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ARTICLE

Enhanced Dissipation of Oxyfluorfen, Ethalfluralin, Trifluralin, Propyzamide, and Pendimethalin in Soil by Solarization and Biosolarization

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This study was conducted to assess the effects of solarization and biosolarization on the degradation of oxyfluorfen, ethalfluralin, trifluralin, propyzamide, and pendimethalin. The experimental design consisted of 17 L pots filled with clay–loam soil, which were contaminated with the studied herbicides. Then, soil disinfection treatments were applied during the summer season, including a control without disinfection (C), solarization (S), and biosolarization (BS). Soil from five pots per treatment was sampled periodically up to 90 days. Herbicide dissipation rates were higher in both S and BS treatments with regard to the control. Similar dissipation rates were observed under S and BS for most of the herbicides studied, except oxyfluorfen and pendimethalin, which were degraded to a greater extent in the BS than in the S treatment. The obtained results showed that both solarization and biosolarization can be considered, in addition to soil disinfection techniques, such as bioremediation tools for herbicide-polluted soils.

KEYWORDS: Herbicide disappearance; soil decontamination; solar heating; mulching; biofumigation

INTRODUCTION

Methyl bromide has been the most commonly used chemical product for soil disinfestation. However, this fumigant gas has been forbidden due to international measures to avoid substances involved in the destruction of the stratospheric ozone layer. For this reason, a great deal of research is being conducted worldwide to develop technologies that will substitute methyl bromide fumigation without loss of yield or quality of crops (*1*). Solarization and biofumigation are two alternative techniques to methyl bromide and are currently used in the province of Murcia (southeast Spain) for growing vegetables in greenhouses (*2, 3*). Soil solarization was first described in 1976 by Katan et al. (*4*) for controlling soil-borne pathogens by harnessing solar energy. This simple technique is based on solar heating of the soil by mulching with a plastic cover during the hot season (*5*). Soil biofumigation is based on the use of volatile substances liberated in the biodecomposition of organic matter (*6, 7*). A combination of biofumigation and solarization (biosolarization) is used to enhance the beneficial effect of biofumigation (*3*). Both solarization and biosolarization have produced good results, especially in low-input and organic farming systems (*8*). In addition to the demonstrated suitability of both techniques for controlling soil-borne diseases and pests, evidence about the effect of soil solarization and biosolarization on the accumulation and dissipation of pesticide residues in the soil has also been obtained. While EPTC, vernolate, quinalphos, simazine, terbuthylazine,

isoproturon, and methabenzthiazuron disappeared at faster rates in solarized soils, other pesticides such as bromacil and fluridone were not affected by this technique (*9–12*). In addition, the treatment of soil by biosolarization enhanced the dissipation of the fungicide pirifenox (*13*).

In Spain, oxyfluorfen, ethalfluralin, trifluralin, propyzamide, and pendimethalin are five herbicides that have been used for weed control in pepper cultivation (*14*). Once an herbicide is applied to a soil, it can be influenced by many processes. The fate of an herbicide in soil is governed by transfer and transformation processes. The most commonly studied processes are chemical, photochemical, or biological degradation, adsorption and desorption, runoff, plant uptake, wind erosion, volatilization, and leaching. The adsorption process is essential in the fate of pesticide in soils. The most common quantitative measurement of the sorption of organic pollutants by soils from aqueous solution is the K_{OC}. Thus, compounds with higher K_{OC} values will be less mobile than those with lower values (*12*). Soil factors (soil composition, soil chemistry, and microbial activity), climatic conditions (moisture, temperature, and sunlight), and physical and chemical properties of the herbicide (water solubility, vapor pressure, and the molecule's susceptibility to chemical or microbial alteration or degradation) can all affect each process (*15*).

The main objective of this study was to ascertain the effect of solarization and biosolarization on the rate of loss of five herbicides commonly used in pepper cultivation in Spain. The experiment was carried out in greenhouses, under the particular climatic conditions of Murcia (southeast Spain).

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Table 1. Main Physical–Chemical Characteristics of the Herbicides Studied

herbicide	chemical formula	molecular weight	water solubility (mg L^{-1})	Log K_{ow}	Log K_{oc}
ethalfluralin	$C_{13}H_{14}F_3N_3O_4$	333.3	0.3	5.1	3.9
trifluralin	$C_{13}H_{16}F_3N_3O_4$	335.3	0.2	4.8	4.0
propyzamide	$C_{12}H_{11}Cl_2NO$	256.1	15	3.3	3.2
pendimethalin	$C_{13}H_{19}N_3O_4$	281.3	5.2	0.3	3.4
oxyfluorfen	$C_{15}H_{11}ClF_3NO_4$	361.7	0.1	4.5	4.7

MATERIALS AND METHODS

Herbicides and Reagents. Herbicide standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and were of more than 99% purity. The main physical and chemical characteristics of the herbicides used are shown in **Table 1**. The experimental values of the octanol/water partition coefficient (K_{OW}), soil/organic partition coefficient (K_{OC}), and aqueous solubility (S) were taken from the Estimation Program Interface (EPI) Suite version 4.00 computer program by the U.S. Environmental Protection Agency (16).

Stock solutions (1000 μg/mL) of each pesticide standard were prepared by dissolving 0.025 g of the pesticide in 25 mL of ethyl acetate/cyclohexane (1/1, v/v) and stored in the dark at 4 ± 1 °C. Working standard solutions were freshly prepared by dilution in the same solvent. Solvents for herbicide residue analysis (acetonitrile, dichloromethane, ethyl acetate, and cyclohexane) were supplied by Scharlau (Barcelona, Spain).

Field Procedures and Sampling. Seventy-five 17 L (13.5 cm diameter × 30 cm depth) pots were filled with 8 kg of a clay–loam soil (33% clay, 30% silt, and 37% sand), pH 7.86 (saturated paste extract), 1.59% organic matter content, and electrical conductivity of 3.54 dS m^{-1} (saturated paste extract). Pots were placed in a greenhouse situated in Torre-Pacheco (Murcia, Spain) during the summer season (August–October, 2008). The treatments consisted of solarization and biosolarization techniques carried out on the soils contaminated with the five herbicides. There were three sets of containers: (i) Nonmulched soil (control, C), (ii) soil covered with PE (solarized, S), and (iii) soil plus manure covered with PE (biosolarized, BS) (25 pots per treatment). First, manure was applied to the BS pots at a rate of 400 g/pot and then thoroughly mixed with the soil. In these pots, only 7.6 kg of soil was weighted to avoid a "dilution effect" following organic matter application. The organic matter used for biofumigation was a mixture of sheep and chicken manures [pH 8.46 (1:10, w/v); electrical conductivity, 10.23 (1:10, w/v); and organic matter, 63.1%]. Next, all of the pots (C, S, and BS) were spiked with the herbicides using commercial formulations: Protibel (24% oxyfluorfen, Probelte), Bitram (33% pendimethalin, Dow AgroSciences), Curb Flo (40% propyzamide, Dow AgroSciences), Treflan (48% trifluralin, Dow AgroSciences), and Sonalen (33% ethalfluralin, Dow AgroSciences). Twenty-five milliliters of a solution containing 6 mg of each compound (active material) was applied to each pot, before they were irrigated to field capacity. The water content of the samples was controlled every week and adjusted by weighing the pots. The soil temperature was measured with a data logger HOBO (Onset Technical Support, Bourne, MA). Finally, solarization was initiated in the S and BS pots by covering them with a transparent polyethylene film (Sotrafa, 50 μm thick, low density). Five pots per treatment were sampled at 0, 15, 30, 60, and 90 days after the beginning of the treatments. All of the soil of each plot was air-dried, passed through a 2 mm sieve, and homogenized. The samples were stored at 5 ± 1 °C until extraction (no more than 3–4 days after sampling).

Pesticide Analysis. Herbicides in soils were analyzed according to the procedure described by Fenoll et al. (17). After extraction, pesticides were analyzed in a gas chromatograph (model HP 6890, Agilent, Waldbronn, Germany), using a mass spectrometer detector (MSD) (Agilent 5973N). An HP-5MSI fused silica capillary column (30 m × 0.25 mm i.d.) with 0.25 μm film thickness, supplied by Agilent Technologies, was used. Helium was used as the carrier (constant pressure eluting, bromophos 20.08 min).

Following our QA/QC program, the instruments were calibrated daily with calibration standards. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. Analysis was performed with the selected ion monitoring (SIM) mode using primary and secondary ions. Retention times had to be within ±0.1 min of the expected time, and qualifier-to-target

Table 2. Retention Times (RT, Min), Target (T), Qualifier Ions (Q_1, Q_2, and Q_3) (m/z), and Abundance Ratios (%) of Qualifier Ion/Target Ion (Q_1/T and Q_2/T)[a] of the Studied Herbicides

herbicide	RT	T	Q_1	Q_2	Q_3	Q_1/T	Q_2/T
ethalfluralin	11.28	276	316	292	333	85.3	46.8
trifluralin	11.64	306	264	307	290	70.5	12.9
propyzamide	13.95	173	175	145	255	62.3	29.2
pendimethalin	20.99	252	253	281	162	14.9	12.7
oxyfluorfen	24.73	252	302	331	361	43.2	41.5

[a] Q/T (%) ratios are the results of the abundance values of the qualifier ion (Q_1 and Q_2) divided by the abundance of the target ion (T) × 100.

ratios had to be within a 10% range for positive confirmation. **Table 2** lists the herbicides along with their retention times, molecular mass (MW), the target (T) and qualifier ions (Q_1, Q_2, and Q_3), and their qualifier to target abundance ratios (Q_1/T and Q_2/T). The target and qualifier abundances were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 50 to 500. Calibration curves were constructed between 0.05 and 2 μg/mL with the standard solutions containing all of the studied herbicides. Blank soil samples were used to establish the detection (LOD) and quantification (LOQ) limits for each herbicide by GC/MSD. The LODs and LOQs of the proposed method were determined at a signal-to-noise signal ratio of 3 and 10, respectively, for the individual herbicides in soil. The repeatability of the chromatographic method was determined by analyzing the soil samples spiked at 0.2 μg/g. Finally, to evaluate the accuracy of the method, the recoveries were determined by the standard addition technique at two concentration levels (0.25 and 0.5 μg/g).

Model Used for Herbicide Dissipation. Several models have been used to describe pesticide degradation in soil (18). The first-order model has been widely used to describe the kinetics of multiple herbicides in soils. The dissipation of herbicides could be described by pseudo first-order kinetics:

$$-d[R]/dt = k[R]$$

$$Ln[R_t] = Ln[R_0] + kt \quad \text{(general formula } y = a + kt)$$

where R_0 and k denote y-intercept (residue at time zero) values and the slope of the dissipation lines, respectively, R_t is the concentration of residue in soil, and t is the postapplication time in days (19). The time at which the concentration reaches half the initial level is termed the half-life ($t_{1/2}$).

However, for dissipation of pesticides in the surface soil, the dissipation curve sometimes follows biphasic kinetics in which each phase consists of a single-exponential decline (20). In the two-compartment model, the dissipation proceeds at different rates according to the equation:

$$R_t = ae^{-k_1t} + be^{-k_2t}$$

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. In a biphasic model, the time required for dissipating 50% of the initial level is DT$_{50}$, which does not assume a specific degradation model.

Statistical Analysis. The statistical data were analyzed using the SPSS 15.0: analysis of variance for the main effects and Duncan's multiple range test to determine differences between means.

RESULTS AND DISCUSSION

Analytical Determination. The MSD responses were linear in the assayed concentration (0.05–2 μg/mL) with correlation coefficients of > 0.999 for the herbicides studied. The LODs and LOQs varied from 0.2 to 0.8 μg/kg and 0.8 to 2.8 μg/kg, respectively. The method showed good repeatability, as expressed by the relative standard deviation (RSD, %) ranging from 1.2 to 2.6% for peak areas and from 0.01 to 0.02% for the retention time. The average recovery by the GC/MSD methods obtained for these compounds varied from 74.8 to 93.6%, with RSDs of less than 4.7%.

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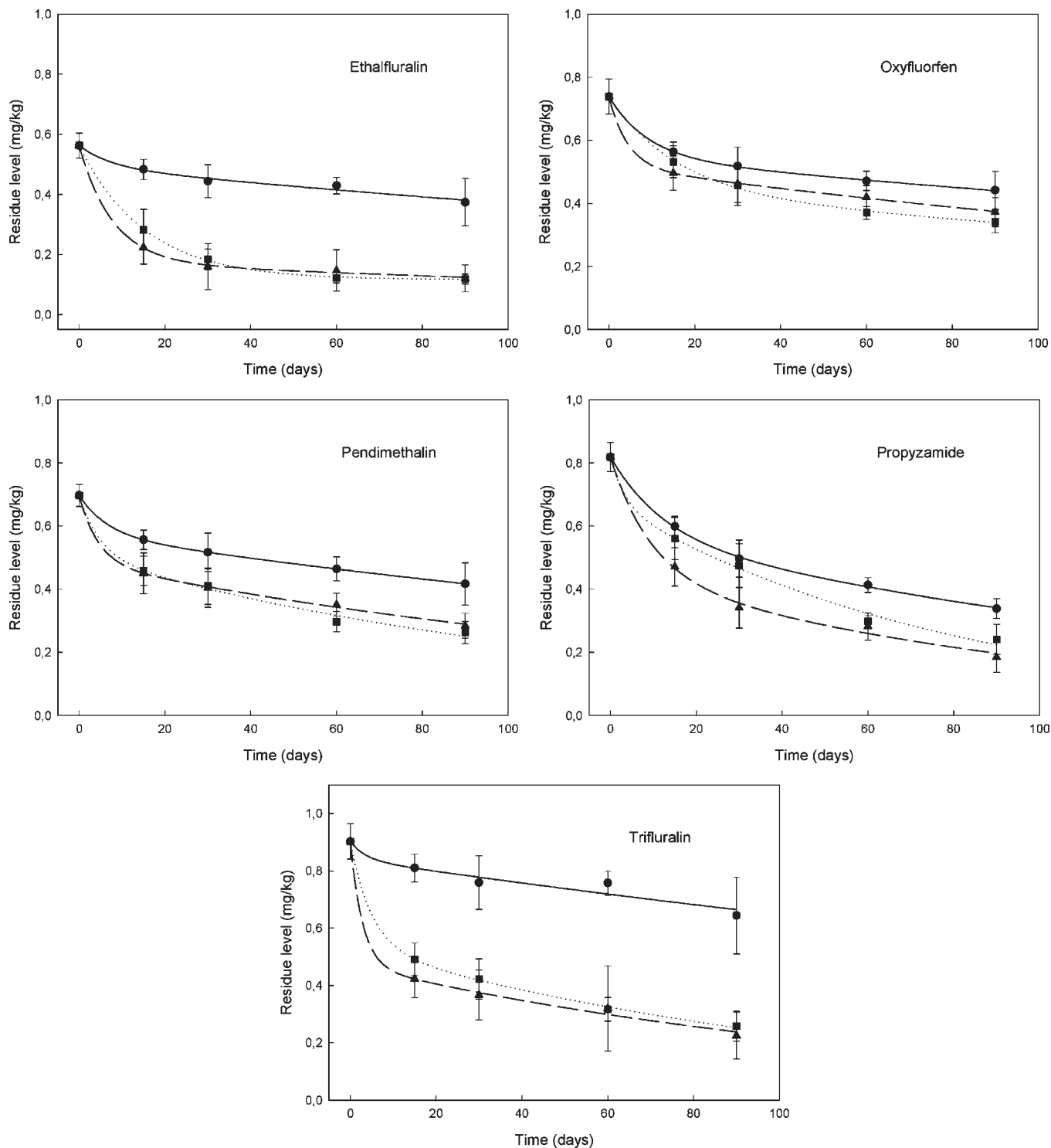
Figure 1. Dissipation curves of herbicide residues (mg/kg), fitted to the biphasic kinetics model, in nondisinfected (●), solarizated (▲), and biosolarizated (■) soils. Data are means ± SDs (*n* = 5).

Dissipation Study in Field. Figure 1 shows the residual values of the herbicides studied in nondisinfected, solarized, and biosolarized soils during the study in greenhouse. The first-order model satisfactorily explained the dissipation process, but biexponential equations were more appropriate for the herbicides studied, with correlation coefficients > 0.991 (except for trifluralin under control treatment).

Ethalfluralin, trifluralin, and pendimethalin are dinitroaniline herbicides used mainly in pepper crops for pre-emergence control of annual broad-leaved weeds. These herbicides act via inhibition of microtubule formation, disrupting cell division and causing microfibril disorientation. The fate of the dinitroanilines is extremely complex because of the different factors (multisubstitution, number of different functional groups used, multistep biotransformations of some of these groups, and their proximity). It is impossible to predict which reactions will predominate and which of the possible hundred or more metabolites will be formed (*21*, *22*). After application, the initial soil concentration for these three herbicides ranged from 0.6 to 0.9 mg/kg (**Figure 1**). Trifluralin showed the highest DT_{50} of all of the

Table 3. Parameters Obtained from the First-Order and Biphasic Kinetics for Herbicides Studied as Affected by Nondisinfection, Solarization, and Biosolarization

	$\ln R_t = \ln R_0 + kt$ (first-order kinetics)					$R_t = ae^{-k_1 t} + be^{-k_2 t}$ (biphasic kinetics)						
	r	TEE[a]	$R_0 \pm$ CI[b] (95%)	$k \pm$ CI[b] (95%)	DT$_{50}$	r	TEE[a]	$a \pm$ CI[b] (95%)	$k_1 \pm$ CI[b] (95%)	$b \pm$ CI[b] (95%)	$k_2 \pm$ CI[b] (95%)	DT$_{50}$
					ethalflurain							
control	−0.951	0.054	0.530 ± 0.020	−0.0040 ± 0.0007	174 b	0.991	0.015	0.070 ± 0.047	0.137 ± 0.275	0.492 ± 0.044	0.0029 ± 0.0013	193 b
solarization	−0.834	0.389	0.353 ± 0.089	−0.0141 ± 0.0054	49 a	0.999	0.010	0.387 ± 0.027	0.128 ± 0.024	0.175 ± 0.025	0.0039 ± 0.0021	10 a
biosolarization	−0.902	0.325	0.399 ± 0.062	−0.0163 ± 0.0045	42 a	0.999	0.006	0.445 ± 0.026	0.065 ± 0.006	0.117 ± 0.026	0.0001 ± 0.0027	15 a
					trifluralin							
control	−0.944	0.047	0.873 ± 0.027	−0.0032 ± 0.0006	217 b	0.967	0.048	0.062 ± 0.097	0.285 ± 6.271	0.841 ± 0.084	0.0026 ± 0.0016	240 b
solarization	−0.894	0.265	0.654 ± 0.123	−0.0127 ± 0.0037	54 a	0.999	0.026	0.432 ± 0.062	0.350 ± 1.349	0.471 ± 0.056	0.0076 ± 0.0021	10 a
biosolarization	−0.929	0.206	0.701 ± 0.097	−0.0123 ± 0.0028	56 a	0.999	0.011	0.365 ± 0.029	0.2021 ± 0.079	0.537 ± 0.027	0.0084 ± 0.0009	22 a
					propyzamide							
control	−0.964	0.104	0.725 ± 0.049	−0.0091 ± 0.0014	76 b	0.999	0.009	0.249 ± 0.042	0.082 ± 0.022	0.570 ± 0.042	0.0057 ± 0.0010	59 b
solarization	−0.955	0.192	0.657 ± 0.078	−0.0148 ± 0.0027	47 a	0.998	0.030	0.369 ± 0.130	0.108 ± 0.070	0.450 ± 0.128	0.0092 ± 0.0043	21 a
biosolarization	−0.981	0.109	0.732 ± 0.042	−0.0133 ± 0.0015	52 a	0.998	0.0310	0.148 ± 0.090	0.292 ± 2.099	0.670 ± 0.084	0.0122 ± 0.0024	40 a
					pendimethalin							
control	−0.946	0.073	0.637 ± 0.033	−0.0051 ± 0.0010	135 c	0.999	0.0005	0.124 ± 0.001	0.153 ± 0.005	0.573 ± 0.001	0.0036 ± 0.0000	139 c
solarization	−0.925	0.147	0.582 ± 0.061	−0.0086 ± 0.0020	81 b	0.999	0.010	0.216 ± 0.023	0.223 ± 0.160	0.481 ± 0.021	0.0057 ± 0.0007	57 b
biosolarization	−0.950	0.139	0.593 ± 0.053	−0.0101 ± 0.0019	68 a	0.997	0.024	0.191 ± 0.064	0.204 ± 0.346	0.505 ± 0.060	0.0078 ± 0.0020	48 a
					oxyfluorfen							
control	−0.897	0.102	0.652 ± 0.046	−0.0050 ± 0.0014	139 c	0.999	0.003	0.191 ± 0.009	0.111 ± 0.013	0.548 ± 0.009	0.0024 ± 0.0002	164 c
solarization	−0.879	0.143	0.619 ± 0.063	−0.0063 ± 0.0020	109 b	0.999	0.004	0.223 ± 0.008	0.230 ± 0.061	0.516 ± 0.007	0.0036 ± 0.0002	93 b
biosolarization	−0.934	0.127	0.639 ± 0.052	−0.0080 ± 0.0018	87 a	0.999	0.012	0.298 ± 0.070	0.063 ± 0.020	0.440 ± 0.070	0.0029 ± 0.0019	65 a

[a] Typical error of estimate. [b] Confidence intervals. Different letters in the "DT$_{50}$" column indicate significant differences between means according to Duncan's test.

studied herbicides in C soils. For ethalfluralin, trifluralin, and pendimethalin, a lower dissipation rate and higher DT$_{50}$ were observed in the control than in disinfected soils (**Table 3**). However, no significant differences between S and BS treatments were observed when studying ethalfluralin and trifluralin degradation. Pendimethalin was degraded faster in BS than in S, the latter reducing the DT$_{50}$ by 82 days with respect to the control and BS reducing by 91 days.

Oxyfluorfen is used to control annual broad-leaved weeds in peppers and other fruits and vegetables crops. The mode of action of oxyfluorfen is inhibition of protoporphyrinogen oxidase (*22*). After the application, the residue of oxyfluorfen was 0.74 mg/kg (**Figure 1**). The residue of this herbicide tended to decrease in the C, S, and BS treatments, showing biphasic kinetics with an *r* higher than 0.999 in all cases (**Table 3**). Under control conditions, the dissipation rate was lower for ethalflralin and trifluralin than for oxyfluorfen. In contrast, oxyfluorfen showed the highest DT$_{50}$ of all of the studied herbicides in S and BS soils. In general, oxyfluorfen is persistent in aerobic soils but more rapidly transformed in anaerobic conditions (*21*). Soil disinfection by S and BS led to a significant increase ($p < 0.001$) in oxyfluorfen degradation in soil as compared with the control treatment. This was evident from the values found for DT$_{50}$, which were higher for C than for S and BS (**Table 3**). Significant differences between S and BS treatments were observed. This compound was degraded faster in BS than in S, reducing the DT$_{50}$ by 28 days.

Propyzamide belongs to the amides family and is used for the control of some broad-leaved weeds in pepper crops (*22*). Propyzamide is a systemic herbicide that is absorbed by the roots and translocated. It inhibits the growth of sensitive species by disrupting the mitotic sequence in dividing cells. Cyclization to an oxazoline is a common metabolic feature that plays a part in both abiotic degradation and biotransformation (*21*). In a similar way to most of the herbicides studied, the dissipation rate of
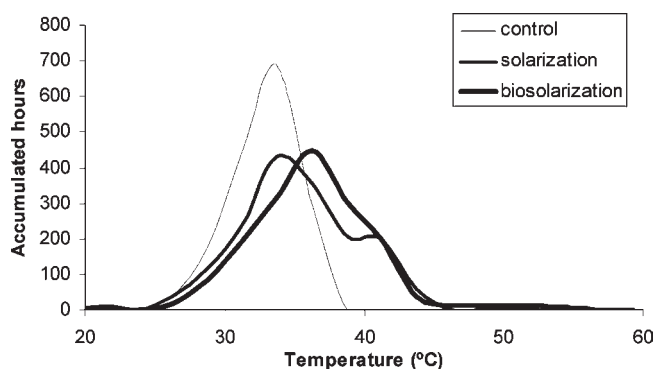
Figure 2. Accumulated hours for the different soil temperatures reached during the experiment. The temperature was measured every 8 min at 0−15 cm depth.

propyzamide in disinfected soils was higher than in the control treatment, and no significant differences between S and BS treatments were observed.

An increase in the soil temperature of about 14 and 16 °C, respectively, was observed in S and BS treatments with regard to the control treatment (**Figure 2**). In addition, the number of accumulated hours at high temperature was higher in both S and BS than in control. The effect of S and BS treatment on soil temperature can be attributed to the solarization process, which captures radiant energy from the sun (*15*), and it may be responsible for the observed general enhancing of the residue dissipation rate. The effect of temperature on pesticide degradation is based on increasing desorption, microbial activity, and/or enhancing the action of catalytic substances (*23*). With regard to the effect of soil temperature on the microbial activity, most mesophilic organisms have thermal damage from 38 to 40 °C. However, some thermophilic and thermotolerant organisms can

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survive higher temperatures or even increase their activity. Thus, soil temperature during solarization can create a new microbial population, which can contribute to herbicide biodegradation (*24*). Information about the effect of solarization on pesticide degradation is still limited. Some authors have reported increasing pesticide degradation (organophosphorus insecticides and benzimidazole fungicides) in soils with this disinfection technique (*11, 25*). In addition, a well-established influence of the film was observed in the dissipation of some triazine and phenylurea herbicides from the soil (*12*). On the other hand, the role of the organic matter for use in bioremediation has been reported in soil, and it has been attributed to the large populations of microorganisms that are generally contained within it (*26−28*). Because BS involves the application of a relatively high rate of organic matter, a higher dissipation rate of herbicides in BS than in S treatment would be expected. However, only pendimethalin and oxyfluorfen showed a higher degradation rate under BS, as compared to S. The reasons that the effect of BS was similar to the S treatment could be the inactivation of microbial activity by solarization or the higher resistance of some herbicides (or of other complexes formed with some components of the environment) to microbial degradation (*26, 29*). In addition, the application of organic matter to the soil may also affect pesticide degradation by increasing soil pesticide adsorption (*15*) and then masking the enhancing effect of microbial activity on pesticide degradation.

In conclusion, the biexponential equation describes adequately the dissipation of all herbicides studied. In addition, the results obtained show that both solarization and biosolarization can be considered not only as suitable soil disinfection techniques for controlling soil-borne diseases and pests but also as a sustainable and effective alternative for pesticide-polluted soils. The increased dissipation effect of both methyl-bromide alternative techniques can be attributed mainly to an increase in soil temperature. The behavior of some compounds (pendimethalin and oxyfluorfen), which showed lower dissipation rates under solarization than under biosolarization, suggests that, in some cases, organic matter application by biosolarization can enhance the bioremediation effect of solarization. The different behavior observed within herbicides suggests that specific studies for other compound are needed to assess the effect of these disinfection techniques on pesticide degradation.

In summary, the use of a renewable source of energy, inexhaustible and pollution-free, like sunlight in combination with polyethylene cover and organic matter, may be beneficial in accelerating the dissipation of some pesticides. We can clearly affirm that under the experimental conditions followed in this work, soil solarization and soil biosolarization have a significant effect on the fate and behavior of the studied herbicides.

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