



Rate of loss of insecticides during soil solarization and soil biosolarization

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ABSTRACT

This paper reports the use of solarization and biosolarization to decontaminate a soil polluted with six insecticides (buprofezin, pirimicarb, pirimiphos methyl, pyridaben, pyriproxyfen and tebufenpyrad). In the experiment, 17-L pots filled with clay-loam soil were placed in a greenhouse during the summer season and then contaminated with the insecticides of interest. Treatments consisted of different solarization and biosolarization treatments, including a control without disinfection. For both solarization and biosolarization treatments, low-density polyethylene film was used as cover; the biosolarization treatment involving application of a mixture of sheep and chicken manures at a rate of 400 g pot⁻¹. Five pots per treatment were sampled periodically up to 90 d after the beginning of each treatment. The results showed that both solarization and biosolarization enhanced the degradation rates of most of the insecticides tested compared with the control, probably as a result of the increased soil temperature. Pirimicarb, pirimiphos methyl, tebufenpyrad, pyriproxyfen and pyridaben were degraded to a greater extent in the biosolarization than in the solarization treatment. The results confirm that both solarization and biosolarization can be considered as a remediation tool for soils polluted by these insecticides.

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1. Introduction

In the province of Murcia (southeast Spain) sweet pepper has been a monoculture in greenhouses for many years. Soils are usually disinfected every year with methyl bromide for pathogens control and to avoid soil fatigue effects [1]. Solarization and biosolarization (solarization + biofumigation) are among the disinfection techniques currently used in the province for growing pepper in greenhouses as alternatives to methyl bromide [2]. In this respect, solarization is a relatively new approach for controlling soil-borne pathogens by harnessing solar energy. Basically, the soil is heated by mulching with transparent polyethylene during the hot summer months [3]. Biofumigation, on the other hand, is based on exposing of the pests to toxic volatiles produced upon the decomposition of organic matter (aerobic or anaerobic), which is purposely incorporated in the soil [4,5]. Mulching with transparent polyethylene (biosolarization) prevents the escape of these volatiles and improves the control [6]. These methods have produced good results, especially in low-input and organic farming systems for the control of soil-borne pests and diseases, mostly as pre-planting soil treatments [7].

The presence of pesticides in agricultural soils may be due to treatments applied to the soil directly or, to the aerial part of crops to combat pests, in which case approximately 50% of the product

may reach the soil [8]. Environmental risks derived from such soil contamination include pesticide leaching and subsequent groundwater contamination and even the presence of pesticide residues in untreated crops, such as organic crops, following the absorption of such residues by plants.

In order to solve this problem, several remediation techniques are currently used. Traditional strategies for remediation of contaminated soils such as landfilling or incineration may pose many environmental concerns and the cost of these techniques is often prohibitive. Therefore, alternative simple and inexpensive techniques are needed for the reduction or elimination of pesticide residues in soils [9]. Among them, bioremediation, the use of zerovalent iron [10,11], soil solarization [12–14] and soil biosolarization [15] have been proposed in the recent years as methods to accelerate the degradation and natural attenuation of pesticide residues in soils.

In Spain, buprofezin, pirimicarb, pirimiphos methyl, pyridaben, pyriproxyfen and tebufenpyrad are six insecticides that are widely used for pest control in pepper cultivation [16]. Pirimicarb is a selective systemic insecticide that is widely employed against aphids with a contact, stomach and respiratory action. Pirimiphos methyl is used to control a wide range of insects and mites on agricultural crops, when it may be used alone or together with buprofezin. Buprofezin is an insect growth regulator active against Homoptera. Tebufenpyrad and pyridaben are non-systemic acaricides that inhibit mitochondrial electron transport in complex I. Pyriproxyfen is an insect growth regulator that is mainly employed against whitefly [17]. The risks of residue leaching or uptake by

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plants in successive crops has been reported in connection with some of these insecticides [18,19].

The fate of insecticides in soil is governed by chemical and microbial degradation, adsorption/desorption, plant uptake, diffusion, assimilation by microorganisms, runoff, wind erosion, volatilisation and leaching processes, adsorption being the predominant [8]. The most common quantitative measurement of the adsorption of organic pollutants by soils from aqueous solutions is the soil/organic partition coefficient (K_{OC}). Thus, compounds with higher K_{OC} values will be less mobile than those with lower values [20]. In addition, degradation is one of the processes responsible for the disappearance of insecticides in soil. Chemical degradation takes place mainly through photolysis, hydrolysis, oxidation and reduction reactions, whereas biological degradation occurs when soil microorganisms break down or consume pesticides [8]. Knowledge of the kinetics of biochemical degradation is essential for evaluating the persistence of these compounds. The main objective of this research was to study the effect of soil solarization and biosolarization on the rate of degradation of different insecticides commonly used in the pepper cultivation in Spain. The experiment was carried out in greenhouse, under the climatic conditions of Murcia (Spain).

2. Experimental

2.1. Insecticides and reagents

Insecticide standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and were of more than 99% purity. The main physical and chemical characteristics of the insecticides used are shown in Table 1. The experimental values of the octanol/water partition coefficient (K_{OW}), soil/organic partition coefficient (K_{OC}), aqueous solubility (S), were taken from the Estimation Program Interface Suite version 4.00 computer program by U.S. Environmental Protection Agency [21].

Stock solutions ($1000 \mu\text{g mL}^{-1}$) of each insecticide standard were prepared by dissolving 0.025 g of the insecticide in 25 mL of ethyl acetate/cyclohexane (1/1, v/v) and stored in the dark at $4 \pm 1^\circ\text{C}$. Working standard solutions were prepared freshly by dilution in the same solvent. Solvents for insecticide residue analysis (acetonitrile, dichloromethane, ethyl acetate and cyclohexane) were supplied by Scharlau (Barcelona, Spain).

2.2. Field procedures and sampling

This work forms part of a broader study to assess the effect of solarization and biosolarization on several pesticides commonly used for controlling pests in pepper cultivated under greenhouse conditions. In particular, the present study focuses on the effect of these disinfection techniques on insecticides degradation. To this aim, identical experimental designs to those applied for studying fungicide and herbicide degradation were used [22,23]. The assay was carried out in 2008, in a greenhouse situated in Torre-Pacheco (Murcia, Spain), during the summer season (August–October). 17-L pots were filled with clay-loam soil (33% clay, 30% silt, 37% sand) with a pH of 7.86 (saturated paste extract), 1.59% organic mat-

ter content, and electrical conductivity of 3.54 dS m^{-1} (saturated paste extract). Treatments consisted of a control (C), in which soils were not exposed to any disinfection technique, and the application of solarization (S) and biosolarization (BS). Twenty five pots were used per treatment distributed in a completely randomized design (CRD). For the S treatments the top of the pots were covered with a low-density polyethylene film (LDPE) (Sotrafa, $50 \mu\text{m}$ thick, low density), with a headspace between the film and the soil. For the BS treatments, manure was applied to the pots at a rate of 400 g pot^{-1} (according to the rate recommended for the adequate control of soilborne fungi) and then thoroughly mixed with the soil. Then, soils plus manure were covered with LDPE, similarly to the pots in the S treatment. In all the pots, soil or manure plus soil, weighed 8 kg so that the pots were of a uniform mass. The organic matter used for biofumigation was a mixture of sheep and chicken manures [pH = 8.46 (1/10, w/v), electrical conductivity 10.2 dS m^{-1} (1/10, w/v), organic matter 63.1%]. Afterwards, all the pots (C, S and BS) were spiked with the insecticides of interest using commercial formulations: Aphox (50% pirimicarb), Guardian (8% of buprofezin and 40% of pirimiphos methyl), Comanche (20% tebufenpyrad), Juvinal (10% pyriproxyfen), Sanmite (20% pyridaben). For this, 25 mL of a solution containing 8 mg of each compound (except for buprofezin, 2 mg of compound) was applied to each pot, before irrigating to field capacity. Five pots per treatment were sampled periodically up to 90 d after the beginning of the treatments, for which the whole soil of each pot was air-dried, passed through a 2 mm sieve and homogenized.

2.3. Pesticide analysis

Insecticides were analyzed in a gas chromatograph Agilent model HP 6890 (Waldbronn, Germany), using a mass spectrometer detector (MSD) (Agilent 5973N) and an HP-5MSI fused silica capillary column ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) with $0.25 \mu\text{m}$ film thickness, according to the procedure described by Fenoll et al. [24]. Insecticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. Table 2 lists the insecticides 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). Calibration curves were constructed between 0.05 and $2 \mu\text{g mL}^{-1}$ with the standard solutions containing all the insecticides of interest. The detection limits (LODs) and the quantification limits (LOQs) were determined at a signal-to-noise signal ratio of 3 and 10, respectively, for the individual insecticides in soil. The repeatability of the chromatographic method was determined by analyzing the soil samples spiked at $0.2 \mu\text{g g}^{-1}$. Finally, to evaluate the accuracy of the method, the recoveries were determined by the standard addition technique at two concentration levels (0.25 and $0.5 \mu\text{g g}^{-1}$).

2.4. Model used for fungicide dissipation

Among several models that have been used to describe pesticide degradation in soil, the first-order model is the most widely used [25]. However, the dissipation of pesticides in the surface soil some-

Table 1
Main physical–chemical characteristics of the tested insecticides.

Insecticide	Molecular formula	Molecular weight	Water solubility (mg L^{-1})	Log K_{OW}	Log K_{OC}
Buprofezin	$\text{C}_{16}\text{H}_{23}\text{N}_3\text{OS}$	305.4	0.39	4.8	3.8
Pirimicarb	$\text{C}_{11}\text{H}_{18}\text{N}_4\text{O}_2$	238.3	3000	1.7	1.5
Pirimiphos methyl	$\text{C}_{11}\text{H}_{20}\text{N}_3\text{O}_3\text{PS}$	305.3	11	4.2	2.1
Pyridaben	$\text{C}_{19}\text{H}_{25}\text{ClN}_2\text{OS}$	364.9	0.01	6.4	5.5
Pyriproxyfen	$\text{C}_{20}\text{H}_{19}\text{NO}_3$	321.4	0.37	5.4	5.6
Tebufenpyrad	$\text{C}_{18}\text{H}_{24}\text{ClN}_3\text{O}$	333.9	2.61	4.9	4.0

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 tested insecticides.

Insecticide	RT	<i>T</i>	<i>Q</i> ₁	<i>Q</i> ₂	<i>Q</i> ₃	<i>Q</i> ₁ / <i>T</i>	<i>Q</i> ₂ / <i>T</i>
Buprofezin	24.58	105	106	104	172	48.2	46.7
Pirimicarb	15.69	166	72	238	167	50.4	25.3
Pirimiphos methyl	18.31	290	276	305	233	80.1	36.9
Pyridaben	31.52	147	117	148	132	13.2	12.7
Pyriproxyfen	29.93	136	96	78	137	10.7	10.2
Tebufenpyrad	29.16	318	333	171	276	82.2	78.5

^a *Q*/*T* (%) ratios are the results of abundance values of the qualifier ion (*Q*₁, *Q*₂) divided by the abundance of the target ion (*T*) × 100.

times better fits a biphasic kinetics, in which each phase consists of a single-exponential decrease [26], according to the equation , where *R*_{*t*} is the concentration of residue in soil and *k*₁ and *k*₂ are the dissipation rate constants of each phase. In this equation, the sum of the two constants, *a* and *b*, is approximately equal to *R*₀ (concentration of residue in soil at time zero) and expresses the quantitative partition between the two compartments.

2.5. Statistical analysis

The curve fitting was obtained using SigmaPlot version 8.02 statistical software (Systat, Software Inc., San Jose, CA). Main effect (disinfection treatment) and differences between means were analyzed statistically using the SPSS 15.0 software (SPSS Inc., Chicago, IL) package, by ANOVA and Tukey's Multiple Range Test, respectively.

3. Results and discussion

3.1. Analytical determination

The MSD response was linear in the assayed concentration range, with correlation coefficients (*r*) of >0.999 for all the insecticides studied. The LOD and LOQ varied from 0.1 to 4.2 μg kg⁻¹ and 0.4 to 14.0 μg kg⁻¹, respectively. The method showed good

repeatability, as expressed by the relative standard deviation (RSD, %) ranging from 1.7 to 3.2% for peak areas, and from 0.01 to 0.03% for the retention time. The average recovery by the GC-MSD method obtained for these compounds varied from 70.9 to 100.9%, with relative standard deviations of less than 4.8%.

3.2. Dissipation study in greenhouse

Fig. 1 shows the residual values of the insecticides studied in non-disinfected, solarized and biosolarized soils during the greenhouse study. The first-order model satisfactorily explained the dissipation process, but biexponential equations were more appropriate for the tested insecticides, with *r* > 0.993. These results can be explained because the first-order equation predicts slower initial and more rapid later dissipation compared with what normally occurs. After application, the initial soil concentration for the insecticides ranged from 0.8 to 1.3 mg kg⁻¹, except for buprofezin, which was 0.4 mg kg⁻¹ (Fig. 1).

The metabolism of pirimiphos methyl can be represented by initial hydrolysis to yield 2-diethylamino-6 methyl-pyrimidin-4-ol, which may be conjugated or successively N-de-ethylated [27]. Pirimiphos methyl showed the highest DT₅₀ (time required for dissipating 50% of the initial level) of all the insecticides in C, S and BS soils. The residue of this insecticide tended to decrease in the C, S and BS treatments, showing a biphasic kinetics with an *r* higher

Table 3
Parameters obtained from the first-order and biphasic kinetics for tested insecticides as affected by non-disinfection, solarization and biosolarization.

	Parameter						
	$R_t = a \cdot e^{-k_1 t} + b \cdot e^{-k_2 t}$ (biphasic kinetics)						
	<i>r</i>	TEE ^a	<i>a</i> ± CI ^b (95%)	<i>k</i> ₁ ± CI ^b (95%)	<i>b</i> ± CI ^b (95%)	<i>k</i> ₂ ± CI ^b (95%)	DT ₅₀
Buprofezin							
Control	0.999	0.002	0.104 ± 0.007	0.110 ± 0.017	0.258 ± 0.007	0.0040 ± 0.0004	89b
Solarization	0.996	0.013	0.095 ± 0.032	0.203 ± 0.357	0.267 ± 0.029	0.0058 ± 0.0018	67ab
Biosolarization	0.998	0.010	0.226 ± 0.121	0.036 ± 0.020	0.136 ± 0.123	0.0000 ± 0.0088	45a
Pirimicarb							
Control	0.999	0.015	0.255 ± 0.055	0.116 ± 0.053	0.760 ± 0.053	0.0072 ± 0.0011	56c
Solarization	0.999	0.020	0.258 ± 0.055	0.231 ± 0.322	0.757 ± 0.052	0.0100 ± 0.0012	40b
Biosolarization	0.999	0.0001	0.437 ± 0.0007	0.102 ± 0.0003	0.578 ± 0.007	0.0104 ± 0.0000	22a
Pirimiphos methyl							
Control	0.997	0.061	0.499 ± 0.178	0.189 ± 0.281	0.806 ± 0.167	0.0094 ± 0.0036	24c
Solarization	0.999	0.048	1.204 ± 0.265	0.078 ± 0.025	0.103 ± 0.264	0.0063 ± 0.0338	10b
Biosolarization	0.999	0.002	1.287 ± 0.008	0.095 ± 0.001	0.018 ± 0.008	0.0073 ± 0.0060	7a
Pyridaben							
Control	0.999	0.008	0.221 ± 0.022	0.145 ± 0.045	0.710 ± 0.020	0.0033 ± 0.0004	128c
Solarization	0.999	0.015	0.329 ± 0.032	0.234 ± 0.174	0.601 ± 0.028	0.0030 ± 0.0007	85b
Biosolarization	0.999	0.016	0.347 ± 0.066	0.089 ± 0.030	0.583 ± 0.065	0.0042 ± 0.0015	55a
Pyriproxyfen							
Control	0.993	0.038	0.124 ± 0.091	0.242 ± 1.500	0.690 ± 0.083	0.0065 ± 0.0020	81c
Solarization	0.999	0.0002	0.236 ± 0.0005	0.184 ± 0.002	0.578 ± 0.0005	0.0090 ± 0.0000	39b
Biosolarization	0.998	0.034	0.309 ± 0.242	0.163 ± 0.261	0.504 ± 0.240	0.0258 ± 0.0102	13a
Tebufenpyrad							
Control	0.999	0.007	0.258 ± 0.017	0.138 ± 0.027	0.652 ± 0.016	0.0024 ± 0.0004	150c
Solarization	0.999	0.023	0.227 ± 0.005	0.355 ± 0.232	0.683 ± 0.004	0.0045 ± 0.0001	90b
Biosolarization	0.999	0.022	0.206 ± 0.057	0.234 ± 0.448	0.704 ± 0.052	0.0080 ± 0.0013	55a

Different letters in the "DT₅₀" column indicate significant differences between means according to Tukey's test.

^a Typical error of estimate.

^b Confidence intervals.

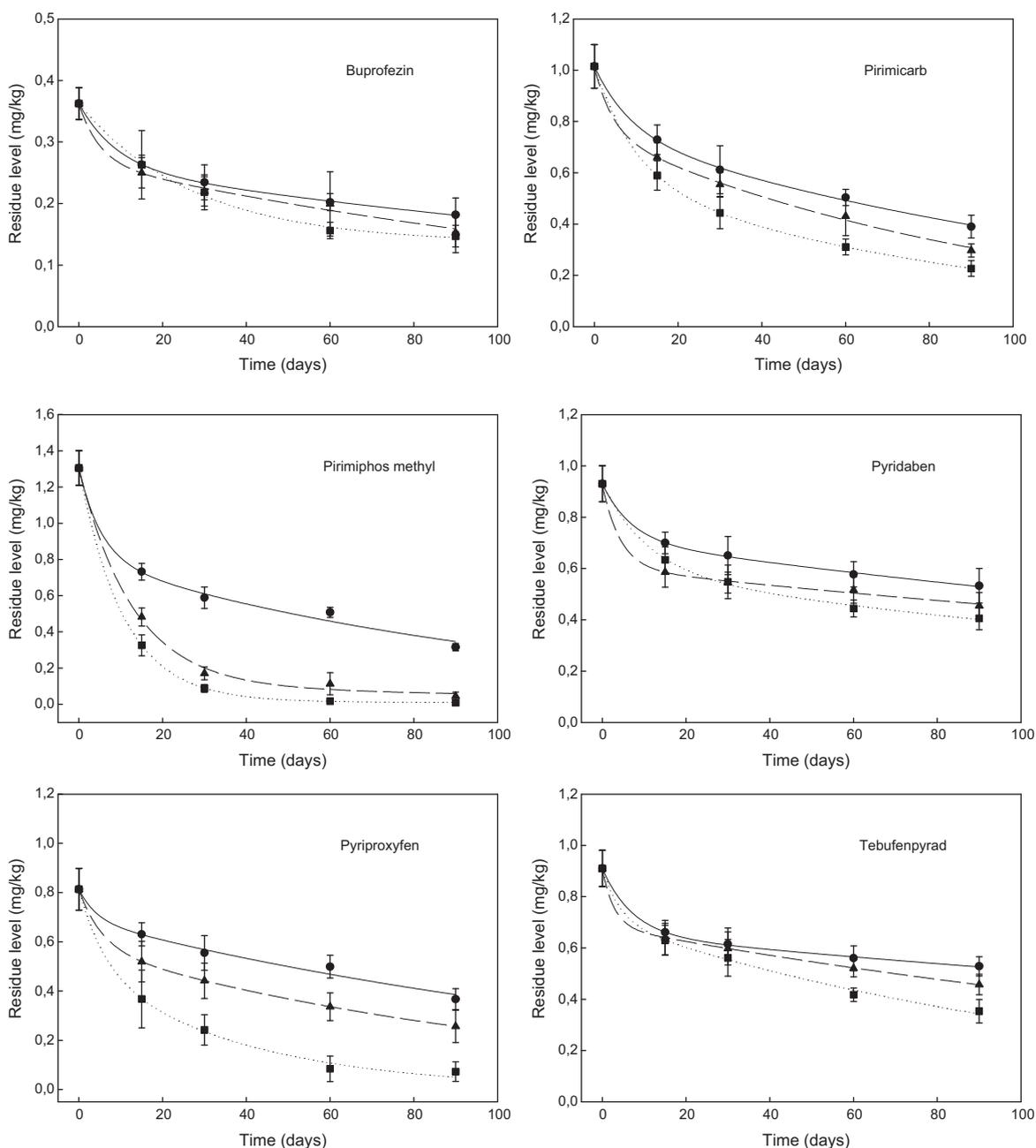


Fig. 1. Dissipation curves of insecticide residues (mg kg^{-1}), fitted to the biphasic kinetics model, in non-disinfected (\bullet), solarized (\blacktriangle) and biosolarized (\blacksquare) soils. Data are means \pm SD ($n=5$).

than 0.997 in all cases (Table 3). In contrast, tebufenpyrad and pyridaben showed the highest DT_{50} of all the insecticides in C, S and BS soils, probably because the compound shows a high K_{OC} value (Table 1). The metabolic and degradation pathways for pirimicarb are mainly via N-demethylation, hydrolysis of the carbamate ester function, ring opening to form guanidines and conjugation. Pyriproxyfen does not persist in soils and is rapidly metabolized by a variety of organisms. The general pathway in soils involves fission of ether linkage and hydroxylation of the phenoxyphenol [27]. Under control conditions, the dissipation rate was lower for pyriproxyfen than for pirimicarb. In contrast, in disinfected soils, pyriproxyfen showed a higher degradation rate than pirimicarb. Opening of the thiadiazinane ring appears to be the initial degradation and metabolic pathway for buprofezin [27]. The residue of buprofezin tended to decrease in the C, S and BS treatments according to a biphasic kinetics with an r between 0.996 and 0.999.

Soil disinfection by solarization (S) and biosolarization (BS) led to a significant higher dissipation rate and lower DT_{50} of pirimicarb, pirimiphos methyl, tebufenpyrad, pyriproxyfen and pyridaben, compared with the control treatment (Table 3). No significant differences between C and S treatments were observed when studying buprofezin degradation. In addition, most of the insecticides were degraded faster in BS than in S. Thus, the S treatment reduced the DT_{50} by 16, 14, 60, 42 and 43 d with regard to the control treatment for pirimicarb, pirimiphos methyl, tebufenpyrad, pyriproxyfen and pyridaben, respectively, whereas BS treatment reduced it by 34, 17, 95, 68 and 73 d, respectively.

In agreement with previous works in which the effect of S and BS on several fungicides and herbicides were studied, the application of these soil disinfection techniques tended to enhance the dissipation rate of the tested insecticides [22,23]. In addition, other authors have reported the lower persistence of organophosphorus

insecticides and benzimidazole fungicides in soils with solarization [13,28]. As in the previous studies reported by Fenoll et al. [22,23], the effect of S and BS can be attributed to an increase in the soil temperature and also, in the case of BS, to the biocidal activity of the applied manure. Pesticide degradation is enhanced with increased temperatures as a result of increased desorption, microbial activity and/or the action of catalytic substances [29]. In regards to the microorganism population, the temperature achieved during S and BS can cause biological changes in soil on one hand, due to thermal damage that most mesophilic organisms suffer at the temperatures reached, and on the other, to the survival or even increased activity of thermophilic and thermotolerant microorganisms. The new microbial balance so created can contribute to pesticide biodegradation [30]. During BS, the high rate of organic matter application contributes to increasing the soil microbial population and so enhances the potential of S to remediate pesticide-contaminated soils [31–33]. In the present study, pirimicarb, pirimiphos methyl, tebufenpyrad, pyriproxyfen and pyridaben showed a higher degradation rate under BS conditions compared with S, whereas only buprofezin showed a similar degradation rate in both S and BS treatments. The reason for this similar effect of BS and S treatments could be the higher resistance of buprofezin (or of other complexes formed with some components of the environment) to microbial degradation [33,34]. In addition, the application of organic matter to the soil may also affect pesticide degradation by increasing soil pesticide adsorption [8], so masking the enhancing effect of microbial activity on pesticide degradation.

4. Conclusions

A biexponential equation described adequately the dissipation of all insecticides studied under the different disinfection treatments. The general effect of solarization and biosolarization on the tested insecticides was to enhance the residue dissipation rate, except in the case of buprofezin, an effect that could be attributed mainly to an increase in soil temperature. The behavior of some compounds (pirimicarb, pirimiphos methyl, tebufenpyrad, pyriproxyfen and pyridaben) which showed lower dissipation rates with solarization than with biosolarization suggests that, in some cases, organic matter application for biosolarization can enhance the bioremediation effect of solarization. In summary, the use of a renewable, inexhaustible and pollution-free source of energy, 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 tested insecticides.

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