Rate of Loss of Simazine, Terbuthylazine, Isoproturon, and Methabenzthiazuron during Soil Solarization

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This paper reports the use of solar heating by polyethylene mulching for decontamination of a silty clay-loam soil polluted with herbicides. Soil solarization, a natural and hydrothermal method commonly used for disinfesting soils, was tested during the summer season on a Hipercalcic Calcisol located in Murcia (southeast Spain) for dissipation of *s*-triazine (simazine and terbuthylazine) and phenylurea (isoproturon and methabenzthiazuron) herbicides using low-density (LD) and high-density (HD) polyethylene (PE) film as a cover. A well-established influence of the film was observed on the dissipation of all herbicides from the soil, although the density (0.92−0.95 g/cm^3) of the film used (LDPE and HDPE) was not significant in terms of the rate of loss. In all cases, a quick depletion during the first 2 weeks was observed, mainly for terbuthylazine. The first-order model satisfactorily explained the dissipation process, but the Hoerl and biexponential equations were more appropriate, mainly for simazine, isoproturon, and methabenzthiazuron. In all cases, herbicides disappeared at faster rates in solarized soils (DT$_{50}$ = 4−29 days) than in nonmulched soils (DT$_{50}$ = 11−35 days), especially for terbuthylazine and isoproturon.

KEYWORDS: Fitting curves; herbicide dissipation; polyethylene films; solar heating

INTRODUCTION

Soil-borne diseases and pests cause major losses in field and horticultural crops. The search for nonchemical methods of controlling soil-borne pathogens has recently intensified in light of the coming phase-out of methyl bromide (*1*). Soil solarization is a disinfestation method, first described in 1976 by Katan et al. (*2*), for controlling soil-borne pathogens and weeds, mostly as a preplanting soil treatment. This simple technique is a natural, hydrothermal process of disinfecting soil and plant pests that is accomplished through passive solar heating, involving physical, chemical, and biological changes in the soil environment (*3−5*). Increased or decreased crop growth in disinfected soils results from these changes and may be of economic significance in some cases (*6*). Transparent polyethylene plastic placed on moist soil (>70% of field capacity) during the hot summer months increases soil temperatures to levels lethal to many soil-borne plant pathogens, weed seeds and seedlings, nematodes, and some soil-residing mites. Limited cloud cover in arid and semiarid regions of the world results in shorter periods of solarization (4−6 weeks).

Plastic mulches have been used predominantly for management of soil moisture, temperature, nutrients, and weed control (*7*). One of the most common methods of containment, i.e., the retention of more volatile pesticides in the soil environment for a sufficiently long period of time for efficient control of pests, is the use of plastic film to cover the soil surface after treatment. A variety of physical and chemical properties of the polyethylene films such as additives, the length of the monomer side chain, and

the thickness and density and environmental factors, mainly temperature, affect the permeability of plastic film (*8, 9*). However, research on the effect of this method on the persistence of pesticide residues in the soil is limited, and contradictory results have been obtained (*10*). While ethiofencarb and terbutryn persisted for longer periods of time in solarized soils, other pesticides as bromacil and fluridone were not affected by this method; volatile herbicides EPTC and vernolate degraded rapidly (*11*). In addition, for quinalphos (organophosphorus insecticide), the rate of loss was higher in mulched soil (*12*) and the treatment of soil by biofumigation combined with solarization (biosolarization) enhanced the dissipation of the fungicide pyrifenox (*13*).

From an agronomic point of view, it is a desirable characteristic that pesticides persist a sufficient length of time to control pests throughout the cultivation cycle. However, from an environmental point of view, molecules that persist in the environment are undesirable for many reasons. Some are intrinsically toxic and deleteriously affect humans, domesticated animals, agricultural crops, wildlife, fish and other aquatic organisms, or microorganisms. The longer the molecule remains in the environment, the greater the exposure of susceptible individuals or populations and the greater the risk of harmful effects (*14*).

Once a pesticide is introduced into the environment, whether by application, disposal, or a spill, it can be influenced by many processes. When the fate of environmental contaminants like pesticides is modeled, knowledge of physicochemical parameters such as the soil organic carbon sorption coefficient (K_{OC}), octanol−water partition coefficient (K_{OW}), water solubility (S_W), vapor pressure (*P*), and Henry's law constant (*H*) is

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critically important. Furthermore, site characteristics, environmental conditions, crop management systems, and the handling practices of the pesticide user can all affect the fate of pesticides in the environment (15).

Fate processes can be separated into three major types: adsorption, which is the binding of pesticides to mineral or organic matter, transfer processes that move pesticides in the environment, and degradation processes that break down pesticides. The most common and today generally accepted quantitative measure of the sorption of organic pollutants by soils from aqueous solutions is the K_{OC}. In general, compounds with higher K_{OC} values will be less mobile than those with lower values. The three major types of pesticide degradation are microbial, chemical, and photodegradation. Research carried out in recent years has greatly contributed to our knowledge of how these products behave in the environment (16−19).

Traditional strategies for remediation of contaminated soils such us landfilling or incineration exchange one problem for another, and the cost of these methods is often prohibitive. Therefore, alternative low-cost and sustainable methods are needed to accelerate the degradation and natural attenuation of pesticides from multiple chemical classes (20). Clearly, their residual concentrations may well constitute in certain cases an important source of contamination in areas where they have been long used. For this reason, the aim of this work was to study the use of solar heating by polyethylene (low- and high-density) mulching for remediation of soils containing residues of four herbicides: simazine, terbuthylazine, isoproturon, and methabenzthiazuron.

MATERIALS AND METHODS

Herbicides and Reagents. Simazine (6-chloro-*N,N′*-diethyl-1,3,5-triazine-2,4-diamine), terbuthylazine [6-chloro-*N*-(1,1-dimethylethyl)-*N′*-ethyl-1,3,5-triazine-2,4-diamine], isoproturon {*N,N*-dimethyl-*N′*-[4-(1-methylethyl)phenyl]urea}, and methabenzthiazuron [(*N*-2-benzothiazolyl-*N,N′*-dimethyl)urea] were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) in greater than 99% purity.

Table 1 shows the main physical and chemical properties of the herbicides. Experimental values of the octanol−water partition coefficient (log K_{OW}), aqueous solubility (S_W), and Henry's law constant (*H*) were taken from the PHYSPROP Database (www.syrres.com). The soil−organic partition coefficient (K_{OC}) was predicted according to the Molecular Connectivity Index (MCI) model proposed by Meyland et al. (21) using the estimation model KOCWIN version 2.00 to avoid the uncertainties involved in the experimental K_{OC} values, and biodegradability

prediction from BIOWIN version 4.10, all included in the EPI Suite version 4.00 computer program provided by U.S. Environmental Protection Agency (22). Disappearance times (DT$_{50}$) for aqueous photolysis were taken from The Pesticide Properties DataBase (23).
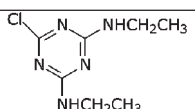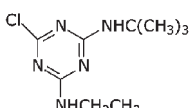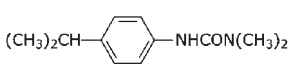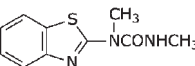
Stock standard solutions of 200 μg/mL were prepared by exact weighing and dissolving in methanol and finally stored in the dark at 4 °C. Working standard solutions were prepared freshly by dilution in the same solvent. Solvents for pesticide residue analysis (methanol, acetonitrile, and dichloromethane) were supplied by Scharlau Chemie (Barcelona, Spain). Reagents for soil analysis were purchased from Panreac Química (Barcelona, Spain).

Soil and Experimental Conditions. A Hipercalcic Calcisol (24) in fallow land located in Campo de Cartagena (Murcia, Spain), developed in quaternary fine silts and characterized by its low organic matter content, was used (bulk density of 1.29 g/mL). All the samples were taken from open terrain. Soil (silty clay-loam) was removed from the plow layer (Ap horizon, 25 cm), air-dried, passed trough a 2 mm sieve, and stored at 5 ± 1 °C. The experimental studies began as soon as possible (not more than 4 days after sampling and storage under cool conditions).

Soil samples (50 g) were placed in polypropylene containers (65 mm × 38 mm inside diameter). Each container was then fortified with 500 μL of a methanol/water solution (20/80, v/v) containing the pesticides (200 μg/mL), which was equivalent to a soil concentration of 2 μg/g (dry weight basis). Finally, 30 min later, distilled water was added to each soil sample to bring it to maximum water holding capacity, and the containers were covered with the film separately and placed in the open air on holes (60 mm depth) dug in the experimental plot. There were three sets of control containers: (i) saturated soil covered with low-density polyethylene (LDPE, 0.92 g/cm³, 20 μm film thickness), (ii) saturated soil covered with high-density polyethylene (HDPE, 0.95 g/cm³, 25 μm film thickness), and (iii) saturated soil but not covered with polyethylene (nonmulched). The experiments were repeated three times. Plastic films, Dow 582E (LDPE) and Hostalen GM 9240HT (HDPE), were obtained from Plásticos Romero (Murcia, Spain).

Field experiments were conducted during the summer season (June 15 to September 10, 2007) at the Service of Agricultural and Forest Experimentation of the University of Murcia (Murcia, Spain) at 38°01′N and 1°09′W at an elevation of 93 m above mean sea level. The maximum air temperature during the experiment was 42 °C. Soil moisture and temperature were recorded at a depth of 5 cm with the help of a Testo 635 portable thermohygrometer (Testo S.A., Cabrils, Spain). For incubations, soil samples were adjusted to 90 ± 2% of the estimated water holding capacity. The water content of the samples was controlled every week and adjusted by weighing the containers. The soil temperature was recorded at 13−14 h every 2 days. The maximum temperature in solarized soil during the outdoor experiment reached 48 °C (10 °C higher than in the control soil). The average number of sunshine hours recorded was 11.4. The maximum global and UV-radiation recorded during the experiment were

Table 1. Main Physical and Chemical Properties of the Studied Herbicides

Compound	Chemical structure	Properties[a]						
		MW	Log K_{OW}[b]	H[b]	S_W[b]	Log K_{OC}[c]	Biodegradability prediction[d]	Aqueous photolysis[e]
Simazine		201.7	2.18	9.42×10^{-10}	6.2	2.16	NRB	MF
Terbuthylazine		229.7	3.21	3.72×10^{-08}	8.5	2.50	NRB	S
Isoproturon		206.3	2.87	1.12×10^{-10}	65	2.29	NRB	S
Methabenzthiazuron		221.3	2.64	2.64×10^{-10}	59	2.93	NRB	S

[a] Molecular weight (MW), octanol−water partition coefficient (K_{OW}), Henry's law constant (*H*, atm m³ mol⁻¹ at 25 °C), water solubility (S_W, mg/L), and soil−organic partition coefficient (K_{OC}, mL/g). [b] Experimental values (PHYSPROP Database). [c] Estimated values (MCI method). [d] NRB, not readily biodegradable (BIOWIN version 4.10). [e] MF, moderately fast, DT$_{50}$ at pH 7, <14 days; S, stable, DT$_{50}$ at pH 7, >30 days (PPDB).

Article

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1020 and 29 W/m^2, respectively. Soil samples were periodically taken from each container (50 g) for residue analysis and soil characteristics starting from the day of spraying (day 0) as well as 7, 14, 47, and 81 days after treatment.

Analytical Procedures. Soil samples were analyzed for pH, total organic carbon (TOC), electrical conductivity (EC), total nitrogen (TN), microelements (Fe, Cu, Mn, and Zn), and available phosphorus (P). EC and pH were measured in soil paste extracts (1/1 soil/H$_2$O ratio). TN was measured following the Kjeldahl procedure. Phosphorus was extracted in 0.5 N NaHCO$_3$ and determined by the Olsen method (*25*). Available Zn^{2+}, Fe^{3+}, Mn^{2+}, and Cu^{2+} were extracted with DTPA (diethylenetriamine-pentaacetic acid) and measured by atomic absorption spectroscopy (*26*). OM content was measured by wet combustion with a mixture of potassium dichromate and sulfuric acid (*27*). **Table 2** lists the main physical and chemical characteristics of the soil.

Herbicide residues were extracted from the soil by sonication using acetonitrile as the extraction solvent according to the method proposed by Navarro et al. (*28*). For analytical determination, 10 μL was injected into the Alliance HPLC-PDA system, which consisted of a Waters e2695 separations module (Waters Co., Mildford, MA) equipped with a vacuum degasser, a quaternary pump, an autosampler, and a Waters 2996 photodiode array detector. Data were collected and integrated with Waters Empower. A reversed-phase Discovery C18 column (150 mm × 4.6 mm inside diameter, 5 μm diameter particle column) with a Supelguard Discovery C18 guard column (20 mm × 4 mm inside diameter, 5 μm, Supelco, Bellefonte, PA) was used. Analyses were performed by UV absorbance detection, at 230 nm using acetonitrile-water/ammonium acetate (1 mM) as the eluant gradient (from 10 to 90% acetonitrile in 35 min, linear, at a flow rate of 1 mL/min and room temperature). The flushing time was 20 min with 90% by volume acetonitrile. Equilibration required 20 min under starting conditions. Under those conditions, the retention times were as follows: 18.43 min for simazine, 21.88 min for methabenzthiazuron, 22.85 min for isoproturon, and 25.68 min for terbuthylazine.

In the QA/QC program, the instruments were calibrated daily with calibration standards. The quantification criteria included confirmation of the retention times and spectra (190−400 nm) of the standard and analyte. Calibration curves were built between 0.001 and 2 μg/mL with the standard solutions containing all studied herbicides. Blank soil samples were used to establish the limit of detection (LOD) and the limit of quantification (LOQ). Both LODs and LOQs were calculated from signal-to-noise (S/N) ratios of 3 and 10, respectively. To test the repeatability of the method, 10 soil samples were spiked at two concentration levels (0.1 and 0.5 μg/g). To evaluate the accuracy of the method, the recoveries were determined by the standard addition technique. The calibration samples by spiking herbicides at two concentration levels (0.1 and 0.5 μg/g) into soil samples were analyzed in five replicates.

Models Used for Herbicide Dissipation. Several mathematical equations have been used to describe herbicide degradation in soil (*29*). The first-order model has been largely used for describing kinetics of multiple herbicides in soils under both field and laboratory conditions. Assuming that herbicide dissipation in surface soil follows first-order kinetics, the pesticide residues, at any time (R_t), can be calculated by the following equation:

$$R_t = R_0 e^{-kt} \tag{1}$$

where R_0 denotes the residue at time zero (*y*-intercept values), k is the dissipation rate constant (slope of the disappearance lines), and t is the postapplication time in days. The time at which the concentration reaches half the initial level is termed the half-life ($t_{1/2}$).

Table 2. Major Physical and Chemical Properties of the Soil ($n = 3$)

parameter	mean value (RSD, %)	parameter	mean value (RSD, %)
sand (%)	19.5 (2)	TOC (g/kg)	5.7 (10)
silt (%)	47.2 (3)	EC (ds/m)	0.14 (9)
clay (%)	33.3 (5)	Fe^{3+} (mg/kg)	20.2 (15)
pH	8.3 (3)	Mn^{2+} (mg/kg)	96.0 (12)
total N (%)	0.07 (9)	Cu^{2+} (mg/kg)	10.1 (9)
phosphorus (mg/kg)	48.6 (5)	Zn^{2+} (mg/kg)	7.5 (13)

In some cases, a modification of the first-order model proposed by Hoerl (*30*) has been advantageously used by some authors (*29, 31, 32*):

$$R_t = a e^{-bt} t^c \tag{2}$$

This is a more general form of both the power function and the exponential function (*33*). The parameters a and b are similar to R_0 and k in the first-order equation, and c is a measurement of the deviation from the exponential behavior.

In addition, for dissipation of pesticides in surface soil, the dissipation curve sometimes follows biphasic kinetics in which each phase consists of a single-exponential decline (*34*). In the two-compartment model, the dissipation proceeds at different rates according to the equation

$$R_t = a e^{-k_1 t} + b e^{-k_2 t} \tag{3}$$

where the sum of the two constants, a and b, is approximately equal to R_0 and expresses the quantitative partition between the two compartments and k_1 and k_2 are the dissipation rate constants of each phase.

Statistical Analysis. The curve fitting and statistical data were obtained using SigmaPlot version 8.02 statistical software (Systat, Software Inc., San Jose, CA).

RESULTS AND DISCUSSION

Analytical Determination. Calibration curves presented excellent correlation coefficients ($R^2 \geq 0.999$) showing the good relationship between concentrations and absorbance intensity in the studied range. The LODs and LOQs were sufficiently low, varying from 0.3 to 1.5 ng/g and from 0.9 to 4.6 ng/g, respectively. The method had a good repeatability expressed by the relative standard deviation (RSD, %) which was less than 9% in the most unfavorable case. The average recoveries were >80% in all cases, ranging from 81.2 to 105.1% with a RSD of <8.6%.

Evolution of Herbicide Residues. Figures 1−4 show the dissipation of herbicide residues during soil solarization under the different experimental conditions. The initial concentration of simazine (day 0, 1 h) ranged from 1.95 to 2.10 μg/g (**Figure 1**). For mulched soils, dissipation was rapid, lowering residual values to ≤0.55 μg/g after 14 days, while for nonmulched soil, the residue level found at this time was approximately double. From this time to the end of the experiment, the concentration decreased continuously, ranging from 0.22 to 0.25 μg/g and from 0.22 to 0.32 μg/g for mulched and nonmulched soils, respectively. For terbuthylazine, the mean initial concentration was 2.05 μg/g (**Figure 2**). For mulched soils, the dissipation was rapid, lowering residual levels to <0.18 μg/g in the first 14 days. Residue levels
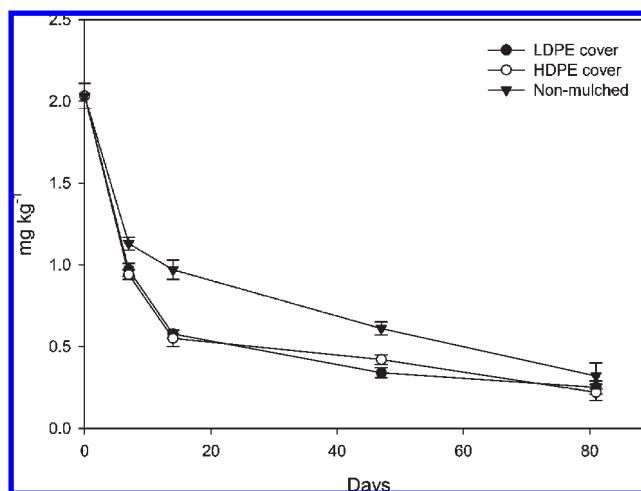
Figure 1. Dissipation of simazine residues during soil solarization (error bars are 95% confidence intervals).
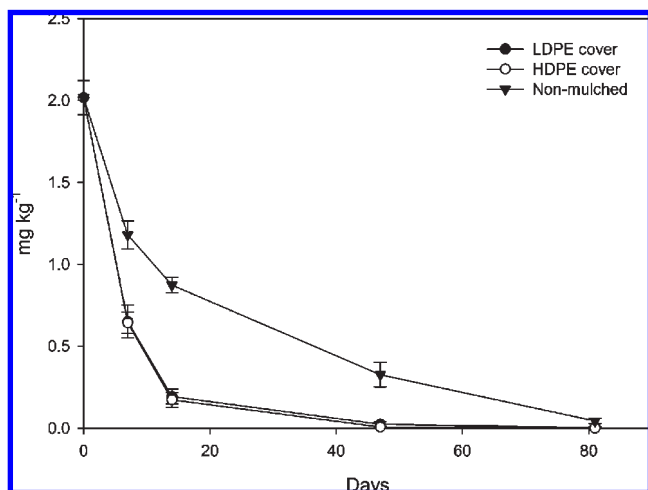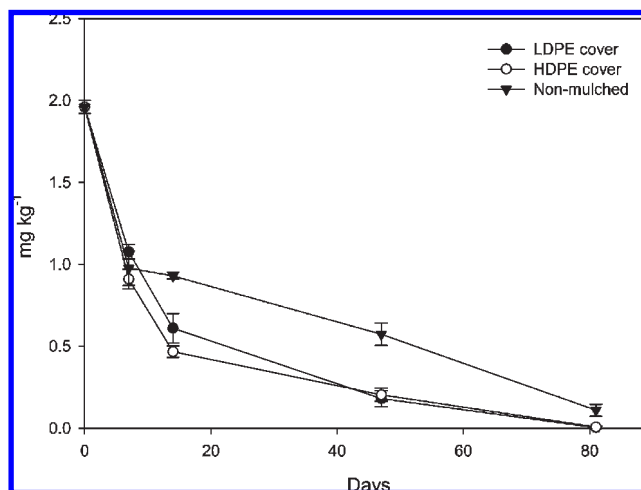
Figure 2. Dissipation of terbuthylazine residues during soil solarization (error bars are 95% confidence intervals).
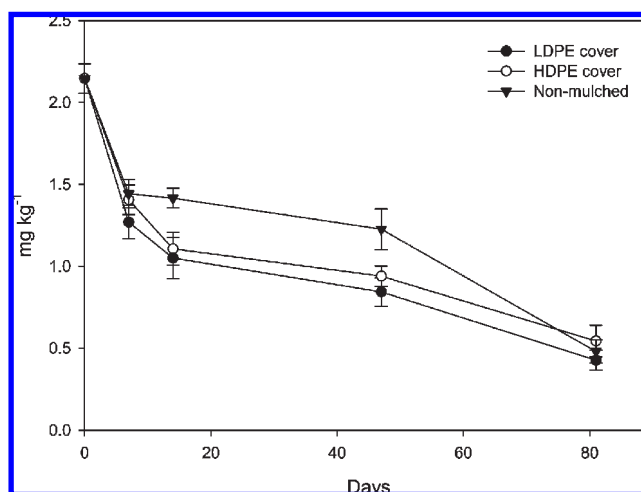

Figure 3. Dissipation of isoproturon residues during soil solarization (error bars are 95% confidence intervals).

Figure 4. Dissipation of methabenztiazuron residues during soil solarization (error bars are 95% confidence intervals).

were nearly 5 times greater in unmulched soil. After 47 days, levels of residues were below detection limit for mulched soils while 0.33 μg/g was recovered from nonmulched soil. No statistically significant differences ($p < 0.05$) were observed for the film cover. In the case of isoproturon (**Figure 3**), 1.96 μg/g was isolated from the soil at the beginning of the experiment (day 0). Seven days later, levels of residues were close to 1 μg/g for mulched and nonmulched soil samples. After this sample point, dissipation was more rapid in the covered soils with residue levels for both LDPE and HDPE decreasing to 0.2 μg/g, while in the noncovered samples, the mean value was 3 times higher (0.6 μg/g) after solarization. Methabenzthiazuron was the more persistent herbicide (**Figure 4**). Its initial concentration (2.16 μg/g) decreased from 36 to 42% during the first week. From this time until 47 days, a low dissipation rate was observed in all cases, mainly for nonmulched soils. At the end of the experiment, ~0.5 μg/g of methabenzthiazuron was recovered in all cases (23% of the initial amount).

Dissipation Kinetics. Figure 5 shows the curves fitted to the proposed models for covered soils with LDPE (0.92 g/cm^3). In each case, two phases can be differentiated, consisting of an initially fast dissipation stage (0–14 days) of the herbicides from soil surface followed by a much slower persistence phase (14–81 days). This agrees with the model proposed by Hamaker and Goring (*35*) that considered two states for pesticides in soils: a labile fraction which is degraded by a first-order process, mainly by volatilization, photolysis, and biodegradation, and a fraction which is slowly but reversibly bound to mineral and organic matter and not degradable.

Photodegradation can be a prominent degradation via for simazine because it is unstable in UV light (DT$_{50}$ = 2 days), while the other herbicides are stable (DT$_{50}$ > 30 days) to photolysis as shown in **Table 1**. According to BIOWIN, owned by the U.S. Environmental Protection Agency, the four studied herbicides are not readily biodegradable (**Table 1**). This estimation is based on the probability of rapid aerobic and anaerobic biodegradation of an organic compound in the presence of mixed populations of environmental microorganisms. The BIOWIN prediction is based on the application of Bayesian analysis (*36*). Therefore, the fast degradation in the first phase can probably be due in all cases to volatilization, mainly for terbuthylazine. The experimental H value (10^{-8} at m^3 mol^{-1}) for this herbicide is 2 orders of magnitude greater than for simazine, isoproturon, and methabenzthiazuron (10^{-10} at m^3 mol^{-1}), which could explain the more

rapid decrease in the level of terbuthylazine residues during the first 2 weeks. Volatilization can be the most important mechanism for the loss of pesticides from soil to the atmosphere during the first days after application, mainly in moist soils (*37*). For pesticides with high vapor pressure, a large fraction of them may exist in the vapor phase at temperatures and pressures that normally occur in the field. High temperatures favor the process, the only exception being when the soil dries quickly. Contrary to some models that require a large number of data parameters, others simpler models for the study of pesticide volatilization from a soil surface have been proposed (*38*). These models use experimental or predicted values of K_{OW}, K_{OC}, H, P, and S_{W}.

According to the models used, the kinetic parameters obtained for the overall period can be found in **Tables 3** and **4**. Fitting with the simple first-order equation shows R^2 values ranging from 0.76 to 0.99, and half-lives agree with experimental data with the exception of that of methabenzthiazuron. Although this model allows the determination of kinetic parameters in a simple way, its use can be recommended for dissipation of terbuthylazine. In contrast, for simazine and isoproturon, this model predicts a dissipation after 14 days faster than that experimentally observed, while for methabenzthiazuron, initial concentrations were overestimated. Many authors have reported failures of this model and of the half-life concept in describing degradation data, especially
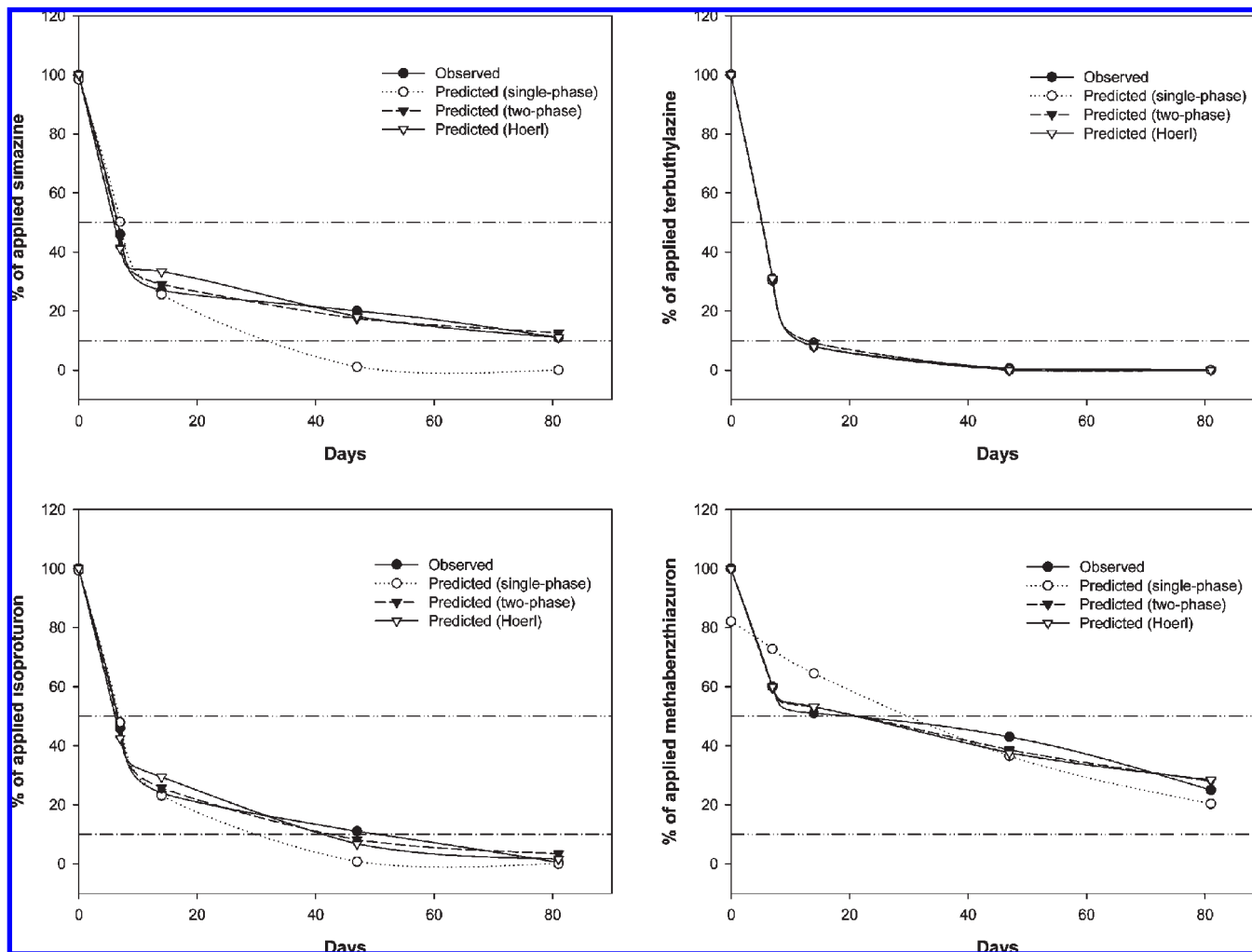
Figure 5. Predicted vs observed values for the percent of herbicide remaining in solarized soil (LDPE) with time using the three kinetics models. Horizontal dashed lines show 10 and 50% of the initial amount.

with microbial adaptation or formation of bound residues (*39*). The first-order equation predicts slower initial and more rapid later dissipation versus what normally occurs, and these deficiencies are not shared by other equations.

In some cases, the decline of pesticides in soils does not follow the first-order kinetics and decelerates with time, possibly due to either adsorption to soil components or movement out of a photic zone. Thus, some researchers have applied two- or three-phase models, but in some cases, the second-order rate constant or Hoerl function has been proposed as a good relationship for different herbicides (*29*, *32*). The values of R^2 obtained from the Hoerl equation (**Tables 3** and **4**) ranged from 0.89 to 0.99, and the standard error of estimation ($S_{y/x}$) was markedly lower than in the previous model (0.35−14.82). In this model, which considers an initial fast dissipation followed by a slower one, the *b* values for terbuthylazine in mulched soils are close to zero, which confirms the simple first-order assumption as a good estimation. On the other hand, in the other cases, the *b* values are less than zero, indicating a biphasic pattern (*29*). The DT_{50} values graphically estimated agree with the experimental data.

The biexponential equation gives the best fit, with the highest values for R^2 (0.91−0.99). Also in this case, the $S_{y/x}$ values are notably smaller (1.22−8.22) than in the case of the single-phase model with the exception of that of methabenzthiazuron in nonmulched soils (24.98). The half-lives are similar to those

estimated by the Hoerl equation, ranging from 4 to 20 days for mulched soils.

Influence of Polyethylene Density and Permeability. Following first-order kinetics, significant differences ($p < 0.05$) were not found for plastic density in the case of triazine herbicides. For both simazine and terbuthylazine, DT_{50} values were the same using LD and HD polyethylene tarps, 7 and 4 days, respectively (**Table 4**). On the other hand, the behavior of phenylurea herbicides was significantly influenced ($p < 0.05$) by film density. Isoproturon was more quickly dissipated under HDPE cover ($DT_{50} = 6$) than LDPE cover ($DT_{50} = 8$), while the behavior of methabenzthiazuron was the opposite, i.e., quicker disappearance under LDPE cover.

Lower density implies higher permeability. Although the permeability of LDPE is greater than that of HDPE, both are permeable to gases and organic vapors. Pesticides with higher vapor pressure such as terbuthylazine and simazine will be able to cross the film and escape to the atmosphere from the soil surface in greater proportions than isoproturon and methabenzthiazuron. The permeability of plastic films to gaseous solutes is due to diffusion and is thought to occur by the solute dissolving into the surface of the film, followed by the diffusion through the film and evaporation from the opposite film surface (*40*). A larger mass transfer coefficient indicates less resistance to diffusion and, therefore, higher emission rates. The permeability of the PE film depends strongly on the environmental conditions, especially

Table 3. Kinetic Parameters for the Dissipation of Triazine Herbicides in Nonmulched (NM) and Covered Soil with Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE)

model[a]	simazine[a]			terbuthylazine[a]		
	NM	LDPE	HDPE	NM	LDPE	HDPE
single-phase $C = a \exp(-kt)$						
a	84.78 (12.65)	98.45 (11.53)	98.43 (12.70)	96.30 (6.60)	100.09 (0.81)	100.11 (0.83)
$-k \, (\times 10^2)$	3.02 (1.28)	9.36 (2.58)	9.62 (2.91)	5.74 (1.04)	16.54 (0.33)	17.07 (0.35)
R^2	0.825[c]	0.919	0.901[c]	0.975[d]	0.999[e]	0.999[e]
$S_{y/x}$ [b]	15.43	11.74	12.92	6.99	0.82	0.83
DT_{50}/DT_{90}	18/71 (0.25)	7/24 (0.29)	7/24 (0.29)	11/39 (0.28)	4/14 (0.29)	4/13 (0.31)
two-phase $C = a \exp(-k_1 t) + b \exp(-k_2 t)$						
a	41.32 (3.44)	76.66 (3.99)	72.91 (11.66)	31.30 (12.40)	50.83 (190.37)	50.89 (194.99)
b	58.68 (2.95)	23.41 (3.87)	27.23 (11.21)	68.70 (12.03)	49.25 (190.37)	49.21 (194.95)
$-k_1 \, (\times 10^2)$	72.86 (162.64)	16.37 (1.61)	18.87 (6.25)	31.11 (30.14)	16.54 (151.77)	17.06 (161.61)
$-k_2 \, (\times 10^2)$	1.52 (0.14)	0.78 (0.28)	0.95 (0.74)	3.35 (0.65)	16.54 (156.62)	17.09 (166.63)
R^2	0.999[c]	0.999[c]	0.997	0.998	0.999[c]	0.999[c]
$S_{y/x}$	1.76	1.22	3.80	3.13	1.41	1.44
DT_{50}/DT_{90}	11/117 (0.09)	6/109 (0.06)	6/106 (0.06)	10/58 (0.17)	4/14 (0.29)	4/14 (0.29)
Hoerl $C = a \exp(-kt) t^b$						
a	74.88 (1.89)	65.84 (5.61)	64.72 (5.24)	83.80 (2.63)	109.10 (5.99)	113.35 (3.61)
$-k \, (\times 10^2)$	1.08 (0.18)	1.38 (0.79)	1.15 (0.68)	3.65 (0.41)	18.36 (1.31)	19.79 (0.76)
$-b \, (\times 10^2)$	12.55 (1.14)	18.32 (3.76)	19.03 (3.58)	7.81 (1.40)	−2.98 (2.33)	−4.58 (1.35)
R^2	0.997[e]	0.986[e]	0.987[e]	0.998[e]	0.999[e]	0.999[e]
$S_{y/x}$	2.38	5.94	5.77	2.38	0.66	0.35
DT_{50}/DT_{90}	11/132 (0.08)	3/80 (0.04)	3/89 (0.03)	11/57 (0.19)	5/13 (0.38)	4/13 (0.31)

[a] Standard deviation in parentheses. [b] $S_{y/x}$ is the standard deviation of the fitting (standard error of estimation). [c] $p < 0.05$. [d] $p < 0.01$. [e] $p < 0.001$.

Table 4. Kinetic Parameters for the Dissipation of Phenylurea Herbicides in Nonmulched (NM) and Covered Soil with Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE)

model[a]	isoproturon[a]			methabenztiazuron[a]		
	NM	LDPE	HDPE	NM	LDPE	HDPE
single-phase $C = a \exp(-kt)$						
a	87.92 (13.28)	99.35 (3.95)	99.36 (5.98)	89.53 (10.53)	83.06 (11.68)	82.10 (11.46)
$k \, (\times 10^2)$	4.07 (1.73)	8.18 (0.79)	10.42 (1.45)	1.65 (0.59)	2.08 (0.85)	1.72 (0.72)
R^2	0.927	0.992[c]	0.982[c]	0.914[d]	0.894[d]	0.765
$S_{y/x}$ [b]	15.05	4.05	6.06	14.43	15.41	15.59
DT_{50}/DT_{90}	14/53 (0.26)	8/28 (0.29)	6/22 (0.27)	35/133 (0.26)	24/102 (0.24)	29/122 (0.24)
two-phase $C = a \exp(-k_1 t) + b \exp(-k_2 t)$						
a	40.63 (12.46)	67.37 (46.78)	73.24 (29.38)	42.91 (2149.00)	34.42 (13.37)	39.78 (11.47)
b	59.36 (9.37)	32.83 (46.99)	26.89 (29.33)	46.61 (2149.00)	61.58 (11.47)	60.23 (10.00)
$k_1 \, (\times 10^2)$	577.86 (351.85)	12.64 (7.76)	16.88 (9.50)	1.65 (246.4)	48.13 (122.37)	35.55 (43.32)
$k_2 \, (\times 10^2)$	1.99 (0.71)	3.24 (2.83)	2.55 (2.39)	1.65 (227.91)	1.22 (0.46)	0.95 (0.36)
R^2	0.993	0.999[d]	0.996	0.914	0.993	0.989
$S_{y/x}$	8.22	3.03	4.55	24.98	6.87	5.70
DT_{50}/DT_{90}	8/89 (0.09)	8/39 (0.20)	6/39 (0.15)	35/133 (0.26)	17/149 (0.11)	20/188 (0.11)
Hoerl $C = a \exp(-kt) t^b$						
a	75.33 (6.04)	87.43 (7.68)	73.32 (8.66)	88.12 (10.85)	77.61 (4.24)	77.72 (3.47)
$-k \, (\times 10^2)$	1.57 (0.69)	5.49 (1.61)	3.95 (1.92)	1.19 (0.79)	0.88 (0.36)	0.65 (0.26)
$-b \, (\times 10^2)$	12.22 (3.60)	6.12 (3.83)	13.70 (5.15)	5.13 (5.67)	10.95 (2.47)	10.90 (2.03)
R^2	0.980[c]	0.995[c]	0.990[c]	0.886[d]	0.982[c]	0.985[c]
$S_{y/x}$	7.02	3.94	5.47	14.82	5.63	4.77
DT_{50}/DT_{90}	9/94 (0.10)	8/36 (0.22)	5/38 (0.13)	33/161 (0.20)	16/169 (0.09)	19/226 (0.08)

[a] Standard deviation in parentheses. [b] $S_{y/x}$ is the standard deviation of the fitting (standard error of estimation). [c] $p < 0.001$. [d] $p < 0.05$.

ambient temperatures, increasing ∼2 times for every 10 °C temperature increase (*41*). The HDPE's effectiveness in controlling emissions of fumigants such as methyl bromide is similar to that of bare soil, deep injection, or application of water to seal the soil surface. New plastic films are nearly impermeable to pesticides with vapor pressures as high as those for fumigants. In an outdoor study, the permeability to methyl bromide of a virtually impermeable film (VIF) like Hytibar was approximately 200 times lower than that of HDPE (*42*).

Effect of Moisture and Temperature. Soil samples were initially adjusted to 90% of the estimated water holding capacity. Soil mulching practically eliminates evaporation because the evaporated soil moisture during the day condenses on the mulch and drips onto the soil surface. Moreover, water absorption by both PE films is very low (0.01%, 24 h). Even in this manner, the variations in volumetric soil moisture content were measured weekly and the containers rewetted to a certain grade. With regard to temperature, an increment of 10 °C was observed in solarized soils in comparison with nonmulched soils, although no significant differences (*p* < 0.05) were observed between both films.

The binomial moisture or temperature is fundamental for both disinfesting and soil decontamination. If the soil is too dry (<70%

of field capacity), weed seed and pathogens may not imbibe enough water to make them vulnerable to the increased heat. Some authors report a decrease in the maximum temperature during soil solarization with increasing moisture contents at different depths in sandy loam and silty clay-loam soils, and they concluded that repeated watering during solarization does not seem to be necessary to eradicate soil pathogens (*43*). On the other hand, the rate of chemical reactions is temperature-dependent. Therefore, increasing temperatures will accelerate reactions rates. As assumed in FOCUS (*44*), an increment of 10 °C in the soil temperature increases the reaction rate 2.2 times for a reaction with an activation energy of 54 kJ/mol.

Although most mesophilic organisms in soil have thermal damage thresholds beginning around 38−40 °C, some thermophilic and thermotolerant organisms can survive temperatures achieved in most types of solarization treatment (*45*). Furthermore, a number of bacterial taxa in solarized soils have been reported to be either reduced or increased. Soil temperatures during solarization are sufficiently high to kill the target pests but also to create a new microbial balance, which is characterized by increased populations of antagonistic and plant growth-promoting rhizobacteria such as *Bacillus* and fluorescent pseudomonads (*4*). Thus, they can contribute to the herbicide biodegradation during the phase of greater persistence.

Bibliographical data show that the rates of degradation (DT_{50}) in soil for simazine vary from 27 to 102 days with temperature and soil moisture being the main factors affecting rates, while for terbuthylazine, half-lives range from 30 to 116 days in biologically active soil (*46*, *47*). For isoproturon, degradation was found to be more sensitive to water content variations than to temperature fluctuations with half-life values ranging from 10 to 12 days in surface soil layers at 22 °C and 90% of the estimated water holding capacity, while at subsurface depths, half-lives were longer than 100 days (*48*). Methabenzthiazuron degrades slowly in soils, but according to some authors (*49*), an increase in temperature can promote the formation of bound residues and enhanced dissipation.

Finally, the effect of soil temperature on organic matter content is remarkable. In our case, a decrease in the TOC was always observed and was more pronounced for mulched soils. Significant differences ($p < 0.05$) were observed for mulched and nonmulched soils. Although in the control (nonmulched) soil the organic matter content decreased to 3.8 g/kg, the value for covered soils was close to 3 g/kg after a solarization period. Several researchers have shown that enhanced decomposition of organic matter takes place during or after a solarization process. Thus, Stapleton et al. (*50*) found that a significant decrease in the level of organic material after solarization in a silty clay soil resulted from heat-generated oxidation in the aerobic portion of the solarized soil. Also, it is important to remember that water is an excellent competitor for any soil surface site. Under dry conditions (nonmulched soils), soils become extremely sorptive for both nonpolar and polar pesticides with clay mineral surfaces being the main sorption sites. Once adsorbed to soil surfaces, pesticides are in general unavailable for microbial degradation.

In conclusion, we can clearly affirm that under the experimental conditions followed in this work, soil solarization may have a significant effect on the fate and behavior of the studied herbicides, although field studies (open air and greenhouse) in appropriate plots are required to corroborate our finding. The use of a renewable source of energy, inexhaustible and pollution-free, like sunlight in combination with polyethylene cover, a tool for capturing solar energy to heat the soil, may be beneficial in accelerating degradation of the studied herbicides, especially for terbuthylazine and isoproturon. Bearing in mind the minimum

differences observed in the effect of both films, we recommend the use of LDPE because it is cheaper than HDPE. The biexponential equation describes adequately the dissipation of all herbicides in the soil covered with HDPE. Therefore, the use of soil solarization mainly in some areas of southeast Spain receiving more than 3000 h of sunlight per year can be a sustainable and effective alternative for pesticide-polluted soils.

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