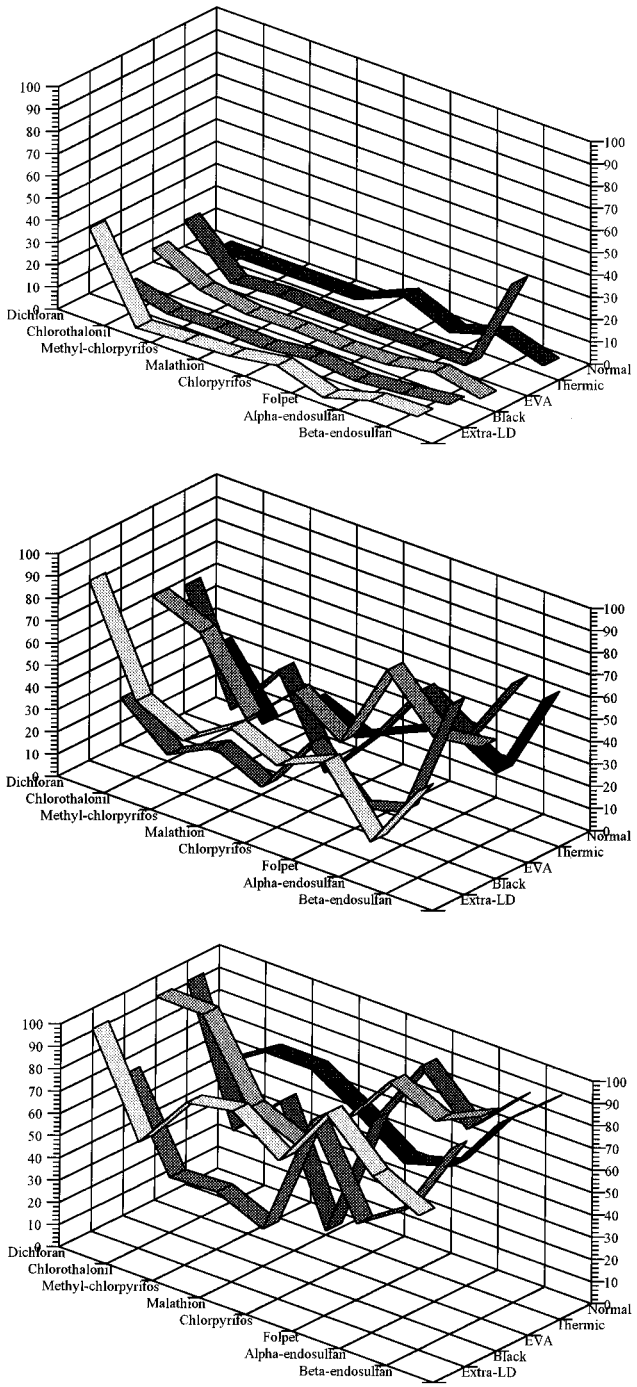

Figure 1. Percentage of absorption of each pesticide on each type of plastic. Exposure conditions were as follows: temperature, 24 °C; time, (a, top) 3 days, (b, middle) 7 days, (c, bottom) 15 days.

Linear range was calculated from the plot of the response obtained per mass unit versus the injected mass. As is well-known, the lower concentration values do not have a linear response with ECD. For this reason multivariate calibration was used in all cases to assure the quantitation.

Selection of Pesticides. The pesticides under study were selected by taking into account several factors, as follows: (a) the usage of each compound and how often they are applied to the crops where plastic films are

Table 2. Results Obtained for the Different Films at 24, 35, and 50 °C[a]

	time	thermic film		extra-LDPE		normal film		black film		EVA	
compound	(days)	ng/g	ng/cm^2	ng/g	ng/cm^2	ng/g	ng/cm^2	ng/g	ng/cm^2	ng/g	ng/cm^2
					A. At 24 °C						
dichloran	3	87.10	0.5	166	1.1	1	0.0	142	0.1	62.71	0.4
	7	282.2	1.8	385	2.5	942	0.9	802	0.8	287.8	1.9
	15	428.6	2.8	430	2.8	1629.9	1.5	1172.3	2.0	419.5	2.8
chlorothalonil	3	0.5	0.0	5	0.0	1	0.0	8	0.0	15.9	0.1
	7	74.10	0.5	178	1.1	123	0.1	307	0.3	242.3	1.6
	15	168.7	1.1	236	1.5	1948.6	1.9	801	0.9	404.0	2.7
methylchlorpyriphos	3	5.2	0.0	7	0.0	9	0.0	1	0.0	1.8	0.0
	7	137.8	0.9	105	0.7	477	0.4	449	0.4	89.5	0.6
	15	196.5	1.3	264	1.7	1507.2	1.4	640	0.7	204.9	1.4
chlorpyriphos	3	0.78	0.0	2	0.1	225	0.2	6	0.0	0.1	0.0
	7	102.9	0.6	136	0.9	576	0.5	910	0.9	119.6	0.8
	15	253.2	1.6	265	1.7	1062.6	1.0	1735.3	2.0	272.1	1.8
folpet	3	2.33	0.0	0	0.0	1	0.0	9	0.0	1.6	0.0
	7	102.9	1.2	155	1.0	731	0.7	380	0.4	240.4	1.6
	15	330.9	2.2	338	2.2	1105.1	1.0	835	0.9	329.2	2.2
α-endosulfan	3	1.17	0.0	1	0.0	104	0.1	3	0.0	10.02	0.0
	7	95.2	0.6	4	0.2	304	0.3	337	0.3	111.1	0.7
	15	178.9	1.1	179	1.1	1152.7	1.1	733	0.8	198.3	1.3
β-endosulfan	3	100.8	0.6	1	0.1	1	0.0	6	0.0	0.7	0.0
	7	168.6	1.1	108	0.7	930	0.9	1121.2	1.2	118.1	0.8
	15	226.6	1.5	158	1.0	1423.5	1.3	1194.9	1.3	221.6	1.5
malathion	3	3.8	0.0	1	0.1	1	0.0	3	0.0	4.40	0.0
	7	21.99	0.1	217	1.4	425	0.4	365	0.3	221.4	1.5
	15	51.55	0.3	406	2.7	1808.3	1.7	696	0.8	262.1	1.7
					B. At 35 °C						
dichloran	3	106.6	0.7	224	1.4	41.7	0.0	219	0.2	73.24	0.5
	7	314.3	2.1	428	2.8	1415.2	1.4	1006.9	1.1	302.1	2.0
	15	441.9	2.9	450	2.9	1844.7	1.9	2087.7	2.2	437.2	2.9
chlorothalonil	3	5.9	0.0	1	0.0	46.7	0.0	9	0.0	63.2	0.4
	7	104.3	0.7	219	1.4	1287.8	1.3	446	0.4	265.7	1.8
	15	202.6	1.3	315	2.0	2218.7	2.3	1637.1	1.7	422.9	2.8
methylchlorpyriphos	3	16.51	0.1	3	0.2	53.03	0.0	159	0.1	13.1	0.0
	7	181.6	1.2	159	1.0	740	0.7	566	0.6	107.8	0.7
	15	237.8	1.6	336	2.2	1656.7	1.7	752	0.8	236.3	1.6
chlorpyriphos	3	5.8	0.0	1	0.1	289	0.3	117	0.1	34.7	0.2
	7	133.9	0.9	157	1.0	846	0.8	997	1.0	162.5	1.1
	15	286.9	1.9	306	2.0	2418.4	2.5	2231.8	2.4	314.6	2.1
folpet	3	3.5	0.0	0	0.0	111	0.1	10.4	0.0	50.2	0.3
	7	202.1	1.3	290	1.9	940	0.9	577	0.6	306.7	2.0
	15	347.1	2.3	354	2.3	2194.8	2.3	1359.5	1.4	343.4	2.3
α-endosulfan	3	2.5	0.0	3	0.2	130	0.1	89.6	0.1	25.3	0.1
	7	118.1	0.7	5	0.3	468	0.4	493	0.5	177.4	1.2
	15	200.1	1.3	194	1.2	1104.4	1.1	1106.0	1.2	223.3	1.5
β-endosulfan	3	108.3	0.7	2	0.1	52.6	0.0	137	0.1	23.1	0.1
	7	190.1	1.2	118	0.7	1178.9	1.2	1211.7	1.3	168.2	1.1
	15	234.6	1.5	174	1.1	1476.2	1.5	1447.7	1.5	232.1	1.5
malathion	3	5.7	0.0	2	0.1	29.9	0.0	6	0.0	8.6	0.0
	7	28.36	0.1	299	1.9	1156.7	1.1	545	0.6	251.5	1.7
	15	82.36	0.5	457	3.0	2227.8	2.3	846	0.9	314.6	2.1
					C. At 50 °C						
dichloran	3	222.6	1.5	360.3	2.3	60.4	0.0	520	0.5	91.5	0.6
	7	396.5	2.6	411.6	2.7	1640	1.6	1627.7	1.7	309.0	2.1
	15	423.9	2.8	409.8	2.8	2155.4	2.2	2466.9	2.6	421.0	2.8
chlorothalonil	3	32.9	0.2	27.5	0.1	161	0.1	278	0.2	73.5	0.5
	7	156.9	1.0	242	1.6	1392.0	1.4	534	0.5	335.7	2.2
	15	247.8	1.6	373	2.6	2622.7	2.7	2018.8	2.1	406.7	2.7
methylchlorpyriphos	3	40.2	0.2	57.9	0.3	163	0.1	228	0.2	55.0	0.3
	7	203.3	1.3	191	1.2	937	0.9	690	0.7	165.0	1.1
	15	271.0	1.8	306	2.1	1817.5	1.8	1148.3	1.2	284.5	1.9
chlorpyriphos	3	31.9	0.2	113	0.7	735	0.7	545	0.5	120.9	0.8
	7	177.9	1.1	188	1.2	1180.8	1.2	1318.6	1.4	251.0	1.7
	15	319.6	2.1	309	2.1	2400	2.4	2312.2	2.4	332.3	2.2
folpet	3	28.79	0.1	42.3	0.2	625	0.6	104	0.1	90.3	0.6
	7	284.7	1.9	312	2.1	1750.5	1.7	1063.7	1.1	304.5	2.0
	15	332.7	2.2	322	2.2	2180	2.2	1553.6	1.6	330.5	2.2
α-endosulfan	3	18.82	0.1	66.0	0.4	151	0.1	201	0.2	35.4	0.2
	7	191.8	1.2	190	1.2	506	0.5	768	0.8	194.2	1.3
	15	222.3	1.5	215	1.5	1224.3	1.2	1285.8	1.3	220.8	1.5
β-endosulfan	3	154.8	1.0	87.4	0.5	122	0.1	204	0.2	90.0	0.6
	7	206.8	1.3	136	0.9	1305.6	1.3	1388.2	1.4	202.3	1.3
	15	223.9	1.5	212	1.4	1467.3	1.5	1413.6	1.5	222.4	1.5
malathion	3	46.8	0.3	130	0.8	70.9	0.0	535	0.5	51.9	0.3
	7	253.7	1.7	348	2.3	1541.3	1.5	894	0.9	256.0	1.7
	15	344.1	2.3	450	3.1	2627.5	2.7	1265.1	1.3	397.6	2.7

[a] The results are expressed as nanograms of pesticide per gram of plastic and nanograms of pesticides per square centimeter of plastic.

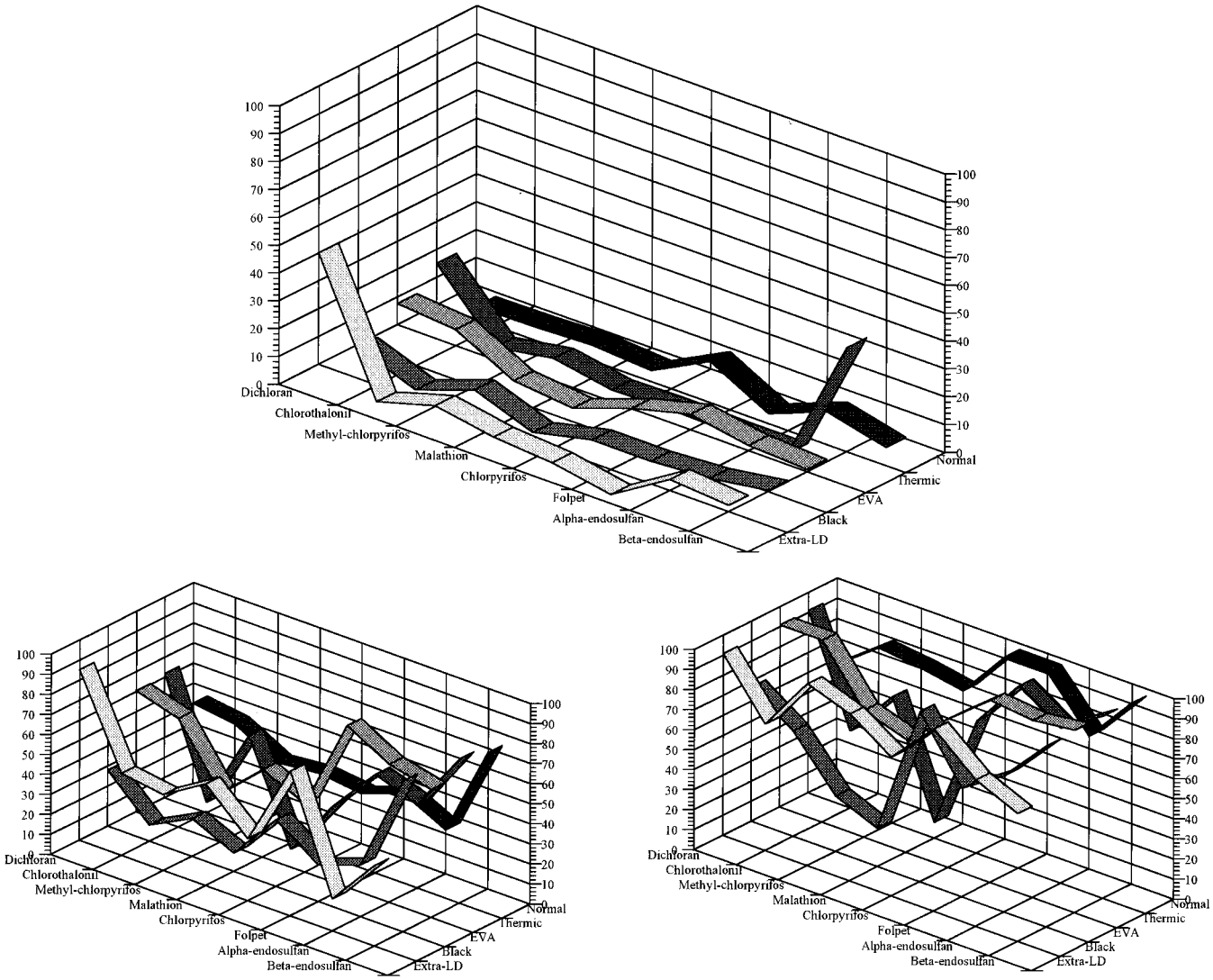

Figure 2. Percentage of absorption of each pesticide on each type of plastic. Exposure conditions were as follows: temperature, 35 °C; time, (a, top) 3 days, (b, lower left) 7 days, (c, lower right) 15 days.

Table 3. Activation Energy (kcal/mol) and Kinetic Constant Values ($Days^{-1}$)

compound	temp (°C)	thermic film	extra-LDPE	normal film	black film	EVA
dichloran	24	2.82×10^{-4}	1.04×10^{-4}	3.24×10^{-4}	4.18×10^{-4}	3.80×10^{-4}
	35	3.64×10^{-4}	2.51×10^{-4}	3.94×10^{-4}	4.46×10^{-4}	4.87×10^{-4}
	50	4.74×10^{-4}	3.00×10^{-4}	4.60×10^{-4}	4.67×10^{-4}	5.22×10^{-4}
E_a		3.31	7.23	2.26	0.72	2.10
chlorothalonil	24	2.45×10^{-4}	3.00×10^{-4}	4.23×10^{-4}	2.38×10^{-4}	4.37×10^{-4}
	35	2.96×10^{-4}	4.27×10^{-4}	5.11×10^{-4}	4.15×10^{-4}	4.94×10^{-4}
	50	3.33×10^{-4}	5.53×10^{-4}	5.94×10^{-4}	4.71×10^{-4}	5.41×10^{-4}
E_a		1.97	3.96	2.20	4.64	1.36
methylchlorpyriphos	24	3.31×10^{-4}	4.66×10^{-4}	4.24×10^{-4}	1.78×10^{-4}	3.84×10^{-4}
	35	4.10×10^{-4}	5.28×10^{-4}	5.06×10^{-4}	2.56×10^{-4}	4.48×10^{-4}
	50	4.49×10^{-4}	5.96×10^{-4}	5.20×10^{-4}	2.99×10^{-4}	4.72×10^{-4}
E_a		2.00	1.60	1.38	3.46	1.35
chlorpyriphos	24	4.06×10^{-4}	3.80×10^{-4}	2.71×10^{-4}	4.40×10^{-4}	2.25×10^{-4}
	35	4.79×10^{-4}	3.93×10^{-4}	4.75×10^{-4}	5.51×10^{-4}	3.64×10^{-4}
	50	5.06×10^{-4}	4.82×10^{-4}	6.01×10^{-4}	5.84×10^{-4}	4.14×10^{-4}
E_a		1.77	1.35	5.28	1.92	4.14
folpet	24	4.57×10^{-4}	4.79×10^{-4}	2.66×10^{-4}	2.75×10^{-4}	4.25×10^{-4}
	35	5.46×10^{-4}	5.12×10^{-4}	4.42×10^{-4}	4.10×10^{-4}	4.27×10^{-4}
	50	6.28×10^{-4}	6.00×10^{-4}	6.54×10^{-4}	4.31×10^{-4}	5.05×10^{-4}
E_a		2.07	1.33	5.83	3.12	0.98
α-endosulfan	24	4.28×10^{-4}	3.19×10^{-4}	4.40×10^{-4}	3.01×10^{-4}	4.36×10^{-4}
	35	5.41×10^{-4}	4.36×10^{-4}	4.46×10^{-4}	4.67×10^{-4}	4.98×10^{-4}
	50	5.46×10^{-4}	4.78×10^{-4}	4.95×10^{-4}	4.99×10^{-4}	5.25×10^{-4}
E_a		1.76	2.71	0.71	3.52	1.28
β-endosulfan	24	1.88×10^{-4}	3.39×10^{-4}	4.34×10^{-4}	3.84×10^{-4}	3.54×10^{-4}
	35	2.56×10^{-4}	3.86×10^{-4}	5.44×10^{-4}	4.97×10^{-4}	4.64×10^{-4}
	50	3.36×10^{-4}	3.99×10^{-4}	5.82×10^{-4}	5.37×10^{-4}	5.56×10^{-4}
E_a		3.73	1.09	1.96	2.23	2.95
malathion	24	1.06×10^{-4}	4.31×10^{-4}	3.56×10^{-4}	1.64×10^{-4}	2.85×10^{-4}
	35	1.34×10^{-4}	4.55×10^{-4}	4.62×10^{-4}	1.68×10^{-4}	3.84×10^{-4}
	50	3.94×10^{-4}	5.43×10^{-4}	5.33×10^{-4}	1.74×10^{-4}	4.72×10^{-4}
E_a		7.76	1.39	2.64	0.31	3.26

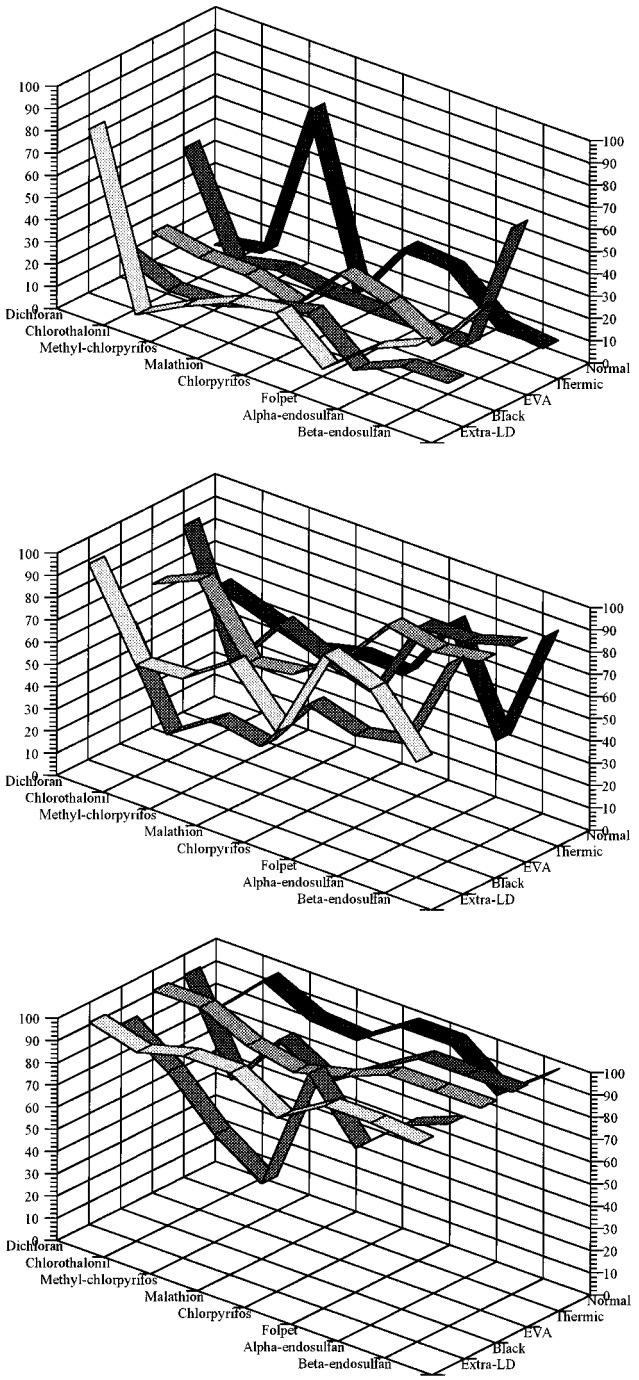

Figure 3. Percentage of absorption of each pesticide on each type of plastic. Exposure conditions were as follows: temperature, 50 °C; time, (a, top) 3 days, (b, middle) 7 days, (c, bottom) 15 days.

used as agricultural soil covers; (b) the lifetime of each pesticide; (c) the mutual compatibility within the group of selected pesticides, to avoid chemical reaction or degradation between them in the same solution or application; (d) the intended analytical procedure sensitivity; and (e) the chemical structure of these pesticides.

Absorption is a process highly dependent on the solubility, which depends on the chemical structure of either the solute or the solvent, the pesticide and the polymer, respectively.

On the other hand, if the chemical structure was the main factor affecting the absorption, compounds having similar structure should behave similarly in the absorption process. To demonstrate the effect of structure on absorption, two isomers such as α- and β-endosulfan and other two compounds, chlorpyriphos and methylchlorpyrifos, were included in this study.

Absorption Studies. The absorption process is expected to be influenced by both the temperature and contact time between the pesticides and the polymer. Both parameters were varied in the kinetic study. In an attempt to simulate the real temperature that could be reached on the film surface when the plastic is used as agricultural soil cover, three values of temperature (24, 35, and 50 °C) were selected to carry out the study. At each value, the plastic film was held in contact with the aqueous solution of pesticides for 3, 7, 15, and 20 days.

Table 2 shows the results obtained, and Figures 1−3 show some of them in three-dimensional diagrams.

Several interesting aspects can be emphasized from these data. First, there are the different performances of the plastic films under study. The black LDPE contains black carbon, and it could be expected to have a higher absorption ability than the other films. However, it behaves similarly to normal LDPE film. Consequently, it can be assumed that the presence of black carbon in the polymer does not affect the absorption of pesticides. On the other hand, thermic LDPE film and extra-LDPE films show a similar performance, whereas EVA, which is a copolymer, behaves quite differently from the rest of the LDPE films. This agrees with the idea of the relationship between structure and absorption ability.

The second aspect to be pointed out from the figures is the maximum absorption value, which is, in nearly all cases, about 100% of absorption with the longest contact time between pesticides and plastic films. This means that the absorption is kinetically slow. It is also necessary to take into account the liposolubility of these pesticides, which is responsible for the high partition coefficient between the polymer and the aqueous phase.

Finally, the third factor observed from the results obtained is the relationship between the chemical structure of the pesticides and the absorption ability of the plastic film. The two optical isomers α- and β-endosulfan behave differently on the same films, and the same phenomenon can be observed with chlorpyriphos and methylchlorpyriphos. Consequently, it can be confirmed that there is not a close relationship between chemical structure and absorption.

Kinetic Study. From all of the results obtained, the corresponding kinetic equations have been calculated. The first-order equation should be

$$\ln C_f/C_i = -Kt$$

where C_f is the final concentration (mol L^{-1}) of each pesticide in aqueous phase after the absorption process, C_i is the initial concentration (mol L^{-1}) of each pesticide in aqueous phase before the absorption, K is the kinetic constant, and t is the contact time (days) between the plastic film and the pesticide in aqueous phase. When the values of $\ln C_f/C_i$ were plotted versus the contact time, a straight line was obtained in all cases.

When the Arrhenius equation was applied at each temperature value, the activation energy was calculated. Table 3 shows the activation energy values as well as the kinetic constants obtained for all of the pesticides under study. As could be expected, when the activation energy increases, the absorption process is slower. From a general point of view it could be established that the absorption of pesticides on plastic films is an easy process which has low values of activation energy.

CONCLUSIONS

From the study carried out, several interesting conclusions are drawn:

(1) All of the pesticides under study were absorbed on the plastic films used as agricultural soil covers. This absorption is a kinetically slow process with kinetic constants of the order of 10^{-4}−10^{-3} and activation energy values ranging from 0.3 to 7.7 kcal when the pesticides are applied in aqueous phase.

(2) The absorption process on the plastic film is practically independent of the chemical structure of pesticides, since pesticides with very similar chemical structures or even optical isomers behave differently versus the absorption.

(3) The pesticides absorbed on the plastic films have great stability and do not seem to spontaneously degrade, even those whose decomposition in aqueous phase has been described elsewhere (Gray, 1994). This suggests that the plastic film remains contaminated by pesticides. This fact should be taken into account in the likely reuse or recycling of these plastic films.

LITERATURE CITED

Brydson, J. A. *Materiales Plásticos*, Instituto de Plásticos y Cauchos del CSIC: Madrid, 1995.

Desriac, P. The effect of pesticides on the life of greenhouse films. *Plasticulture* **1991**, *89*, 9−16.

Gray, N. F. *Drinking Water Quality. Problems and Solutions*; Wiley: New York, 1994.

Grob, K.; Kaelin, Y.; Artho A. Coupled LC-GC: the capacity of silica gel columns for retaining fat. *J. High Resolut. Chromatogr.* **1991**, *14*, 373−376.

Leidy, R. B.; Wright, C. G.; Dupree J. Exposure levels to indoor pesticides H. E. *Am. Chem Soc. Symp. Ser.* **1993**, *No. 522*, 282−295.

Nerín, C.; Tornés, A. R.; Domeño, C.; Cacho, J. Determination of OCPs in animal diet. A comparative study of clean-up procedures. *Fresenius' J. Anal. Chem.* **1995**, *352*, 364−371.

Plásticos en la Agricultura; Reciclado de Plásticos en España, ANAIP (Confederación Española de Empresarios de Plásticos), 1993; p 18.

Roy, P. C. Las industrias del reciclaje. *Tec. Ind.* (*Madrid*) **1994**, *No. 125*, 13−17.

Topp, E.; Smith, W. Sorption of the herbicides atrazine and metholachlor to selected plastics and silicone rubber. *Environ. Qual.* **1992**, *21*, 316−317.

Van der Hoff, G. R.; Gort, S. M.; Baumann, R. A.; Van Zoonen, P. Clean-up of some OCPs and pyrethroid insecticides by automated solid phase extraction cartridges coupled to capillary GC-ECD. *J. High Resolut. Chromatogr.* **1991**, *14*, 465−470.

Vuik, J.; Poll, J. M.; Vink, R.; de Vos, R. H. Absorption experiments of etridiazole and oxamyl on polyethylene sheets and PVC tubing used in horticulture. *J. Agric. Food Chem.* **1990**, *38*, 328−330.

Yeary, R. A.; Leonard, J. A. Measurements of pesticides in air during to lawns, trees and shrubs in urban environments. *Am. Chem. Soc. Symp. Ser.* **1993**, *No. 522*, 275−281.

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