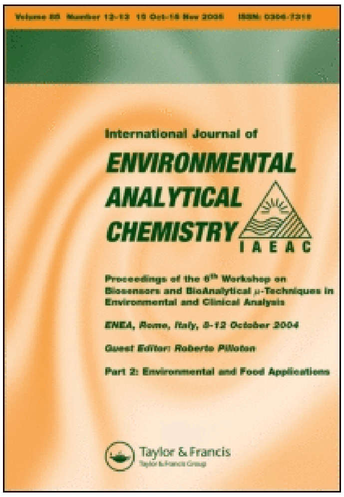

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Persistence of trifluralin in soil of oilseed rape fields in Western Greece

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The persistence of trifluralin, a herbicide exhibiting persistent organic pollutant properties, was investigated in a clay loam (CL) type soil under conventional tillage of oilseed rape and in bare soil. Trifluralin residues were determined with high performance liquid chromatography (HPLC) with diode array detection (DAD) after extraction with acetonitrile using sonication. Trifluralin dissipation was followed for a time period of 150 days and it was characterised by a relative fast initial loss followed by slow dissipation. More rapid loss within the plots of conventional cultivation in comparison to bare soil was observed. The half-life of trifluralin calculated from first-order kinetics dissipation ranged from 53.3 to 56.8 days in the plots with oilseed rape while in bare soil it ranged from 67.9 to 71.4 days. One month after application a considerable loss of about 30% was observed in all fields. Two months later a loss of 40% was observed in bare soil and 60% in the plots cultivated with oilseed rape, indicating the role of crop in the dissipation of trifluralin. Sixteen to 23 per cent of the initial applied trifluralin still remained in soil 150 days after application.

Keywords: trifluralin; oilseed rape; half-life; dissipation

1. Introduction

Oilseed rape (*Brassica napus* L.) is one of the most important crops in Europe. The area of rapeseed cultivation in Europe is approximately 4.6 million ha, a quarter of worldwide production [1]. About 14,000 ha of this crop are cultivated in Greece although that rapeseed production is lower than other European countries. In recent years, globally increased demand for biodiesel render the oilseed rape production important. The beneficial effects of a temperate climate lead to high productivity of this crop in Western Greece. It seems that it can replace crops of the region, which are limited, such as tobacco, and thus it can be used in existing non-cultivated areas.

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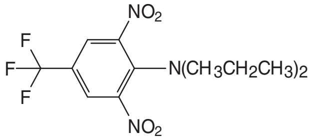
Herbicides are one of the most important groups of crop protection products applied all over the word. Trifluralin, the oldest representative compound for the important chemical family of dinitroanilines, has been commonly used as pre-emergent herbicide, for the control of a variety of weeds in arable crops [2]. Particularly in oilseed rape crop is one of the most widely used herbicides [3]. The compound has limited water solubility (0.221 mg/L), high volatility ($V_p = 9.5$ mPa) and K_{oc} ($\log K_{oc} = 3.90$) (Table 1). Thus, trifluralin is essentially immobile towards leaching and can be transported off-site via volatilisation or may move with particulate matter in surface run-off. The environmental fate of trifluralin has been previously reviewed by Grover *et al.* [5]. Trifluralin is readily degraded by sunlight in all media while volatilisation represents also a major dissipation pathway [8–10]. The persistence (half-life, DT_{50}) of trifluralin in soils under a variety of agronomic conditions ranged between 0.9 and 300 days. According to available scientific information and review reports, trifluralin exhibits characteristics of Persistent Organic Pollutants (POPs). As a result of evaluation process under the Council Directive 91/414/EEC concerning the placing of plant protection products on the market, plant protection products containing trifluralin should have been totally and definitely withdrawn by December 2008 [11]. In Greece the use of trifluralin commercial formulations was allowed till the end of March 2009. Some previous studies have been dedicated to the persistence of trifluralin in soil [3,5,12] but since trifluralin exhibits characteristics of POPs and the persistence of trifluralin in agricultural soils is highly variable depending on several factors, the study of trifluralin dissipation under additional and specific conditions has significant environmental importance.

The environmental fate of pesticides is mainly regulated by their behaviour in soils where various physicochemical and biological processes control their dissipation and movement towards other environmental compartments (air, water, biota). Thus, information on the retention and dissipation of trifluralin are among the key steps in risk assessment of its persistence and contribution to pollution that may deteriorate soil, water and air quality. In addition, trifluralin appears on the lists of pesticides to be monitored as far as water quality is concerned (Water Framework Directive, EC, 2000) and it is detected in surface waters [13–15], thus it is necessary to determine the risk of trifluralin transfer from soil to water by experiments at various scales. Few data have been published regarding the dissipation of trifluralin in soils in the Mediterannean area cropped with oilseed rape [3,16]. The goal of this study was to investigate persistence of trifluralin in soil cultivated with oilseed rape.

Table 1. Physicochemical properties[a] and field half-life of trifluralin.

Structure/Herbicide	MW ($g\,mol^{-1}$)	$\log K_{ow}$	$\log K_{oc}$	Solubility in water ($mg\,L^{-1}$)	Vapour pressure (mPa)	Field half-life (days)
 Trifluralin	335.3	5.07	3.90	0.221 (pH = 7)	9.5 (25°C)	25 to >201 [5] 45–180 [6] 60–132 [7] 1.5–350 [3]

[a]Compiled using data from Tomlin [4]; Hornsby *et al.* [7].

2. Experimental

2.1 *Field experiment*

The experimental field was located in the area of Arta (20.56E, 39.07N) in Western Greece, in a site with no history of pesticide use for the last 10 years. The soil of the field was a clay loam (CL) type and its physicochemical characteristics are shown in Table 2. The total area of the field was approximately 500 m^2 and it was divided into two groups (cultivated with oilseed rape and bare soil, respectively) of three plots each (approximately 40 m^2). Three soil cores were randomly taken and pooled together from three sampling points in each plot. A drainage trench around the experimental field protected the plots from lateral surface run-off. One group of plots was used as replicates for the cultivation of oilseed rape 'Vectra'; the other one was used as replicates for the control plot where herbicide was applied without cultivation in bare soil.

Trifluralin was applied in the experimental field on 21 November 2007 as a water emulsion of the commercial EC formulation Treflan 48 EC (48% w/v) at a rate of 1.2 kg a.i./ha according to recommended agricultural practices. Treflan EC herbicide is a pre-emergent herbicide that is incorporated into the soil to provide long-lasting control of many annual grasses and broad-leaved weeds. Treflan herbicide controls susceptible weeds by killing seedlings as they germinate; however, it does not control established weeds. A conventional tractor-mounted sprayer equipped with a 10 m galvanised boom with 20 spray nozzles and a pressure regulator was used for the application of trifluralin formulation in calm weather. Before use, the spraying device was calibrated in respect to spray beam and pumping volume per time unit. The incorporation of trifluralin into the soil to a depth of 5–6 cm was performed just after application, as recommended, in order to avoid volatilisation [5,8].

Oilseed rape was sown in rows 45 × 5 cm one day after application (22 November 2007) and the plots received all the usual cultural practices (e.g. fertilisation: 10N, $4P_2O_5$ *και* $6K_2O$). Irrigation was not necessary for the development of the plants because the frequency and the volume of precipitation is particularly high in the Western region of Greece, and especially during March and April (Table 3). The meteorological data (Meteorological station of Technological Educational Institute of Epirus, Arta) comprising temperature, relative humidity, precipitation, solar radiation and frost days, from the first spray to final sampling (21 November 2007 to 9 April 2008), are presented in Table 3.

2.2 *Soil sampling*

Nine samplings (Table 4) were performed within the cultivation period (November 2007–April 2008). Soil samples were taken at 0 (three hours after incorporation), 7, 14, 28, 48, 60, 90, 120 and 150 days after application (DAA) by combing five random cores

Table 2. Main characteristics of the soil samples from the experimental site.

Depth (cm)	EC (mS/cm)	pH (water)	Clay (%)	Silt (%)	Sand (%)	OC (%)	$CaCO_3$ (%)
0–30	0.4	7.6	33.84	40.40	25.76	1.86	8.5
30–60	0.5	7.8	35.20	39.58	25.22	1.57	11.2

Table 3. Meteorological data[a] during the experimental period.

Month	Precipitation (mm)	Solar radiation (W/m^2)	Mean daily temperature (°C)	Frost days	Relative humidity (%)
November	201	138	12	0–1	78
December	152	135	8	5	72
January	114	153	9	12	74
February	127	130	9	7	68
March	92	166	12	3	69
April	69	198	15	0–1	67

[a]From the meteorogical station of Technological Educational Institute of Epirus, Arta.

Table 4. Sampling days of soil samples during the experimental period.

Sampling days	Time after application (days)
21 November 2007	0 (three hours after application)
28 November 2007	7
5 December 2007	14
19 December 2007	28
8 January 2008	48
20 January 2008	60
19 February 2008	90
20 March 2008	120
19 April 2008	150

(8 cm diameter) from 0–20 cm depth in each plot. Samples were also taken from control plots at the same experimental periods. The sampling in the cultivated plots was performed near the rootzone of the oilseed rape plants. Soil samples from each plot were put in paper bags, immediately placed in a cooler and taken to the laboratory where they were frozen at −20°C until analysis.

The soil samples from each experimental plot air dried in shade, homogenised, screened through 2 mm mesh sieve to achieve uniform mixing and sampled in duplicate (10 g) prior to extraction or storage (−20°C) until analysis. The moisture content of the soil sample was determined by oven drying at 105°C. The main characteristics of the soils from the experimental site are illustrated in Table 2.

2.3 *Soil extraction*

A soil sample (5 g) was transferred in screw cap glass tube, 20 ml of acetonitrile (HPLC-grade, Merck, Germany) was added and the suspension was shaken in a vortex for 1 min and then in a sonication bath for 10 min. The extraction was repeated twice with 15 ml acetonitrile. Mechanical shaking and sonication-assisted extraction were successfully applied for the analysis of pesticides in soils and sediments [17]. Sonication provides an

Table 5. Mean recovery (average of three replicates for each level) and relative standard deviation (RSD) of trifluralin from spiked soils fortification levels.

	Recovery (%) ± RSD				
	Fortification level (mg/kg)				
Field site (soil type)	1.5	1.0	0.5	0.1	Overall mean
Arta (CL)	96 ± 5	92 ± 3	90 ± 4	89 ± 7	92 ± 4

efficient contact between the solid and solvent usually resulting in a greater recovery of analyte. Acetonitrile has been proved as an extraction solvent with good efficiency for many pesticides including trifluralin while the extracts were purer and there were fewer peaks of co-extractives in the chromatograms [18,19]. The combined extracts were successively centrifuged at 4000 rpm for 10 min and the supernatant was rotary evaporated to 5 ml and concentrated to 0.5 ml under a nitrogen stream. Finally they were filtered through 0.45 μm filters (Millipore, HV, Waters) and analysed by HPLC. For all soil samples, laboratory blanks, spiked and blank soil samples were included.

The efficiency of the method was checked by spiking control air-dried soil samples from the field with trifluralin at four fortification levels (0.1, 0.5, 1 and 1.5 μg/g) by the addition of a suitable volume of trifluralin standard solution in acetone. After thorough mixing, the spiked soils were equilibrated in the dark at laboratory temperature (20°C) for eight hours before extraction. Trifluralin recovery ranged from 86 to 96% for the low and high fortification level. Mean recovery and relative standard deviation (RSD) of trifluralin spiked soils at the previous fortification levels was 92 ± 4.2 (Table 5).

2.4 *Residue analysis*

All solvents were HPLC-grade from Merck (Darmstadt, Germany) and trifluralin standard was obtained from Riedel-de Haen (Germany). Residues were determined by high performance liquid chromatography using a Dionnex P 680 instrument equipped with a Photodiode Array Detector PDA-100 and a Thermostated-100 oven, equipped with a C18 column (SupelcoSil^{TM} ABZ+, 25 cm × 4.6 mm × 5 μm, Supelco). The analysis of the samples was performed at the following conditions: mobile phase of acetonitrile-water (ACN : H_2O–70 : 30, 0–30 min) and the temperature was set at 32°C. The injection volume was 20 μL, and the mobile flow rate was 1 mL min^{-1}. A UV detector response was obtained at 235 nm (trifluralin retention time: 9.81 min) by injecting triplicate standard solutions ranging from 0.1–10 mg L^{-1}. Determination of trifluralin residues in samples was done by comparing the area of the trifluralin peak in the sample chromatogram with the areas of trifluralin standard solution chromatograms and quantified using the external standard calibration method. A good linearity of response was obtained ($R^2 = 0.9963$) in the range 0.1 to 10 mg L^{-1} of trifluralin. The limits of detection and quantification of the method were 0.02 μg/g and 0.07 μg/g dry soil considering a signal-to-noise ratio equal to 3 and 10, respectively. Representative chromatograms of soil sample extracts at days 0 and 90 DAA are given in Figure 1.

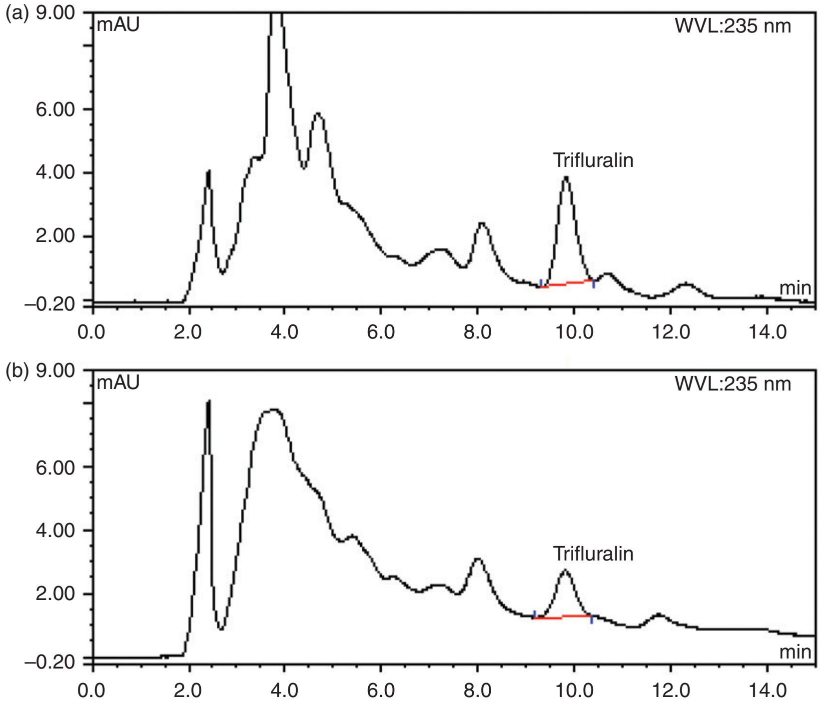


Figure 1. HPLC chromatograms of extracted soil samples at 0 days (a) and 90 DAA (b) from plots tilled with oilseed rape.

2.5 *Data analysis*

Herbicide dissipation was described using first-order kinetics:

$$C(t) = C_0 \exp(-kt)$$

where t is the time (days) after application of the pesticide, $C(t)$ is the residue of the pesticide at time t, C_0 is an initial residue after application (at $t = 0$), k the first-order rate constant of dissipation (day^{-1}).

The herbicide dissipation half-life $T_{1/2}$ was calculated with the following equation:

$$T_{1/2}(days) = \ln(2)/k$$

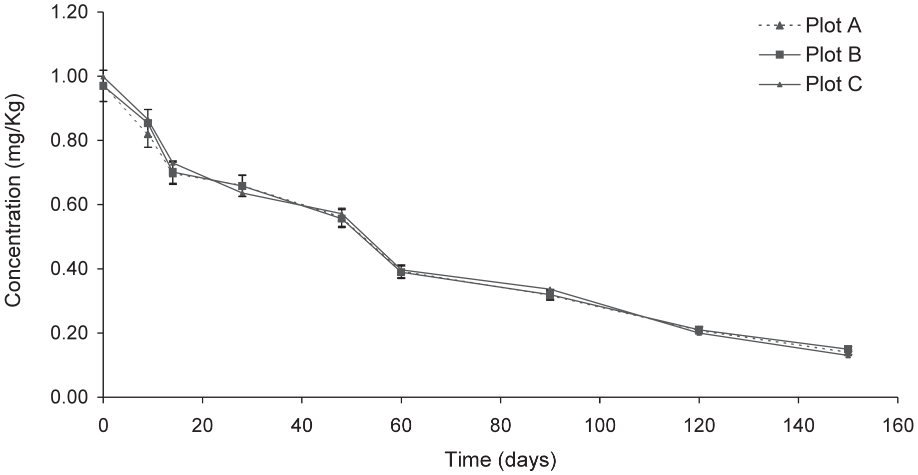
where $T_{1/2}$ is the time required for the pesticide residue level to fall to half the initial application level, k is a dissipation coefficient. Second-order kinetics were also tested for describing the dissipation of trifluralin in the present study; however, the fitting of the model to the experimental data was worse than first-order model.

Concentrations were compared by one-way ANOVA test and mean differences were determined using Duncan's test ($p < 0.05$). The data were analysed using SPSS 14.0 program for Windows.

3. Results and discussion

Trifluralin was not detected in the soil samples that were collected from the soil layer of 0–20 cm before the application of trifluralin. The results obtained from the analysis of soil

(a) plots tilled with oilseed rape "Vectra" (soil layer 0-20 cm)



(b) Plots on bare soil (soil layer 0-20 cm)

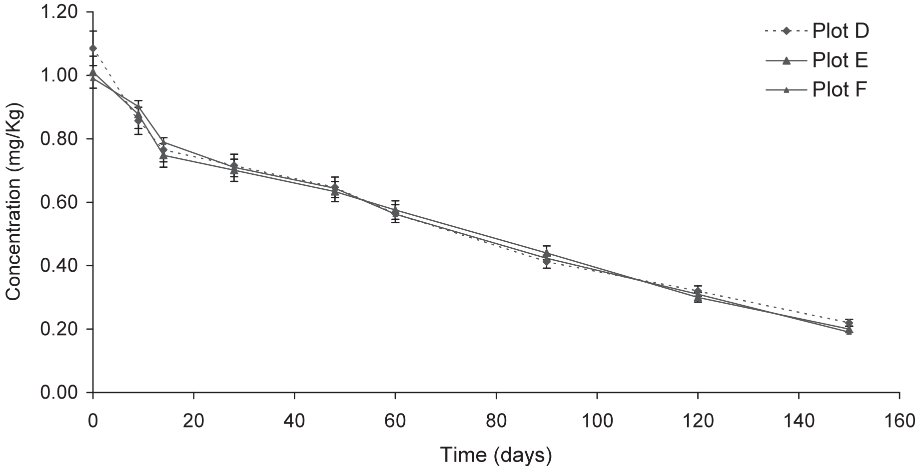


Figure 2. Residual concentrations of trifluralin in the soil layer of 0–20 cm of experimental plots: (a) plots on bare soil and (b) plots tilled with oilseed rape var. Vectra.

samples for the period November 2007–April 2008 are illustrated in Figure 2. Three hours after application, trifluralin concentrations in the soil depth (0–20 cm) were estimated almost at 1 mg kg^{-1}. In preliminary experiments, the analysis of deeper soil layers showed no significant trifluralin residues in accordance with other studies that showed no significant downward transfer of trifluralin [5,16,20–22].

Trifluralin dissipation was followed for a time period of 150 days and was characterised by an initial phase of rapid dissipation followed by a second phase of slower dissipation in agreement with previous findings [3,23]. The first phase was probably dominated by volatilisation [8,16] and the second phase by chemical and biological degradation, and a decrease in the bioavailability of the substance due to an increase in its adsorption over time that make it less accessible to dissipation processes [3,16].

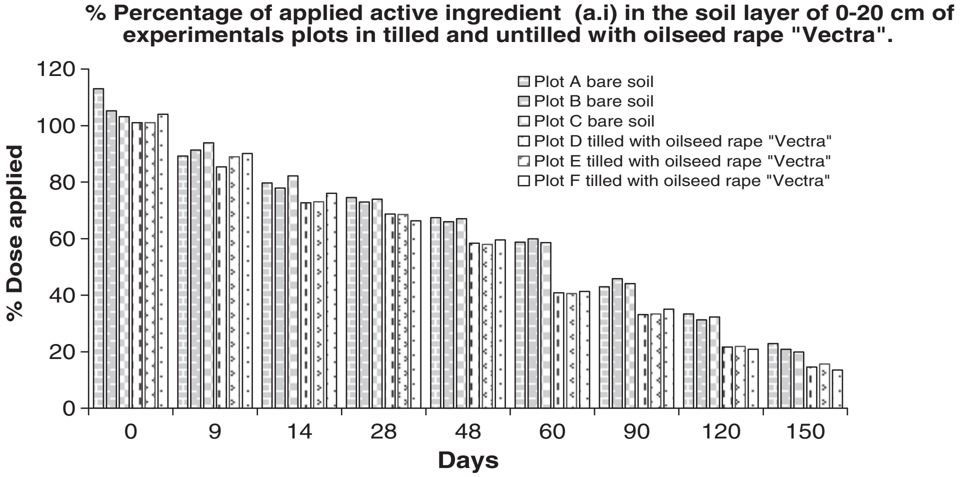


Figure 3. Per cent of applied active ingredient in the soil layer of 0–20 cm of experimental plots in tilled and on bare soil.

Fourteen days following herbicide application the observed loss was about 20% for the bare soil plots and and 26% for the oilseed rape plots. About 10% of volatilisation contribution to trifluralin dissipation was estimated for the time period after incorporation according to Bedos *et al.* 2006 [16] while 26.5% volatilisation losses were reported after 21 days without incorporation [24]. Finally, 60 days after application a considerable loss about 41% and 59% was observed, respectively. 150 DAA of trifluralin about 22% and 15% of applied active ingredient were detected in bare soil plots and oilseed rape plots, respectively (Figure 3), while the corresponding concentration levels were 0.141 and 0.205 mg/kg. Twenty-eight per cent of the applied dose was detected in oilseed rape plots 235 DAA according to Mamy *et al.* [3] while 3.9 ± 0.5% up to 29.9 ± 1.9 % were recorded elsewhere for bare soil 57 DAA for trifluralin sprayed alone and with different adjuvants, respectively [25].

The residual amount and half-life of trifluralin were determined assuming that the dissipation follows first-order kinetics for the investigated period, a model that is usually applied for the evaluation of pesticide persistence [26]. In all cases trifluralin dissipation can be described by first-order kinetics with correlation coefficients $r^2 > 0.9784$. The calculated constant k is the overall apparent persistence rate that expresses the sum of first-order rate constants of the dominant dissipation processes in soil such as volatilisation, biodegradation, hydrolysis and photolysis. The first-order constant k was derived from the slopes of the linear regression of the logarithm of concentration against the time (Table 6).

Our results showed that trifluralin half-life in the group of plots with conventional cultivation of oilseed rape was lower than that in bare soil. The half-life of trifluralin in the plots with oilseed rape ranged from 53.3 to 55.9 days (mean value ± SD = 55.3 ± 1.8 days) while in the plots on bare soil was from 67.9 to 71.4 days (mean value ± SD = 69.8 ± 1.7 days), indicating the role of the crop in the dissipation of trifluralin. However, a much longer period, about 354–378 days for the cropped soil and 452 to 475 days for the bare soil respectively, is needed for the dissipation of trifluralin residues to undetectable levels (0.01 mg/kg or 99% dissipation) according to the observed kinetics. Trifluralin can be

Table 6. Kinetic parameters for the first-order dissipation of trifluralin in plots tilled with oilseed rape and in plots on bare soil.

Plot	Crop	Equation	R^2	k	$t_{1/2}$ (days)
A	Oilseed rape	$C = 0.9191e^{-0.0124x}$	0.9888	0.0124	55.9
B	Oilseed rape	$C = 0.9186e^{-0.0122x}$	0.9881	0.0122	56.8
C	Oilseed rape	$C = 0.9576e^{-0.0130x}$	0.9863	0.0130	53.3
D	Bare soil	$C = 0.9798e^{-0.0097x}$	0.9816	0.0097	71.4
E	Bare soil	$C = 0.9744e^{-0.0099x}$	0.9784	0.0099	70.0
F	Bare soil	$C = 0.9936e^{-0.0102x}$	0.9841	0.0102	67.9

carried over at the end of the growing season and in general such carryover was found to be less than 10% of the applied amount [27].

Other studies for the dissipation of trifluralin in soil (sandy surface) in a South Australian vineyard field [28] demonstrated that the dissipation half-life for trifluralin in surface soil was from 27 to 30 days. The reason for this short dissipation half-life is probably the fact that the herbicide was applied without incorporation into soil. This emphasises the need for caution when calculating the dissipation half-life from field data for volatile pesticides such as trifluralin especially if it is not incorporated upon application. It was found that 18, 29 and 36% of the dose are lost by volatilisation 3, 6 and 12 h after application of trifluralin, respectively [16]. These results show that incorporation of trifluralin has to be done as soon as possible after application in the field. Finally, Bedos *et al.* [16] demonstrated that volatilisation was the major part (71%) of the total soil dissipation measured before incorporation under the experimental conditions in a field cultivated with oilseed. A longer half-life of 204.8 days was found in an oilseed rape field experiment (clay-loam soil) in Eastern France [3], but in this case the average temperature for the experimental period was 6.9°C and the total precipitation was 392.2 mm. In our experiment higher values for total precipitation (755 mm), and temperature (10.8°C) were recorded. In addition, the organic carbon and clay content of the soil in France was higher than in our experiment. The significant differences in trifluralin half-lives between the two studies can be explained taking into account that trifluralin losses generally increase with temperature and soil moisture [29] while trifluralin bound residues in soils are pronounced with time and %OC of soil [3]. It is also possible that microbial degradation reduces with %OC due to reduced bioavailability although that enhanced soil microbial activity was also reported in soils with greater %OC content [30]. Volatilisation decreases when soil organic carbon content increases because it enhances trifluralin sorption. In addition, trifluralin persisted longer in soils with high organic matter and clay content [31]. Moreover, the half-life of trifluralin was found 54.7 ± 10.2 days in clay loam soil tilled with soybeans near Louisiana, USA [22]. In general, it is reported an average field half-life of 45 days on most soils is reported and less than 10% of applied trifluralin remains 1 year after application [27]. The trifluralin half-lives determined by Wauchope *et al.* [32] ranged from 60 to 132 days in several soils. A summary of data on field persistence of trifluralin in different conditions is given in Table 7.

The comparison of trifluralin concentrations among plots with oilseed rape and bare soil is shown in Table 8. Significant differences ($p < 0.05$, Duncan's test) were observed for a time period higher than 28 days when the plants were growing. It is further supported

Table 7. Summary data of dissipation half-lives of trifluralin in various field conditions.

Soil characteristics			Conditions					
Texture	OC %	Country (Region)	Precipitation	T (°C)	Type of study	Agricultural practice	Half-life (days)	Reference
Sandy clay	2.63	Brazil	100 mm[a]	19–42	Bare soil/Field	Without incorporation	0.9	[33]
Sandy	0.86	South Austalia	nr	nr[e]	Vineyard/Field	Without incorporation	27–30	[28]
Sandy	7.1–10.2	Brazil (Mato Grosso)	8.4 mm[b]	19.7–34.8	Bare soil/Field	nr	1.5	[23]
Clay	16–30.6	Brazil (Mato Grosso)	8.4 mm[b]	19.7–34.8	Bare soil/Field	nr	4	[23]
Silt loam	1	USA (Beltsville)	100 mm[c]	8–30	Bare soil/Field	Without incorporation	13.5	[24]
Clay loam	1.63	France (Dijon)	392.2 mm[c]	6.9	Oilseed rape/Field	Immediately incorporated	203.8	[3]
Clay loam	nr	USA (Louisiana)	nr	nr	Soybeans/Field	nr	54.7 ± 10.2	[22]
Clayey silt	nr	Germany (Reinshof)	nr	nr	Oilseed rape/Field	After preplant incorporation	>300	[12]
Loamy sand	nr	Germany (Eickhorst)	nr	nr	Oilseed rape	After pre-emergence	<150	[12]
Loamy sand	0.14	Northern Israel	50%* and 100%[d]	15	Soil columns/Greenhouse	incorporation	59–105*	[34]
Sandy loam	0.31						73–104*	
Sandy clay loam	0.31						101–131*	
Sandy clay loam	0.52						169–198*	
Sandy clay loam	0.59						148*–165	
Sandy loam	0.82						178–257*	
Sandy loam	2.00	France (Chalons)	nr	28 ± 1	Bare soil/Laboratory	Incubation	25.2	
Clay loam	1.63	(Dijon)					24.2	[35]
Sandy loam	0.96	(Toulouse)					14.2	
Clay	11.63	Taiwan	60%[d]	25	Plant material amended soil/Laboratory	Incubation	17.1	[36]

[a]Maximum precipitation; [b]daily precipitation; [c]total precipitation; [d]water holding capacity; nr = not reported; *half-lives for 50% water holding capacity.

Table 8. Comparison of trifluralin concentrations (mg/kg) and dissipation percentages (Mean ± SE) in cropped and bare soil.

Days after application	Trifluralin concentrations in oilseed rape plots	Cumulative dissipation (%) in oilseed rape plots	Trifluralin concentrations in bare soil plots	Cumulative dissipation (%) on bare soil in plots
0	1.010 ± 0.027	–	1.031 ± 0.043	–
9	0.846 ± 0.010	8.51 ± 1.35	0.878 ± 0.013	11.85 ± 1.43
14	0.736 ± 0.017	20.06 ± 1.25	0.767 ± 0.011	26.06 ± 1.06
28	0.657 ± 0.007*	26.16 ± 0.47	0.707 ± 0.004*	32.15 ± 0.78
48	0.571 ± 0.005*	33.18 ± 0.42	0.638 ± 0.007*	41.35 ± 0.48
60	0.404 ± 0.011*	40.92 ± 0.43	0.567 ± 0.008*	59.07 ± 0.23
90	0.323 ± 0.010*	55.70 ± 0.83	0.424 ± 0.006*	66.17 ± 0.61
120	0.215 ± 0.008*	67.70 ± 0.61	0.310 ± 0.007*	78.54 ± 0.32
150	0.141 ± 0.006*	78.79 ± 0.89	0.205 ± 0.007*	85.42 ± 0.60

*Differences are statistically significant at $p < 0.05$ among treatments in the same row. Each point is the mean ± SE of 9 measurements.

that the initial dissipation of trifluralin is mainly owed to volatilisation and to a minor extent photolysis while the cultivation of oilseed rape seems to affect the dissipation rates for time periods longer that 28 days when the dissipation could be owed also to chemical, biological decomposition (plants, root zone) and/or microbial decomposition [37] which is higher in the root area of plants.

Furthermore, soil moisture is also an important factor influencing the dissipation of trifluralin. Although direct moisture measurements in the field were not performed, higher moisture percentages can be ascribed to the cropped soil for similar time periods and fertilisation according to previous studies on water budget in oilseed cultivations [38]. An inverse relationship has been reported between dissipation of trifluralin and soil water content [29,35,36]. When the soil surface dries down to low water content ($0.02–0.05\,\mathrm{kg\,kg^{-1}}$ depending on the soil) the volatilisation of incorporated pesticide is strongly reduced and may cease due to an increase adsorption in soil [16]. A similar effect was reported in dissipation studies of another dinitroaniline herbicide, pendimethalin, that was dissipated faster in the wet regions of soil (along the drip line) compared to dry regions (off the irrigation line) [39]. Soil moisture enhances trifluralin dissipation through microbial breakdown due to increased microbial population and decreased sorption onto soil colloids.

In addition, measurements of soil microbial biomass revealed significant differences in the microbial populations between bulk soil and oilseed rape planted soil as reported elsewhere [40]. The increase in microbial biomass in the rhizosphere associated with an increase in the microbial activity is characteristic of the so-called rhizosphere effect. Planted soil mineralises herbicide faster than bulk soils probably because of a better maintenance of the soil microflora due to the production of root exudates.

Oilseed rape is proposed to replace other crops of the region and the fact that our harvest was too early, it is possible for the winter crops to be used on systems of crop rotation. On the contrary, according to the present and previously published studies detectable concentrations of trifluralin could remain in the soil about 1 year after application [27] while half-lives of trifluralin after repetitive use could be about 10 months [28,29].

So, residues may persist into the following season to injure certain rotational crops. The estimated half-lives of trifluralin in the present and previously published studies under a variety of agronomic conditions cannot be extrapolated for trifluralin dissipation on non-target areas where trifluralin would be surface deposited and, unlike soil-incorporated residues, would dissipate faster subjected to photolysis and volatilisation. Thus, a better understanding of the herbicide behaviour under a variety of conditions and matrices is useful in assessing environmental impact.

4. Conclusions

The persistence of trifluralin in oilseed rape cultivated fields under representative agronomic practices in Greece was studied. The mean field dissipation half-life of trifluralin calculated from first-order kinetics dissipation was 55.3 days in the plots with oilseed rape while in the plots on bare soil it was 69.8 days. Dissipation followed an initial rapid phase, which probably dominated by volatilization, while in the second slower phase, chemical and biological degradation and a decrease in the bioavailability were considered as the major processes. Compared to bare soil, dissipation of trifluralin residues was faster in oilseed planted soil, probably due to enhanced dissipation in the rhizosphere and the greater soil water content that favours its volatilisation. The data generated from this study could be helpful for environmental risk assessment of trifluralin.

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