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Environmental fate of the insecticide cypermethrin applied as microgranular and emulsifiable concentrate formulations in sunflower cultivated field plots

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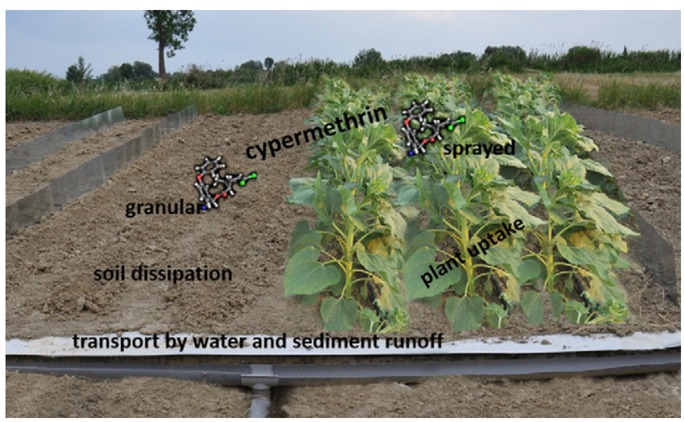
HIGHLIGHTS

- Fate of granular and emulsifiable cypermethrin in sunflower cultivation field study
- The dissipation rate was described better by simple first order kinetics.
- Cypermethrin was found below the 10 cm soil layer occasionally in very few samples.
- Cypermethrin from microgranular formulation was not transferred by runoff water.
- Minor cypermethrin losses by runoff sediment were determined.

GRAPHICAL ABSTRACT



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ABSTRACT

A field dissipation and transport study of the insecticide cypermethrin applied as microgranular (MG) and emulsifiable concentrate (EC) formulations has been conducted in field sunflower cultivations and bare soil plots with two different slopes (1% and 5%). The dissipation of insecticide in soil (on planting rows) was monitored for a period of 193 days. Cypermethrin residual concentrations in the upper soil layer (0–10 cm), 2 days after soil application (DASA), ranged from 0.53 to 0.73 μg g^{-1} when the maximum values were observed 7 DASA, ranged from 1.06 to 1.23 μg g^{-1}. The dissipation rate was better described by first-order kinetics. The average half-life in cultivated (tilled and planted) plots was 23.07 and 24.24 days for soil slopes 5% and 1%, respectively. In uncultivated (tilled but not planted) plots the respective values were 22.01 and 22.37 days. The insecticide was found below the 10 cm soil layer occasionally in few samples at low concentrations (<0.02 μg g^{-1}). In runoff water it was detected once (7 days after foliar application, at levels below LOQ), when in sediment it was detectable for seven samplings. The maximum values were observed 7 days after foliar application, when they reached 0.097 and 0.143 μg g^{-1} in cultivated plots with soil slopes 1% and 5%; and 0.394 and 0.500 μg g^{-1} in uncultivated plots,

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Runoff water
Sediment

respectively. The amount of cypermethrin which was transferred by the sediment remained at low levels (less than 0.01% of the totally applied active ingredient), even in plots with 5% inclination. The insecticide was detected in leaves and stems of the sunflower plants after the foliar application up to the day of harvest. On the contrary, in roots it was detectable during the whole cultivation period. No residues were detected in flowers or seeds.

1. Introduction

Greece, as an EU member, in the effort to reduce greenhouse gas emissions (according to EU directive, 2009/28/EC) has undertaken the obligation to replace, until 2020, the 10% of fuel consumption in transport section with biofuels. Sunflower (*Helianthus annuus*) (commonly cultivated world-wide for edible oil, feedstuff and biofuel production) is the main energy crop in Greece. Its cultivation has been increased the last decade from 5000 to 59,000 ha, replacing other conventional crops such as tobacco and cotton (FAOSTAT, 2011).

As a recently developed crop, very few insecticides have been registered in Greece for sunflower protection against insect pests (GMRDF, 2015). Cypermethrin ((*RS*)-α-cyano-3-phenoxybenzyl (1*RS*,3*RS*;1*RS*,3*SR*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate) has been registered against foliar insects as water emulsion formulations and against soil insects (*Agriotes* genus) as a microgranular formulation. It is a synthetic pyrethroid, not systemic, stomach and contact insecticide with a broad spectrum of activity. It is commonly used world-wide for agricultural, industrial and domestic applications for more than 30 years (USEPA, 2006; FAO, 2009). Due to its wide use and despite the fact that is almost insoluble in water (0.009 mg L^{-1} at 20 °C) (USEPA, 2006) cypermethrin residues have been detected in aquatic environments (surface water, sediment and fish tissue) all over the world (Jabeen et al., 2015; Mahboob et al., 2015; Marino and Ronco, 2005; Vryzas et al., 2011).

Cypermethrin has very low vapor pressure ($2.3 \cdot 10^{-4}$ mP at 25 °C), very high octanol-water K_{ow} ($\log K_{ow} = 5.90$) and high to very high organic carbon K_{oc} ($\log K_{oc} = 3.21–5.58$) partition coefficients (USEPA, 2006; Ismail et al., 2013). In soil, under aerobic conditions, it is biodegraded and it is susceptible to photolysis at a relatively slow rate ($DT_{50} = 28.9$ days) (EFSA, 2008; FAO, 2009; USEPA, 2006). It is very well sorbed in most soils and the binding is increased as the soil organic matter grows (Liu et al., 2009). Cypermethrin is moderately persistent in soil and it is considered as slightly mobile to immobile, therefore it is not likely to leach into deeper soil layers or groundwater (Fenoll et al. 2011; USEPA, 2006). In aqueous solutions and under normal environmental conditions the insecticide presents half-life between 9 and 17 days. Surface waters can be contaminated through spray drift, surface runoff water and soil erosion. In water-sediment systems the concentration of cypermethrin in water rapidly decreases due to the adsorption by the sediment and suspended particles. Furthermore, it is considered highly toxic for aquatic organisms and fish (USEPA, 2006). In plants, cypermethrin remains on the surface and the external tissues (Chavarri et al., 2005; Rasmussen et al., 2003) and its half-life ranges from 0.7 to 8.0 days (Battu et al., 2009; Sadlo et al., 2014).

As far as it is known, there are no reports of insecticide's behavior in the environment when it is applied in microgranular form. In addition, no reports have been found about cypermethrin's persistence in soil or plants of sunflower cultivations. Instead many studies in the literature deal with cypermethrin's persistence on other plants (e.g. Chai et al., 2009; Gupta et al., 2011; Pramanik et al., 2012; Singh et al., 2015), while fewer ones concern the fate of the insecticide in soil, both in laboratory (Gu et al., 2008; Liu et al., 2013; Xie and Zhou, 2008) and field (Battu et al., 2009; Mohapatra, 2014; Mukherjee et al., 2012) conditions. In addition, although many studies refer to the occurrence of cypermethrin in surface water and sediment (Jabeen et al., 2015; Mahboob et al., 2015; Marino and Ronco, 2005; Vryzas et al., 2011), there is a lack of data on insecticide's transport through runoff water and sediment under controlled field conditions (Paracampo et al., 2012).

Herein, the results of an integrated field dissipation and transport study of cypermethrin are presented in order to investigate its environmental fate when it is applied as microgranular (MG) and emulsifiable concentrate (EC) formulations in sunflower cultivations. The objectives of the present work are: (a) to investigate cypermethrin dissipation in bare and sunflower cultivated soil taking into account soil inclination and to study the dissipation kinetics; (b) to study the insecticide transport through runoff water and sediment and (c) to determine the persistence of the insecticide in sunflower plants.

2. Materials and methods

2.1. Chemicals and materials

Analytical standard of cypermethrin (≥98% purity) was procured by Riedel-de-Haën (Pestanal) (Seelze, Germany). HPLC-grade acetonitrile (AcN), ethyl acetate (EtOAc), methanol (MeOH) and water, as well as analytical grade anhydrous magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), sodium citrate tribasic dehydrate, sodium citrate dibasic sesquihydrate and sodium sulfate (Na_2SO_4) were supplied from Sigma-Aldrich (Steinheim, Germany). Primary secondary amine (PSA, 40–60 μm in size), graphitized carbon black (GCB, 40–60 μm in size) and octadecyl silica (C_{18}, 40–60 μm in size) sorbents were obtained from Supelco (Bellefonte, PA, USA), while Oasis HLB solid phase cartridges (6 mL, 200 mg) were purchased from Waters (Mildford, MA, USA).

2.2. Field trials

Sunflower cultivation was conducted between May and August of 2011, at the research farm of the Technological Educational Institute of Epirus (TEIE), Arta (North-Western Greece, latitude 39°07 N, longitude 20°56E). The experimental field (about 700 m^2) was established in a site with no history of pesticide use before the beginning of the sunflower cultivation. The soil type of the field was silty clay (SiC) and its main physicochemical characteristics were as follows: pH 7.9; organic carbon 2.8%; $CaCO_3$ 11.6%; sand 14.9%; silt 39% and clay 46.1% (for sediment the respective values were: 7.7; 4.1%; 10.7%; 7.4%; 42.5% and 50.0%).

The field was divided in two groups of six plots each, with a plot dimension of 4×10 m. The first group was cultivated (tilled and planted), while the other remained uncultivated (tilled but not planted). Two soil slopes, 1% and 5%, were formed in each group, with three plots in each slope. In the lower side of each plot a runoff and sediment collection system was established. The system was constructed so as to collect the runoff water of the whole plot surface. A close loop irrigation system was established as shown in Fig. 1 (Mantzos et al. 2014).

Sunflower seeds were sown in rows at a depth of 3 to 5 cm (0.7 m between each row; 22 cm between the seeds in a row). At the same time, 8 g of a cypermethrin commercial MG formulation (BELLEM 0.8 MG, 0.8% *w*/*w*) was dispersed homogeneously in each 10 m row (96 g of active ingredient per ha (a.i. ha^{-1})) and incorporated into the soil. The insecticide was also applied in the uncultivated plots in furrows (3 to 5 cm depth) that were made for this purpose. After that, the fields were fertilized with 220 g of N, 131 g of P and 249 g of K were added in each plot. Fifty days after the application of MG formulation the