

Assessing the Suitability of Recycled Plastics Used as Agricultural Soil Covers: Migration Study and Experimental Harvest

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The present work is focused on evaluating the suitability of recycling postconsumer agricultural plastic films again for the same use. The criteria to assess the suitability was based on migration study. Both overall and specific migration tests were performed, and the results obtained (ranging from 0.14 to 1.27 mg/dm² for overall migration and from not detectable to 6.98 µg/dm² for specific migration) show how, from this point of view, the recycled material can be safely proposed to be used again as agricultural soil covers. A theoretical discussion about the migration process is also presented and a simple mathematical model was applied to the data obtained, showing how total migration which is experimentally detected is theoretically predictable. These conclusions found were used to design and develop a controlled crop of tomato by using this recycled film. The use of the recycled plastic in the whole process and the behavior and properties of the pesticides absorbed in the postconsumer film are discussed.

Keywords: Pesticides; recycled postconsumer agricultural plastic; migration testing; diffusion; controlled crop

INTRODUCTION

One of the areas in which the plastic use is very important is in agriculture. In 1994, 126 000 tons of plastic material were used in Spain in the agricultural field which represents the 5.2% of the total plastic consumed in that year. The most important plasticulture technique used in Spain is mulching, and it consists of covering the agricultural fields with plastic at the earlier stage of the season to prevent loss of moisture and to protect the harvest from the destructive action of the wind (Llop and Pérez, 1992). In the 1991/92 season (last official figures), the surface covered by using this technique in Spain was 655 845 600 m². The plastic material used is mainly low-density polyethylene with an increasing volume of linear low-density polyethylene and copolymers such as ethylene–vinyl acetate copolymer from greenhouses and small tunnels (ANAIP, 1995).

Most of these films, once their role has finished, are recovered and recycled (ANAIP, 1995) to avoid environmental and economical problems, and because of the good mechanical properties of these recycled films (Campos et al., 1994; Roy, 1994), the best alternative is to reuse it again as agricultural soil cover (NFPA, 1995).

Nevertheless, the plastic films used in agricultural applications absorb pesticides and other chemicals sprayed on the crops (Nerín et al., 1996). Moreover, when these plastics are recycled, the pesticides remain in the plastic even after five recycling steps (Nerín et al., 1997). Pesticides are accumulative and toxic compounds (Worthing and Hance, 1991; Ballschmiter, 1996), and the possibility of using these recycled films implies a deep study about the likely contamination of the crop or the water in contact with them.

This way, migration testing is not an academic pursuit but a practical issue which can ensure that the

plastics materials are fit for their intended uses (Ashby, 1992; Castle, 1994). There are two proposed ways to carry out the migration testing: overall and specific migration tests (85/572/EEC; 90/128/EEC; 93/8/EEC) working with the established food simulants (85/572/EEC). Active research is focused on both topics (Sarriá et al., 1997; Komolprasert and Lawson, 1997; Philo et al., 1997; Suominen et al., 1997; Biles et al., 1997).

There are some situations in which the polymeric material is not in direct contact with food. In such cases, migration could occur in the vapor phase, and there is a general lack of work focused on this particular issue (Nielsen and Jägerstad, 1994; Gavara et al., 1997; Nerín et al., 1998). However, this mode of transfer has been proposed for the migration of packaging components to dry foods (Schwope and Reid, 1988) and has been shown to be possible for styrene migration from polystyrene (Linssen et al., 1991; Lehr et al., 1993).

The determination of migration into the fatty simulants defined in EC Directives (85/572/EEC; 93/8/EEC) such as olive oil is, for some packaging materials, difficult to carry out, while for other materials this fat test is virtually not applicable due to practical difficulties (de Kruijf and Rijk, 1997; Reeves, 1997). For this reason, various other volatile solvents have been proposed as alternatives to the commonly used fatty food simulants, including ethanol–water mixtures (Figge and Hilpert, 1991; Baner et al., 1992; EEC, 1993).

On the other hand, one of the major drawbacks of migration tests is that they are time-consuming—usually the time required is about 10 days, depending on the plastic application—and it is clear that predictive migration modeling offers advantages (Begley, 1997). There are a lot of studies which showed that migration is highly predictable for several migrants in several matrixes (Figge, 1980; Gandek et al., 1989; Goydan et al., 1990), and several mathematical methods have been proposed (Mercer et al., 1990; Laoubi and Vergnaud,

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1995; Limm and Hollifield, 1996; Baner et al., 1996, Piringer et al., 1998).

The aim of the work presented in this paper is multiple: first, to ensure that the postconsumer recycled plastic film is appropriate for a second use in the field as an agricultural soil cover according to its migration behavior; second, to evaluate the behavior of some volatile simulants proposed to replace the fatty simulants legislated; third, to check if the migration is predictable by using a simple physico-mathematical model; and finally, to use the results obtained by both migration and model estimation by developing an experimental harvest.

Safety Considerations. All handling of pesticide standards should be performed while wearing disposable, impervious laboratory gloves. Skin contact with highly concentrated pesticide compounds can be extremely harmful. Many of these highly toxic materials are toxic by dermal route. All handling of neat standards should be performed within a chemical fume hood or a glovebox to minimize inhalation of vapor and potential skin contact.

If primary standard material comes in contact with skin, thorough washing with copious amounts of soap and water should be performed immediately. Such an exposure should always be reported to supervisory personnel and a physician consulted at once. Delayed effects are characteristics of pesticides, and prompt reporting of exposure is essential.

Hydrogen is practically nontoxic. In high concentrations, this gas is a simple asphyxiant, and ultimate loss of consciousness may occur when oxygen concentrations fall below 18%. If large amounts of hydrogen are inhaled, move the person to fresh air and seek medical attention at once. In the event of a leak, remove all ignition sources and allow the gas to disperse with increased ventilation. Hydrogen disperses rapidly in normal open environments. Respiratory protection may be necessary in the event of a leak in a confined area.

Hydrogen is a highly flammable gas that burns with an almost invisible flame and low heat radiation. Hydrogen forms explosive mixtures with air from 4 to 75 vol %. These explosive mixtures of hydrogen with air (or oxygen) can be ignited by a number of finely divided metals (such as common hydrogenation catalysts). Hydrogen is a reducing agent and reacts explosively with strong oxidizers such as halogens (fluorine, chlorine, bromine, or iodine) and interhalogen compounds. Moreover, expansion of hydrogen released rapidly from a compressed cylinder will cause evolution of heat due to its negative Joule–Thompson coefficient.

Thus, hydrogen cylinders should be clamped or otherwise supported in place and used only in areas free of ignition sources and separate from oxidizers. In the event of a fire, shut off the flow of gas and extinguish with carbon dioxide, dry chemical, or halon extinguishers.

MATERIALS AND METHODS

Pesticide Standards. Chlorpyrifos, procymidone, malathion, β -endosulfan, vinclozolin, tolclofos-methyl, 4,4'-dichlorobenzophenone, bromopropylate, and tetradifon (purity > 98.5%) were from Dr. S. Ehrenstorfer GmbH (Augsburg, Germany). *o,p*-DDE was from Certified Reference Material (Terdington, U.K.). Chlorobenzilate, 99.0%, was supplied by Riedel de Håen (Seelze, Germany). 2,4,5,2',3',4'-Hexachlorobiphenyl, PCB 138, was used as the internal standard and was from Chem Service (West Chester, PA).

Solvents. All the solvents used were supplied by Merck (Darmstadt, Germany) in gradient grade for chromatography quality.

Plastic Material. The recycled plastic films (90% w/w low-density polyethylene (LDPE) and 10% w/w ethylene–vinyl acetate copolymer (EVA)) of several thicknesses (35, 60, and 90 μ m) were obtained from the Empresa de Gestión Medioambiental (EGMASA) (Sevilla, Spain).

The virgin plastic films were utilized in the Huelva region of Spain for strawberry farming and were produced of black LDPE for mulching and of EVA for small tunnels. After finishing the season, in which the pesticides detected were sprayed on the crop, the postconsumer plastic was recycled by using the following procedure: size reduction, washing, drying, and pelletizing. These contaminated recycled resins were used to produce the plastic films used in the present work.

Apparatus. A Varian (Harbor City, CA) Star 3400 CX gas chromatograph equipped with an electron capture detector (ECD) (^{63}Ni) and a Varian 8200 autosampler was used. A temperature programmable septum-equipped-programmable injector (SPI) was used with the following program: initial temperature, 50 $^{\circ}\text{C}$; held for 0.10 min; ramped at 150 $^{\circ}\text{C}/\text{min}$ to 240 $^{\circ}\text{C}$; and held for 35.5 min.

The capillary column used was a MFE-73 (cross-linked 5% phenyl methyl silicone) with 60 m \times 0.25 mm \times 0.25 μ m film thickness supplied by Análisis Vinicos (Madrid, Spain). The temperature program used was as follows: initial temperature, 50 $^{\circ}\text{C}$ for 1 min; ramped at 25 $^{\circ}\text{C}/\text{min}$ to 215 $^{\circ}\text{C}$; and held for 2 min. A second ramp was programmed at 2 $^{\circ}\text{C}/\text{min}$ up to 250 $^{\circ}\text{C}$, which was held for 1.5 min. A third ramp at 25 $^{\circ}\text{C}/\text{min}$ increased the temperature to 280 $^{\circ}\text{C}$, which was held for 5 min. The detector temperature was 300 $^{\circ}\text{C}$. The carrier gas was hydrogen (C-50 quality) with a flow rate of 1.35 mL/min. The makeup gas was nitrogen at a flow rate of 35 mL/min.

Overall Migration Test Procedure. The test procedures for aqueous simulants are similar in all the published methods. In this work, we use the scheme reported by Tice and Cooper (Tice and Cooper, 1994), according to the guidelines given by the European Directive (90/128/EEC). The overall migration value is determined gravimetrically. All of the overall migration results shown in this paper are the mean of four determinations and have an accuracy of ± 0.1 mg.

Specific Migration Test Procedure. Migration of selected pesticides from recycled postconsumer plastic was measured in two established simulants, distilled water and 15% ethanol (v/v) in aqueous solution (85/572/EEC). To accomplish one of the objectives described in the Introduction, which is to evaluate some proposed food simulants to substitute the fatty food simulant olive oil (EEC, 1993), the test was also carried out by using 30%, 50%, and 95% ethanol/water (v/v) simulants. The test conditions, i.e., time and temperature, were selected according to those established in the legislation (10 days at 40 $^{\circ}\text{C}$) (Shorten, 1992).

The film surface used in each test was 126 cm², and the volume of simulant used was 20 mL. Three independent studies (each one having two replicates) were performed for each plastic and migration conditions.

Simulant and Plastic Analysis. Three different procedures were carried out in order to analyze the pesticides present in each type of sample.

I. Analysis of Pesticides in Distilled Water, 15% Ethanol, 30% Ethanol, and 50% Ethanol Used as Simulants. Ten milliliters of simulant was extracted three times, each one with 2 mL of dichloromethane. Variable amounts of ammonium sulfate (ranging from 1.8 g for water to 0.5 g for 50% ethanol) were added to break the emulsion. The mixture was automatically shaken for 10 min, and the organic extracts were collected together.

The extracts were then dried with anhydrous sodium sulfate and filtered through a polytetrafluoroethylene (PTFE) syringe filter of 0.2 μ m pore size. The filtered extract was then carefully evaporated to dryness (40 $^{\circ}\text{C}$) by using a nitrogen stream, and the solid residue was redissolved into 2 mL of *n*-hexane. This final extract was concentrated up to 1 mL under a nitrogen

Table 1. Pesticides Detected in the Postconsumer Recycled Plastic^a

compound (CAS number)	function	log K_{ow}^b	concn (plastic thickness)		
			(35 μm)	(60 μm)	(90 μm)
vinclozolin (50471/44/8)	fungicide	3.0	2.32	2.20	2.25
tolclofos-methyl (57018/04/9)	fungicide	4.6	1.17	1.17	1.35
malathion (121/75/5)	insecticide/acaricide	2.7	1.07	1.00	1.15
chlorpyrifos (2921/88/2)	insecticide	5.0 (4.7–5.3)	0.42	0.40	0.48
4,4'-dichlorobenzophenone (90/98/2)	metabolite of keltane	na	1.24	1.19	1.21
<i>o,p</i> -DDE (3424/82/6)	metabolite of DDT	6.4 (5.7–7.0)	0.03	0.01	0.01
chlorobenzilate (510/15/6)	acaricide	4.6	0.51	0.50	0.50
procymidone (32809/16/8)	fungicide	3.1	5.46	5.12	5.51
β -endosulfan (32213/65/9)	insecticide	2.9 (2.2–3.6)	0.40	0.42	0.54
bromopropylate (18181/80/1)	insecticide/acaricide	na	10.5	10.2	10.6
tetradifon (116/29/0)	acaricide	na	2.39	2.23	2.28

^a The concentration results are the average of three replicates; RSD < 7%. The results are expressed as μg of pesticide/g of plastic.
^b na: not available (RS&ML, 1998).

Table 2. Stability Study Results and Validation of the Methods: Recovery Percentages^a

compound	simulants				
	distilled water	15% ethanol	30% ethanol	50% ethanol	95% ethanol
vinclozolin	95.9 \pm 2.4	94.4 \pm 2.2	93.2 \pm 2.4	96.6 \pm 2.0	96.9 \pm 2.2
tolclofos-methyl	94.9 \pm 2.6	95.9 \pm 3.0	95.4 \pm 2.8	92.9 \pm 2.9	96.7 \pm 2.7
malathion	89.0 \pm 3.7	90.8 \pm 4.0	88.0 \pm 4.1	87.8 \pm 3.6	89.9 \pm 4.2
chlorpyrifos	91.1 \pm 2.5	92.3 \pm 2.4	94.2 \pm 2.6	93.6 \pm 2.6	89.3 \pm 2.6
4,4'-dichlorobenzophenone	90.7 \pm 2.4	85.2 \pm 2.1	95.0 \pm 2.6	85.9 \pm 2.4	90.0 \pm 2.4
<i>o,p</i> -DDE	96.5 \pm 2.0	97.2 \pm 1.8	99.8 \pm 2.2	96.2 \pm 2.1	98.1 \pm 2.1
chlorobenzilate	92.9 \pm 3.6	91.6 \pm 3.4	90.1 \pm 4.2	91.9 \pm 4.4	93.7 \pm 4.1
procymidone	91.7 \pm 3.8	93.8 \pm 4.1	85.8 \pm 4.0	91.9 \pm 3.7	90.7 \pm 4.0
β -endosulfan	90.0 \pm 3.1	92.1 \pm 3.0	87.5 \pm 2.8	94.0 \pm 2.6	91.9 \pm 2.9
bromopropylate	85.2 \pm 4.0	87.9 \pm 3.8	88.2 \pm 3.6	86.9 \pm 4.1	91.9 \pm 3.9
tetradifon	82.5 \pm 5.2	75.0 \pm 5.7	78.4 \pm 6.4	75.3 \pm 6.2	75.6 \pm 6.8

^a Results expressed as follows: $x_m \pm ts$, where x_m is the average of four replicates; t is the t value at 95% confidence level for three degrees of freedom, namely 3.18 (Miller and Miller, 1988), and s is the standard deviation.

stream (40 °C) and filtered through the PTFE syringe filter to an autosampler (2 mL) vial. Finally, the standard used for chromatographic quantitation, PCB 138, was added, and the solution was analyzed by GC-ECD under the chromatographic conditions previously described.

II. Analysis of Pesticides in 90% Ethanol Used as Simulant. In this case, all the simulant was filtered through a Whatman No. 1 P/S filter to separate the water. Taking into account the octanol/water coefficients for these pesticides (Noble, 1993), no losses due to the water solubility of the pesticides are likely expected in the filtration process.

The ethanolic phase was then evaporated to dryness under a nitrogen stream, and the residue was dissolved into 2 mL of *n*-hexane. This solution, after filtering and adding the quantitation standard, was analyzed by GC-ECD.

III. Extraction of the Remaining Pesticides from Recycled Film. The extraction of pesticides from the recycled film was carried out by using a previously developed method (Nerin et al., 1997) based on supercritical fluid extraction, and the final determination was made using GC-ECD.

Blank analyses were carried out for the methods proposed above.

Validation of the Methods. Obviously, it is essential to confirm if the values obtained by the proposed methods are the true concentration values of the pesticides in the plastic or in the simulant.

First, the raw postconsumer plastic was analyzed by using three different methods, namely supercritical fluid extraction (SFE), total dissolution in boiling toluene, and ultrasonic extraction (Nerin et al., 1997). The recovery percentages obtained between the methods were in all the cases >92%, the only exception being *o,p*-DDE (80% working with SFE and 70% by using sonication) due to its extremely low concentration on the sample. The concentration found for each pesticide in each plastic is shown in Table 1.

To check the stability of these pesticides under the migration conditions as well as to validate the analytical methods proposed for the selected simulants, the procedure was applied

as follows. In a glass vial containing 20 mL of each simulant, 40 μL of an *n*-hexane solution containing 150 $\mu\text{g}/\text{mL}$ of each pesticide was added. The vial was placed into an oven at 40 °C for 10 days. Then the analysis of each simulant was carried out following the methods that are listed above. Table 2 shows the recovery percentages obtained. As can be seen, all of them seem to be stable under the migration conditions used and the analytical methods applied are quantitative, with the only exception of tetradifon in the most ethanolic simulants. But even in this case, the recovery obtained (>75%) is enough to accomplish our objectives.

Balance of Pesticides. Once the methods are validated, it is important to know the behavior of the pesticides in the migration test. For this specific purpose, the balance of pesticides between the plastic and the simulant was carried out for all the pesticides in all the simulants.

Considering the content of each pesticide in the raw plastic material as its maximum concentration (100%), the sum of the concentration remaining in the plastic and that obtained in the simulant should be equal to this initial value. The results obtained in the analysis of 90 μm thickness plastic are shown in Table 3, while Figure 1 shows the behavior of one selected compound, namely vinclozolin, which represents the general performance of the pesticides.

Controlled Crop. Three parallel rows of 80 m \times 0.8 m each were covered by plastic. Two of them were covered by using the postconsumer recycled plastic whereas virgin black LDPE was applied to the other. The minimum distance between two test rows was about 20 m. Therefore, no interaction between the plastic test rows is likely expected.

The variety of tomato used was an industrial one, UC-82, used for juice and canning purposes. The plants were planted every 30 cm on the three rows. The maximum height of the plant is about 50 cm, so most of the fruits were in direct contact or very near to the plastic film.

The experiences were designed as follows: one of the postconsumer recycled experiences was carried out without

Table 3. Balance of Pesticides^a

compound	1		2		3		4		5	
	A	B	A	B	A	B	A	B	A	B
vinclozolin	82.9	15.3	28.6	60.6	6.5	82.9	6.5	78.6	6.1	87.4
tolclofos-methyl	79.7	8.9	75.4	13.2	66.9	23.3	59.6	25.3	6.9	79.9
malathion	79.4	1.4	1.0	70.0	0.1	78.0	ND	79.7	ND	81.8
chlorpyrifos	75.4	4.1	82.1	12.0	83.0	6.3	78.4	20.8	ND	97.4
4,4'-dichlorobenzophenone	87.5	ND	82.6	1.0	64.0	12.8	66.8	18.3	ND	95.3
<i>o,p</i> -DDE	85.0	ND	ND	ND	ND	ND	ND	ND	ND	ND
chlorobenzilate	96.7	ND	20.7	48.8	ND	79.3	ND	77.5	ND	97.3
procymidone	85.4	0.3	25.7	56.8	21.7	62.3	18.1	65.4	0.4	91.6
β -endosulfan	98.0	ND	60.2	26.2	44.3	53.2	37.1	53.0	ND	95.8
bromopropylate	98.2	ND	100.4	ND	86.2	13.4	60.4	38.0	6.3	90.7
tetradifon	87.5	12.5	85.2	12.0	66.2	11.1	49.4	12.4	ND	17.4

^a All the results are expressed as percentages, considering the concentration in the raw postconsumer recycled plastic as 100%. Simulants codified as follows: 1, distilled water; 2, 15% ethanol; 3, 30% ethanol; 4, 50% ethanol; 5, 95% ethanol. A: plastic. B: simulant. ND: not detectable.

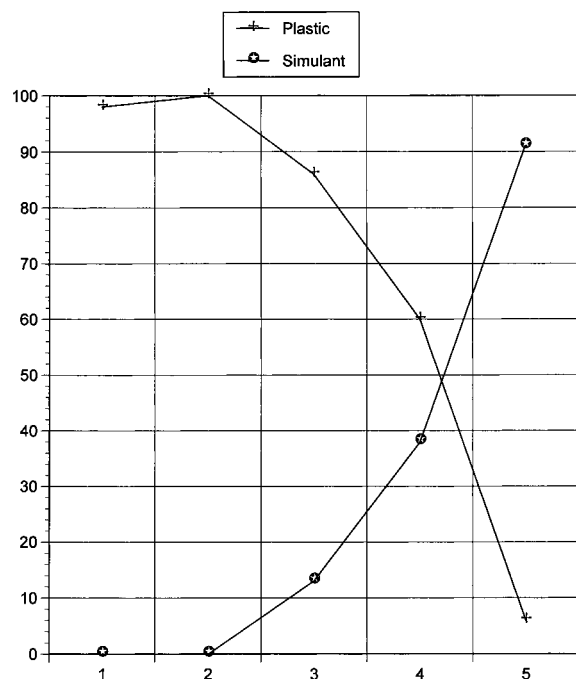


Figure 1. Balance of pesticides: bromopropylate. Simulants codified as follows: 1, distilled water; 2, 15% ethanol; 3, 30% ethanol; 4, 50% ethanol; 5, 95% ethanol.

further application of pesticides whereas the other two experiences (postconsumer and virgin plastic) were treated as usual.

Analysis of Tomato Samples. Two methods were tested to analyze the concentration of pesticides in the tomato samples. One of the methods (IV) was a slight variation of the usual methods for pesticide residues analysis in a vegetable matrix described in the literature (Valverde et al., 1991; Kadenzcki et al., 1992; Holstege et al., 1995). The other method (V) was developed in our laboratory. It consists of applying two sequential ultrasonic extractions of 10 min, each one by using 100 mL of dichloromethane to a mixture of tomato sample:anhydrous sodium sulfate:florisil (1:1:1, w/w/w). All the organic extracts were collected together and evaporated to dryness by using rotary evaporation (40 °C) and nitrogen stream (40 °C). The solid extract was then redissolved in *n*-hexane in the ultrasonic bath for 5 min and concentrated up to 1 mL in the nitrogen stream (40 °C). The extract was filtered through a PTFE syringe filter (0.2 μ m pore size) to an autosampler (2 mL) vial. This solution, after adding the internal standard, PCB 138, was analyzed by using the GC-ECD.

Figure 2 shows the results obtained in the comparison of the two methods in extracting a 250 ng/g spiked tomato sample for each pesticide. The spiking procedure was as follows. The

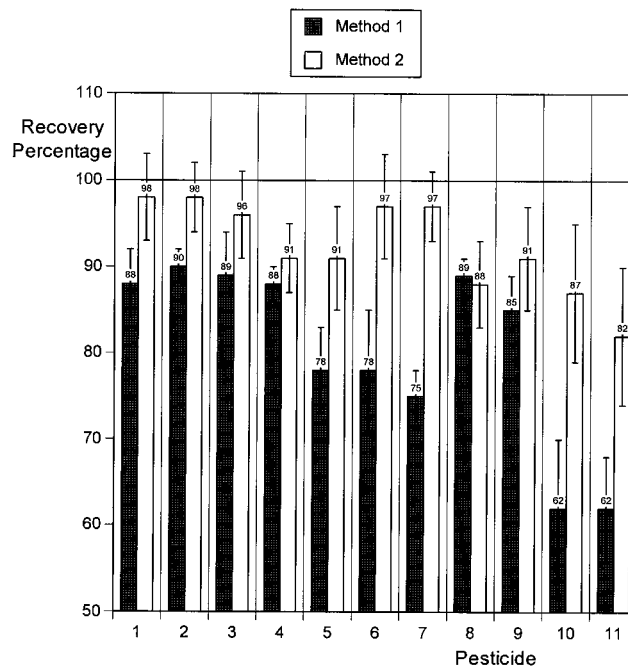


Figure 2. Recovery percentage comparison for the two analytical methods proposed for the tomato samples analysis. Pesticides codified as follows: 1, vinclozolin; 2, tolclofos-methyl; 3, malathion; 4, chlorpyrifos; 5, 4,4'-dichlorobenzophenone; 6, procymidone; 7, *o,p*-DDE; 8, chlorobenzilate; 9, β -endosulfan; 10, bromopropylate; 11, tetradifon.

tomato sample (20–25 g) was triturated, and a solution of pesticides in methanol were added giving a final concentration of 250 ng/g of each compound. The mixture was mechanically shaken for 30 min, and it was stored at 4 °C for 72 h prior to the analysis.

Table 4 shows the detection and quantitation limit for all the procedures developed, expressed as the concentration which gives a signal/noise ratio of 3 and 10, respectively.

RESULTS AND DISCUSSION

The pesticides were selected according to those previously detected in the postconsumer recycled plastics (C. Nerín et al., 1995). Table 1 shows the compounds identified in which 10 pesticides and 2 metabolites, 4,4'-dichlorobenzophenone and *o,p*-DDE, were reported. As can be seen in this table, a quite complex mixture of insecticides, acaricides, and fungicides was found, as can be expected due to the fact that these plastic films have been used mainly for strawberry and cotton cultivation.

Overall Migration Results. The results obtained are shown in Table 5. The overall migration test

Table 4. Detection (DL) and Quantification (QL) Limits for All the Proposed Methods^a

compound	I		II		III		IV		V	
	DL	QL	DL	QL	DL	QL	DL	QL	DL	QL
vinclozolin	0.1	0.15	0.2	0.3	0.06	0.08	0.07	0.1	0.1	0.16
tolclofos-methyl	0.12	0.18	0.2	0.3	0.03	0.045	0.12	0.19	0.15	0.25
malathion	0.15	0.3	0.35	0.65	0.07	0.15	0.07	0.14	0.04	0.09
chlorpyrifos	0.1	0.2	0.07	0.15	0.05	0.1	0.04	0.1	0.04	0.1
4,4'-dichlorobenzophenone	0.09	0.15	0.2	0.3	0.11	0.17	0.085	0.13	0.09	0.14
procymidone	0.1	0.23	0.3	0.7	0.13	0.3	0.1	0.25	0.15	0.35
<i>o,p</i> -DDE	0.008	0.013	0.05	0.08	0.007	0.011	0.002	0.003	0.006	0.01
chlorobenzilate	0.04	0.13	0.08	0.27	0.01	0.04	0.03	0.12	0.08	0.27
β -endosulfan	0.02	0.08	0.1	0.3	0.012	0.04	0.005	0.02	0.01	0.05
bromopropylate	0.07	0.29	0.15	0.6	0.04	0.2	0.01	0.05	0.05	0.2
tetradifon	0.05	0.17	0.25	0.78	0.05	0.15	0.015	0.04	0.06	0.25

^a Data expressed as μg of pesticide/g of matrix. Methods (I–V) identification and description in the text.

Table 5. Overall Migration Results^a

plastic	simulant	overall migration value (mg/dm ²)	overall migration value (mg/kg)
35 μm	distilled water	0.439	1.656
	15% ethanol	0.382	1.037
	30% ethanol	0.278	1.089
	50% ethanol	0.146	0.577
	95% ethanol	0.715	2.715
60 μm	distilled water	0.481	1.049
	15% ethanol	0.439	0.807
	30% ethanol	0.292	0.609
	50% ethanol	0.141	0.528
	95% ethanol	0.564	1.045
90 μm	distilled water	0.549	0.843
	15% ethanol	0.420	0.596
	30% ethanol	0.284	0.333
	50% ethanol	0.140	0.176
	95% ethanol	1.266	1.817

^a All the results are the average of four determinations. %RSD < 5%.

determines the total amount of substances which are able to be transferred from the plastic material or article to specific foodstuffs. So, the overall migration value affords some idea about the degree of alteration (toxic and/or organoleptic) of the food to be expected and about the likely behavior of the food packaging material. As shown in Table 5, there is a considerable increase in the overall migration value working with the high ethanol content simulant, due to its high solvent strength.

However, the highest value obtained is 1.3 ± 0.3 mg/dm², working with 95% ethanol as simulant and the plastic of 90 μm thickness. Article 2 of European Union Directive 90/128/EEC (90/128/EEC) established an overall migration limit of 10 mg/dm² or 60 mg/kg, so none of the simulants tested exceed this overall migration

limit. Consequently, the plastic material seems to be appropriate to be used again as agricultural soil cover.

Specific Migration Results. The overall migration test makes no attempt to identify the nature of the substances, and consequently the result has no significance about the possible hazardous contamination of the foodstuffs by the substances. So, when substances such as pesticides which have a clear toxicological interest are present in the plastic material, the safety of the food in contact with the plastic material should be controlled by individually checking the migration behavior of these compounds.

Table 6 shows the results obtained in the migration test. As can be seen, the migration values are quite different from one pesticide to another. These differences can be attributed to both their chemical structure and solubility properties (expressed by the octanol/water partition coefficients in Table 1). All of the pesticides can be distributed into two groups: those which have very low or even not detectable migration values in water or in the most aqueous simulant, behavior represented by chlorpyrifos in Figure 3a, and those which have significant migration values in all the simulants, similar to vinclozolin in Figure 3b. However, all the pesticides increase their migration values with the content of ethanol in the simulant as could be expected according to their K_{ow} values.

From a theoretical point of view, migration processes can be divided in two steps: first, the diffusion of the migrant across the polymeric matrix, and second, the solvation of this migrant into the simulant (Begley, 1993; Gavara, 1996). In the case of the aqueous simulant or even that with low ethanol content the migration seems to be controlled by both the diffusion of the migrant across the polymeric matrix and by the rela-

Table 6. Specific Migration Results^a

compound	plastic 35 microns					plastic 60 microns					plastic 90 microns				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
vinclozolin	0.11	0.36	0.51	0.48	0.53	0.16	0.55	1.10	0.94	1.10	0.20	0.70	1.33	1.27	1.53
tolclofos-methyl	0.03	0.04	0.07	0.08	0.24	0.05	0.08	0.11	0.16	0.53	0.04	0.18	0.23	0.22	0.95
malathion	0.01	0.19	0.22	0.22	0.26	0.01	0.37	0.44	0.40	0.51	0.01	0.38	0.46	0.48	1.01
chlorpyrifos	0.01	0.01	0.01	0.02	0.10	ND	0.01	0.02	0.03	0.22	0.01	0.01	0.02	0.07	0.43
4,4'-dichlorobenzophenone	ND	0.01	0.05	0.08	0.40	ND	ND	0.11	0.13	0.59	ND	0.01	0.06	0.23	0.97
<i>o,p</i> -DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
chlorobenzilate	ND	0.06	0.10	0.10	0.13	ND	0.11	0.22	0.22	0.27	ND	0.18	0.30	0.30	0.35
procymidone	0.01	0.77	0.88	0.92	1.29	ND	1.54	1.66	1.80	2.73	ND	1.52	2.60	2.88	3.85
β -endosulfan	ND	0.03	0.05	0.05	0.10	ND	0.06	0.11	0.11	0.20	ND	0.16	0.30	0.26	0.38
bromopropylate	ND	ND	0.36	1.03	2.47	ND	ND	0.49	2.08	5.03	ND	ND	0.23	4.77	6.98
tetradifon	0.09	0.07	0.07	0.08	0.11	0.01	0.14	0.14	0.14	0.22	0.02	0.12	0.12	0.20	0.34

^a ND: not detectable. Simulants are codified as follows: 1, distilled water; 2, 15% ethanol; 3, 30% ethanol; 4, 50% ethanol; 5, 95% ethanol. All the results are the average of four determinations. %RSD < 7 except for tetradifon (%RSD < 9). All the results are expressed as μg of pesticide/dm² of plastic.

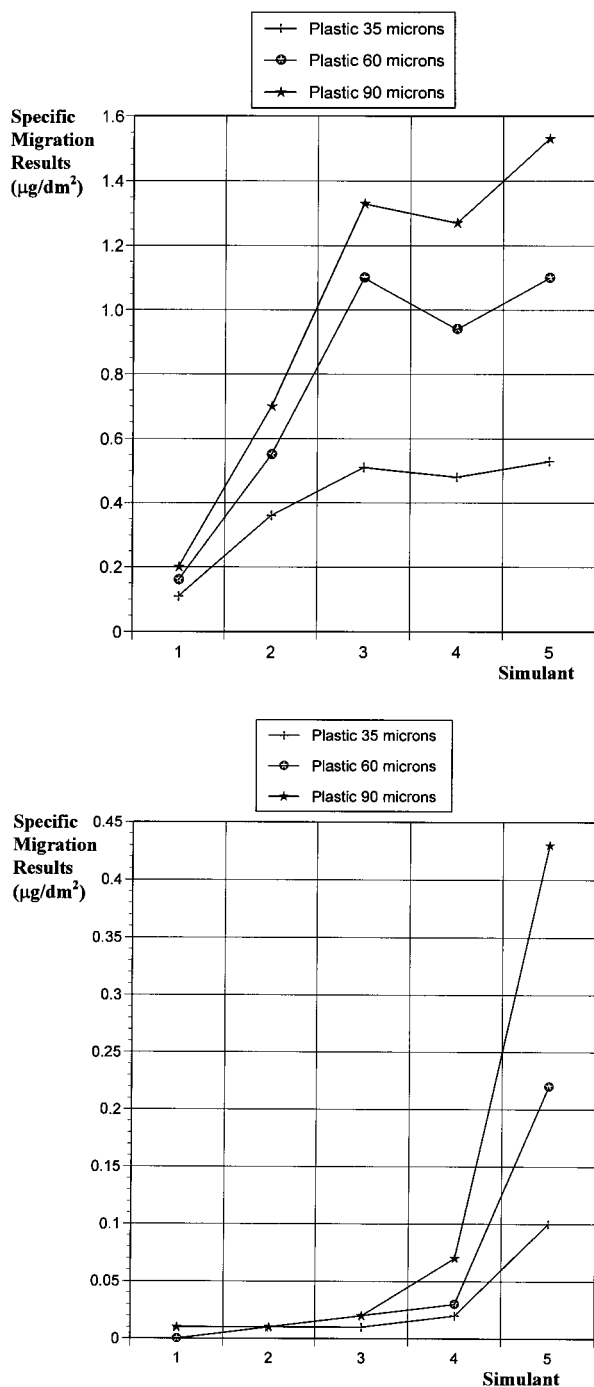


Figure 3. Specific migration results: (a, top) vinclozolin, (b, bottom) chlorpyrifos. All of the results are expressed as $\mu\text{g}/\text{dm}^2$ of pesticide/ dm^2 of plastic. Simulants codified as follows: 1, distilled water; 2, 15% ethanol; 3, 30% ethanol; 4, 50% ethanol; 5, 95% ethanol.

tively slow solvation of the migrant, pesticide in this case, in the simulant. This situation can be compared to those in which the food dissolves badly the migrant.

On the other hand, in simulants with higher ethanol content, the partition equilibrium for the migrant between the simulant and the matrix for the migrant is clearly very favorable to the simulant. So, in this case, there is no solvation limitation, and once the migrant reaches the polymer/simulant interface, it is immediately solvated. This phenomenon implies that the migration value only depends on the diffusivity of the migrant through the polymer, and consequently, the

migration process depends on just the polymer–migrant interaction.

However, the test time, 10 days, seems to be enough to allow the migrants to diffuse through the polymeric matrix and reach the interface. Working with the more ethanolic simulants, the concentration of migrants detected in the simulant is higher for the thicker film, according to the hypothesis stated above; the thicker film has the higher mass/surface ratio, and therefore the total amount of migrants found in the simulant depends, for these simulants, only on the plastic mass under study.

Modeling Migration. As was mentioned above, probably the major drawback of migration testing is that it is time-consuming. So, a number of mathematical models have been proposed to predict the migration of chemicals from packaging to food (Pugh, 1994). Most of these methods are based on Fick's laws for the diffusion (Begley, 1997).

In the present work, we try to check if, by using a simple and easy-to-use migration model, one can achieve a reasonable estimation of the diffusion for one chemical. This way, the solution proposed by Crank (Crank, 1975) for Fick's second law, i.e., in this case for the diffusion-controlled migration, was used. This equation was as follows

$$M_T = 2C_0\rho\sqrt{D_P t/\pi} \quad (1)$$

where M_T is the mass that migrates per unit surface area, C_0 is the concentration (w/w) of the migrant in the plastic, ρ is the polymer density (for this test plastic, $0.84 \text{ g}/\text{cm}^3$), D_P is the diffusion coefficient of the migrant in the polymer, and t is the package lifetime (i.e., the migration test time) in seconds. This equation assumes that there is no solubility effects and that other external phase effects (mixing or reaction effects) are minimal. This assumption lead to a significant overestimation (Baner et al., 1996), but this is not a problem but an advantage when human health considerations are involved.

All parameters in eq 1 are generally known or are easy measured except the diffusion coefficient. This can be measured by carrying out kinetic experiments, which are time-consuming and costly, or by using empirical equations proposed to this particular issue. According to our "simplest" start point, one of the latter was used. In particular, we use the relationship proposed by Piringer (Piringer, 1994)

$$D_P = 10^4 \exp[A_P - aMW - b(1/T)] \quad (2)$$

where A_P is the contribution of the polymer's characteristics on the diffusivity (A_P value for LDPE is 9), MW is the migrant molecular weight, T is the temperature in K, and a and b are correlation constants with values of 0.010 and 10 450, respectively.

Table 7 shows the diffusion coefficients and the theoretical migration values obtained for the three plastics evaluated. All model values exceed the theoretical maximum values for mass balance, which are also listed in the table. So, total migration of pesticides can be expected. For comparison purposes, the experimental migration data found for the pesticides in the 95% ethanol simulant, the simulant with less solvation limitations, are presented in the same table.

Table 7. Diffusion Coefficients and Theoretical Migration Values^a

compound	D_p ($\times 10^{-10}$) (cm^2/s)	plastic 35 μm			plastic 60 μm			plastic 90 μm		
		model	balance	expt	model	balance	expt	model	balance	expt
vinclozolin	15	0.078	0.007	0.005	0.082	0.011	0.011	0.076	0.017	0.015
tolclofos-methyl	13	0.040	0.003	0.002	0.040	0.006	0.005	0.042	0.010	0.010
malathion	9.9	0.030	0.003	0.003	0.030	0.005	0.005	0.032	0.010	0.010
chlorpyrifos	8.2	0.010	0.001	0.001	0.011	0.002	0.002	0.012	0.004	0.004
4,4'-dichlorobenzophenone	22	0.050	0.004	0.004	0.050	0.006	0.006	0.049	0.010	0.010
procymidone	16	0.180	0.016	0.013	0.200	0.027	0.026	0.190	0.042	0.039
<i>o,p</i> -DDE	11	7.2×10^{-4}	8.8×10^{-5}		3.8×10^{-4}	5×10^{-5}		2.0×10^{-4}	7.6×10^{-5}	
β -endosulfan	4.7	0.014	0.001	0.001	0.016	0.003	0.003	0.014	0.004	0.004
chlorobenzilate	11	0.008	0.001	0.001	0.009	0.003	0.002	0.090	0.004	0.004
bromopropylate	3.8	0.180	0.031	0.025	0.190	0.051	0.050	0.180	0.080	0.070
tetradifon	7.8	0.060	0.007	0.001	0.060	0.011	0.002	0.056	0.017	0.003

^a All the migration results are expressed as μg of pesticide/ cm^2 of plastic.

As can be seen, the total migration hypothesis results obtained by model application and the experimental results are very close, with the only exception of tetradifon, as could be expected from the results obtained in the balance of pesticides (Table 3). This good relationship is another confirmation of the discussion about the migration mechanism developed above: for the more ethanolic simulants, no solubility limitations are noted and the migration process is only controlled by diffusion.

Controlled Crop. Finally, a controlled crop of tomato was developed to check the actual behavior of the postconsumer recycled plastic.

The physical behavior of the plastic was appropriate; neither breaks nor losses of physical properties of plastic were detected along the crop. The agronomic features of the crop were also satisfactory; no differences in quantity or quality of the production were found between the recycled and virgin polymer.

A remarkable point is that even in the recycled plastic without additional treatment no damages from *Heliothis amigera*, a common pest particularly active in the area, were detected. So, one can think about the possibility of using the pesticides previously absorbed in the plastic to protect the following crops, in a way similar to the additives in conventional packaging, reducing or even eliminating further application of pesticides.

However, this fact can be attributed to a particularly good year in terms of pests or even to a protection of this row from the others despite the long distance (~ 20 m) between them. Therefore, this statement implies a deeper study along following harvests.

Sampling of tomato were carried out at two heights, fruit in direct contact with the plastic row and fruit without any contact with it for the three test rows. The two methods described in the Experimental Section were applied to the tomato samples. None of the pesticides were detected at all.

CONCLUSIONS

From the study described in this paper, several interesting conclusions can be highlighted. The post-consumer recycled plastic is appropriate to be reused again as agricultural soil cover according to both mechanical and chemical properties.

The last statement was checked by carrying out overall and specific migration tests. Concerning the overall measurements, in all the cases the overall migration values are well below the legislated migration limit of the EU regulation. From the specific migration test for aqueous simulants, no migration or migration

at very low levels were detected. The migration is higher in the ethanolic simulants than in the aqueous ones but, as was demonstrated by carrying out a controlled crop, no significant migration to the fruit was detected at all. From this point of view, the reuse of recycled postconsumer agricultural plastics as agricultural films again on crops can be proposed as a good alternative for this waste material.

The study presented here has shown that the migration is predictable. Moreover, this study shows how, by applying a very simple and easy-to-use mathematical model, one can achieve a good prediction of the likely migration of a chemical. However, the overestimation found on the model's application must be corrected by taking into account the maximum migration values obtained from the mass balance.

As was previously mentioned, the use of recycled plastics with pesticides absorbed on it could be a very interesting approach to avoid further application of pesticides on the crops. However, a deeper study is necessary to confirm this fact without any doubt.

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