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PERSISTENCE OF CHLORPYRIFOS AND ENDOSULFAN IN SOIL

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SUMMARY

The effect of different factors, such as temperature and soil moisture content, in the degradation of chlorpyrifos and endosulfan in soil was studied under laboratory conditions. In addition, field experiments were conducted in the Spanish region of Badajoz to determine the levels of chlorpyrifos and endosulfan throughout the growing season and the residual levels of these chemicals after harvest of tomato. In general, an increase of the pesticide degradation rate with temperature was observed while correlation of the degradation rate with the soil moisture content was only observed for chlorpyrifos and α-endosulfan. The presence of rhizosphere soils did not change the pesticide degradation rate under the conditions assayed.

KEYWORDS: chlorpyrifos, endosulfan, soil, temperature, degradation, rhizosphere.

INTRODUCTION

Horticultural crops may be affected by different pests causing serious damages to plants and, consequently, important yield reductions. Several insecticides are applied to tomato crops to control pests. Chlorpyrifos and endosulfan are widely used in Spain, the third largest producer of tomatoes for preserved food in Europe. Chlorpyrifos is a broad-spectrum organophosphorus insecticide controlling a wide range of soil insect and arthropod pests [1], while endosulfan, a mixture of α- and β-isomers, is an organochlorine insecticide used for the control of sucking and chewing insects on fruits and vegetables [2]. Fig. 1 shows the chemical structure of both the insecticides. In the application of endosulfan to tomato plants one part of the insecticide reaches the target, while the other is deposited on the soil, whereas chlorpyrifos is usually soil-applied. Therefore, both pesticides are found in the soil, where they are subjected to different processes that will determine the fate of these agrochemicals. Temperature, soil moisture content and soil microorganisms have been reported to be important factors in the degradation of chlorpyrifos [3-7] and endosulfan in soil [8-10]. In addition, soil microorganisms are influenced by the presence of plant roots, and an increase in the microbial cell number and the microbial activity has been reported [11].

The aim of this work was to study the effect of different factors, such as temperature and soil moisture content, in the degradation of chlorpyrifos and endosulfan in soil under laboratory conditions. The influence of rhizosphere soils in the degradation of these pesticides was also studied. Plants used in this assay were tomatoes and several weeds usually found in tomato crops (*Amaranthus retroflexus*, *Chenopodium album* and *Solanum nigrum*). In addition, field experiments were conducted in the Spanish region of Badajoz to determine the levels of chlorpyrifos and endosulfan throughout the growing season and the residual levels of these chemicals after harvest of tomato.

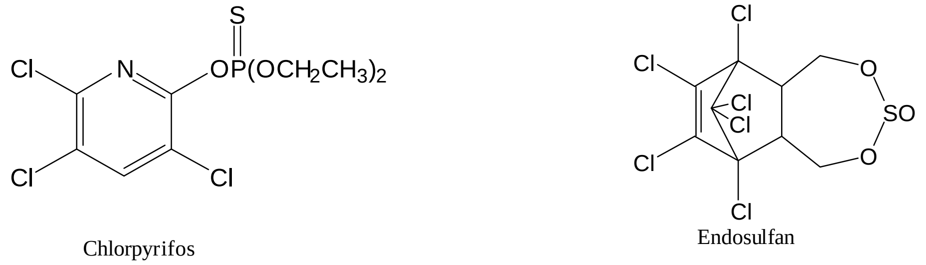

FIGURE 1 - Chemical structure of chlorpyrifos and endosulfan.

MATERIALS AND METHODS

Soils

The main physical-chemical properties of the soil used in the degradation studies were: organic matter 1.75 %, pH 6.7, field capacity 13.3 % (at –33 kPa), density 1.4 g/cm^3, clay 11.54 %, sand 64.81 % and loam 23.65 %. Soil samples were collected from the tilled layer (0-10cm) of an experimental plot located in the region of Madrid (Spain). These samples were sieved (2 mm) and stored at room temperature until treated.

Reagents and solvents

Thimul (α-endosulfan + β-endosulfan 70:30, 35 % w/v suspensible liquid) and Dursban 48 % w/v suspensi-ble liquid (chlorpyrifos), obtained from Rhône Poulenc Química (Madrid, Spain), were used as commercial formulations. Ethyl acetate for pesticide residue analysis and anhydrous sodium sulfate were purchased from Scharlau (Spain) and Merck (Germany).

Laboratory assays

Soil was treated with an aqueous suspension of Thimul and Dursban to reach a final concentration of endosulfan and chlorpyrifos of 1 µg/g. After 24 h of homogenisation, individual samples (24) of 300 g were weighed into screw-top glass jars and distributed in different incubation chambers according to the experimental design to achieve four replicates for each combination of temperature and soil moisture content. To study the temperature effect appropriate amounts of water were added to reach 8 % of soil moisture content (60 % of field capacity) and samples were incubated at different temperatures (5, 15, 25 and 35 ºC). To study the soil moisture effect the temperature was fixed at 25 ºC and samples were incubated at 4, 8 and 13 % of soil moisture content. All the samples were incubated for four months and all the treatments were sampled at intervals of about 20 days. These samples were extracted by a previously described method [12], and the residual concentration of insecticides was determined by means of a Hewlett-Packard Model 5890 gas chromatograph, equipped with an electron-capture detector and automatic injection. A fused silica capillary column, HP-1 (30 m x 0.25 mm i.d. x 0.25 µm film thickness) was employed, with helium as carrier gas at 1 ml/min. The column temperature was maintained at 150 ºC for 1 min, then programmed at 25 ºC/min to 230 ºC, held 0.5 min and programmed at 12 ºC/min to 280 ºC, held 3 min. Injector port and detector temperatures were 270 and 300 ºC, respectively.

Assays with rhizosphere and non-rhizosphere soils

To evaluate the influence of rhizosphere soils in the degradation of the selected insecticides several weeds usually found in tomato crops, *Amaranthus retroflexus, Chenopodium album* and *Solanum nigrum,* together with tomato plants were planted in individual pots (four replicates). Other four replicates of non-rhizosphere soil samples were also placed in pots. All the samples were placed in a growth chamber under controlled conditions (24 ºC and 70 % air humidity) during two months before used in these assays. Plants were removed and the soil remaining was sieved (2 mm) and treated with an aqueous suspension of Thimul and Dursban to reach a final concentration of endosulfan and chlorpyrifos of 1 µg/g. After 24 hrs of homogenisation, individual samples (20) of 300 g were weighed into screw-top glass jars and placed in an incubation chamber at 25 ºC and 8 % of soil moisture content for 3 months. Sampling, extraction and determination of the insecticide residues were performed as described above for the degradation study at different temperatures and soil moisture contents. In addition, microbial biomass was measured in all the soils at the beginning and at the end of the degradation assay by the fumigation-extraction method as described by Joergensen [13].

Field assays

Two tomato fields selected from the Spanish region of Badajoz were periodically sampled from the beginning of the season (May) to the harvesting date (September-October). In addition eighteen commercial fields of the same region were also sampled two months after tomato harvest. Sampling was carried out by taking 10 points from the surface layer (0-10 cm) following the diagonal of the plot and leaving the borders without being sampled. Pesticide residues were determined using the analytical method described above.

RESULTS AND DISCUSSION

Laboratory assays

Various conditions of temperature and soil moisture content were assayed to determine the pesticide degradation rate (Table 1). Results obtained for each treatment fitted well to the first-order kinetic equation $C = C_o \cdot e^{-kt}$, where C_o is the initial concentration of pesticide, C is the concentration at time t and k is the degradation constant.

The determination coefficients (r^2) and the insecticide half-life were calculated by linear regression analysis of the logarithms of the concentration against the incubation time. Half-lives, in the range of temperatures studied at 8 % of soil moisture content, varied from 85 to 25 days for chlorpyrifos, 40 to 27 days for α–endosulfan and 513 to 89 days for the β-isomer (Table 1).

The half-lives obtained for chlorpyrifos and endosulfan are in the range of those reported by other authors [1, 14]. An increase of the pesticide degradation rate with temperature was observed for chlorpyrifos and ß-endosulfan, but for the α-isomer a certain decrease in the degradation rate was observed when temperature changed from 25 ºC to 35 ºC.

TABLE 1
Degradation constants (K), half-lives ($t_{1/2}$) and determination coefficients (r^2) obtained for the insecticides studied [a].

Treatment	T (ºC)	M[b] (%)	Chlorpyrifos (K ± SD)x10^{-2} (day^{-1})	Chlorpyrifos $t_{1/2}$ (days)	Chlorpyrifos r^2	α-Endosulfan (K ± SD)x10^{-2} (day^{-1})	α-Endosulfan $t_{1/2}$ (days)	α-Endosulfan r^2	β-Endosulfan (K ± SD)x10^{-2} (day^{-1})	β-Endosulfan $t_{1/2}$ (days)	β-Endosulfan r^2
T1	5	8	0.81 ± 0.04	85	0.985	1.74 ± 0.08	40	0.984	0.13 ± 0.03	513	0.768
T2	15	8	1.38 ± 0.09	50	0.970	2.15 ± 0.24	32	0.932	0.27 ± 0.04	255	0.813
T3	25	8	2.46 ± 0.18	28	0.972	3.42 ± 0.26	20	0.983	0.57 ± 0.04	121	0.925
T4	35	8	2.82 ± 0.18	25	0.981	2.58 ± 0.18	27	0.974	0.77 ± 0.07	89	0.967
T5	25	4	2.15 ± 0.15	32	0.976	2.68 ± 0.34	26	0.900	0.70 ± 0.11	98	0.909
T6	25	13	2.72 ± 0.27	26	0.951	3.62 ± 0.34	19	0.974	0.70 ± 0.11	98	0.895

[a] Values obtained by linear regression analysis of the logarithms of the concentrations against the incubation time considering eight samplings for each replicate ± standard deviation,
[b] Soil moisture content

TABLE 2 - Effect of temperature and soil moisture content on degradation.

Compounds	Temperature: E_a ± SD (Kjmol^{-1})	Temperature: r^2	Moisture: Log A ± SD	Moisture: A	Moisture: B ± SD	Moisture: r^2
Chlorpyrifos	30.8 ± 4.5	0.960	3.7479 ± 0.0096	42.4	-0.1976 ± 0.0046	0.999
α-Endosulfan	11.9 ± 7.3	0.572	3.5948 ± 0.1317	36.4	-0.2612 ± 0.0637	0.944
β-Endosulfan	42.8 ± 4.3	0.980	4.6208 ± 0.4130	101.6	-0.0182 ± 0.1997	0.008

A decrease of the pesticide degradation rate with temperature is a phenomenon not usually observed, and this fact might be explained by differences in the conversion rate of endosulfan isomers at those temperatures. In fact, a positive correlation of the endosulfan degradation rate with temperature was observed when the α and β isomers were considered together. The effect of temperature on the rate of insecticide degradation was studied using the Arrhenius equation ($k=A_0.e^{-Ea/RT}$). The activation energies (Ea) were calculated by linear regression analysis of the logarithm of the half-life against the reciprocal of the absolute temperature using the results obtained for the treatments, where the moisture content was constant (Table 2).

The influence of the soil moisture content on the degradation of these compounds was studied using the empirical equation $H = A{\cdot}M^{-B}$, where H is the half-life of the insecticide at moisture content M, and A and B are constants. A linear regression analysis of the logarithm of the half-life against the logarithm of the moisture content was accomplished with the data of treatments where temperature was constant (T3, T5 and T6). Results obtained with chlorpyrifos and α–endosulfan fitted well with that equation, while no correlation with soil moisture content was observed for β–endosulfan (Table 2). Constant B gives a measure of degradation dependence with soil moisture content. α-Endosulfan showed the highest negative value, thus degradation of this compound in the soil studied was the most sensitive to the moisture content.

The various rhizosphere soils studied did not affect degradation (at 25 ºC and 8 % of soil moisture content) of pesticides, the half-lives obtained being around 21, 32 and 80 days for chlorpyrifos, α–endosulfan and the β-isomer, respectively. The soil biomass was measured, both at the beginning and the end of the assay, in all the assayed soils and no significant differences (α = 0.05) were found among them (Fig. 2). This fact could explain the similar behaviour observed for the different soils studied.

Field assays

The levels of these chemicals in the soil throughout the season, determined in two tomato fields, varied from 0.15 ± 0.04 to 0.008 ± 0.002 μg/g for chlorpyrifos, from 0.07 ± 0.04 to 0.008 ±0.002 μg/g for α–endosulfan and from 0.15 ± 0.08 to 0.011 ± 0.005 μg/g for β–endosulfan. Pesticide half-lives in the field, determined with these levels, ranged from 14 to 17 days for chlorpyrifos, 21 to 22 days for α-endosulfan and 34 to 73 days for β-endosulfan. These values are lower than those obtained under laboratory conditions. Several factors, such as volatilization, photodegradation and transport, not affecting soil samples during laboratory experiments, may explain the lower half-lives obtained under field conditions. The field half-lives obtained are within the range of those reported by other authors for these compounds [15]. The β-isomer of endosulfan showed the highest half-life both under laboratory and field conditions.

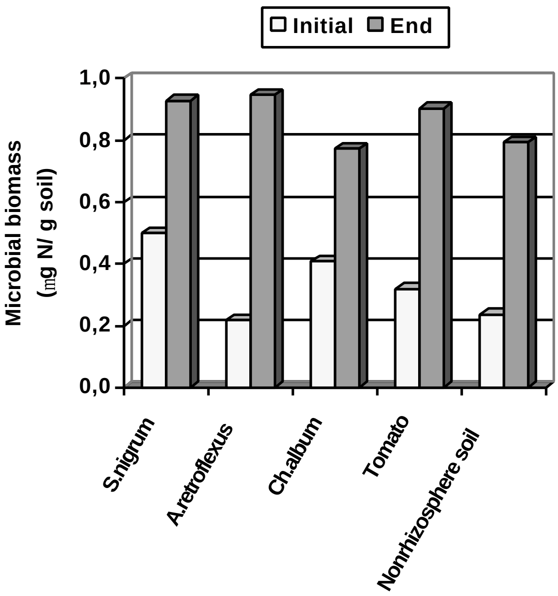

FIGURE 2 - Microbial biomass measured by the fumigation-extraction method in rhizosphere soils (*Amaranthus retroflexus, Chenopodium album, Solanum nigrum* and tomato) and in the non-rhizosphere soil.

A study of residual insecticide levels two months after harvest was carried out in 18 commercial fields. No chlorpyrifos residues were detected, while residual levels of α–endosulfan varied from 0.03 ± 0.02 to 0.0014 ± 0.0007 µg/g and those of β–endosulfan ranged from 0.18 ± 0.06 to 0.009 ± 0.006 µg/g .

CONCLUSIONS

Results obtained in this work indicate an increase of the pesticide degradation rate with temperature for chlorpyrifos and β-endosulfan. The degradation rate of the α-isomer decreased somewhat at the highest temperature assayed. Nevertheless, when the α– and β–endosulfan isomers were considered together, an increase of the degradation rate in the whole range of assayed temperatures was observed. A positive correlation between the pesticide degradation rate and the soil moisture content was found for chlorpyrifos and α-endosulfan, while no correlation between these variables was found for the β-isomer. The rhizosphere soils studied did not affect the insecticide degradation under the conditions assayed.

Results obtained under field conditions pointed out that the half-lives of the insecticides studied were always lower than those obtained under laboratory conditions. β-Endosulfan was the most persistent compound under field and laboratory conditions. No residual levels of chlorpyrifos were detected after tomato harvest, while levels between 0.001 µg/g and 0.18 µg/g were found for endosulfan isomers.

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