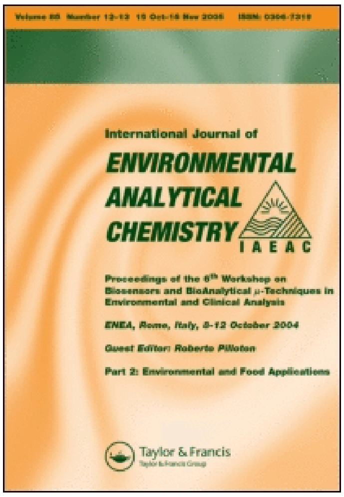

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RUNOFF OF HERBICIDES FROM CROPPED AND UNCROPPED PLOTS WITH DIFFERENT SLOPES

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Losses of the selective herbicides alachlor, metolachlor and EPTC were monitored in runoff waters from experimentally controlled clay-soil plots cultivated with corn. Conditions were selected to simulate agricultural practices employed in the Mediterranean region. Plots were selected to have differing slopes, and uncultivated (control) areas were simultaneously monitored. The duration of the experiment was one year. The surface slopes of the plots, were 0, 1, 2.5, and 5%. Soil erosion was shown to increase with slope from 470 to 1350 kg/ha for slopes of 0 to 5% respectively and the corresponding runoff of surface water was from 6.5 to 26.4% of the total rainfall. Surface runoff herbicide concentrations were highest in the first flush events following the two herbicide applications. Initial concentrations were related to the time that had elapsed between the herbicide application and the runoff event. The maximum concentrations of herbicides in runoff were observed for the plots with the greatest slope (5%) reaching 142 and 154 μg/L for alachlor, 135 and 221 μg/L for metolachlor, and 765 and 1.071 μg/L for EPTC, in tilled and untilled plots, respectively. Cumulative losses of alachlor in surface runoff from tilled and untilled plots (with a slope of 5%) were estimated to be 0.27 and 0.47% of the initially applied active ingredient, respectively. For plots with a slope of 0%, the percentage loss dropped to 0.03 and 0.06% respectively. For metolachlor, the corresponding values from tilled and untilled plots were 0.42 and 1.09% (for a slope of 5%), and 0.08 and 0.16% (for a slope of 0%). In the case of EPTC, the corresponding values from tilled and untilled plots were 0.44 and 0.63% (slope 5%), and 0.04 and 0.07% (slope 0%). Analyses of soil samples from the plots during the period enabled dissipation kinetics to be studied. Results showed that corn cultivation decreased the half-lives of the herbicides [when compared to the control (uncultivated) fields] as follows: for alachlor from 16.7 to 10 days, for metolachlor from 22.3 to 13.3 days and for EPTC from 17.8 to 8 days.

The slope of the soil surface, the compound's solubility and its sorption characteristics are identified as the major parameters that influence alachlor, metolachlor and EPTC transport in the present study.

Keywords: Herbicides; Alachlor; Metolachlor; EPTC; Runoff; Slope; Corn cultivation; Plots

INTRODUCTION

EPTC (*S*-ethyl-dipropylthiocarbamate), alachlor [(2-chloro-2,6-diethyl-*N*-(methoxy-methyl) acetanilide] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-meth-oxyl-1-methylmethyl) acetamide] are herbicides registered for use on several different

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crops. These compounds are the most extensively used in corn production for the control of broadleaf and grassy weeds. In 1990, about 53 tonnes EPTC, 154 tons alachlor and 244 tons metolachlor, in pure form were used in Greece [1]. Residues of alachlor, metolachlor and EPTC and their metabolites have been detected in survey investigations of surface-water samples in the Axios, Loydias and Aliakmon river basins in Central Macedonia (N. Greece) and the Arachthos and Louros river basins in the Epirus region (N.W. Greece) [2–6]. A major source of these chemicals is runoff from nonpoint agricultural sources. Public health concern is also related to their detection in groundwater samples collected in agricultural areas [7]. This presents the possibility of human exposure via consumption of untreated groundwater in these regions. The European Union has set the maximum contaminant level for all pesticides in drinking water at 0.1 μg/L [1].

Alachlor acts as a selective pre- and post-emergence herbicide [8] and is primarily used in corn cultivation to control broadleaf and grassy weeds [9], as well as in cotton and soybean cultivation. Concern has arisen regarding health risks associated with its continued use. This is primarily due to its potential to induce cancer in laboratory animals [10]. The EPA has classified alachlor as a group B2 carcinogen. Alachlor is an acetamide compound showing a soil half-life of 15–20 days [9] and 30–40 days are needed for the degradation of 90% of the compound's initial level by the action of *Chaetomium globosum* bacteria [11]. The fate of alachlor in soil is mainly controlled by photodegradation on the soil surface and sorption to soil with large amounts of organic matter [12,13].

Metolachlor is a selective herbicide, absorbed predominately by the hypocotyls and plant shoots; its herbicidal activity occurs by inhibition of germination [8]. Metolachlor half-life in soil is in the 20–35 day range [9,14]. Although it is a moderately water-soluble compound (530 μg/mL), and may be expected to exhibit some mobility on a light-textured soil, no movement below 10 cm was observed in sand cores during field experiments [15]. Despite the fact that metolachlor is subject to both microbial metabolism [16] and photodecomposition, residues have been detected in well water and soil at certain locations [17]. Its presence in underground water has been detected by different authors at concentrations ranging from 0.08 to 680 μg/mL [18].

EPTC is a selective systemic preplant herbicide with phytohormonic activity for the control of broadleaf and grassy weeds, such as *Chenopodium album*, *Amarantus blitum*, *Avena* spp., *Setaria* spp. It belongs to the carbamate class of compounds. Temperature, moisture and microbial activity greatly affect its rate of degradation in soils [19, 20]. EPTC is adsorbed strongly and more rapidly by dry soils than by moist or wet soils, resulting in a greater loss from moist soils [21]. EPTC is one of the most volatile herbicides in use today [22].

This work presents the results of a one-year study concerning the fate of alachlor, metolachlor and EPTC with emphasis on runoff. The aim was to investigate the effect of different slopes on the runoff of alachlor, metolachlor and EPTC from small plots untilled and tilled with corn. Although studies on the dissipation rates have been reported [14, 23, 24], there are insufficient data on the effect of the soil slope in relation to cultivation on the mobility and runoff losses of these herbicides. The study was performed under real field conditions of cultivation and rainfall, including tilled and untilled plots with different slopes.

EXPERIMENTAL

Experimental Design and Sampling

The location of the field experiment was selected in the Northwestern side of the Ioannina plain at Katsika, a site with no previous history of pesticide use. The field work was conducted on a clay soil (24% sand, 34.7% silt, 41.3% clay) with 1.94% organic matter and pH = 6.5, that was previously plowed to a depth of 25 cm. The total area of the experimental field was 2 hectares.

The experimental field was divided in 2 groups of 4 plots and the experiment run in duplicate. The slope of the plots in each group ranged from 0 to 5%, with three replications. Each plot of the same slope was divided into 4 sub-plots (4×2.4 m) for the applications of the three different herbicides; the spare plot was the reference. Stainless-steel sampling gutters attached to vertically installed metallic collectors were placed at the end of each sub-plot, 8 cm below the lower part of 4-m corn rows to collect the runoff (Fig. 1). The dimensions of each collector were $30 \times 20 \times 220$ cm and two glass containers (carboys) were connected side by side in order to store the water samples. Corn cultivation took place in three rows, with a row spacing of 80 cm. The direction of the corn rows was parallel with respect to the plot slope. The water collector was placed at the end of the central row in order to collect the runoff from the side dikes. In total, 32 such collectors were used in the experimental design.

The corn was sown on the 9 June 1998 at a depth of 5 cm. The same day 82.1 g of EPTC active ingredient was sprayed on a 76.8-m^2 area and the application rate was 10.7 kg/ha. EPTC was incorporated immediately in the soil to a depth of 5 cm, because it is a volatile compound, liable to evaporation [22]. Ten days later, on 19 June, 33.6 g (4.4 kg/ha) of metolachlor active ingredient and 29 g (3.8 kg/ha) of alachlor were applied by spraying at the other sub-plots (Fig. 1).

The first plant growth was observed on 20–21 June 1998. A second application of herbicide was made on 9 July at half the rate of the initial applications, owing to the great amount of weed growth observed. When the plant height reached 55–60 cm after 35 days, the plants were thinned to a spacing of approximately 20 cm, while the flowering of the plants started between the 65th and 70th days. Broadleaf grasses were planted in both tilled and untilled plots after 15 days. These grasses grew more vigorously among the weed species in the untilled plots than among the corn rows.

Sample Collection

Runoff water samples (1 L) were collected after irrigation or rainfall events. The sampling dates and time after the first herbicide application, as well as climatological data of the area are given in Table I. The entire plot area was irrigated four times in total, and the first runoff event from rainfall occurred on 2 August, 54 days after the first application of EPTC and 44 days after the first application of alachlor and metolachlor.

Soil samples were collected with thorough mixing of eight random cores from each sub-plot using a sub-soil probe with a Kodar PETG copolyester liner (4.6 cm in diameter) and were kept frozen (−20°C) until analyzed. They were cut into 5-cm depth increments for the first day samples and 20 cm for all other soil samples. After mixing, 5 g of soil was weighed into a glass vial and kept refrigerated (4°C) until

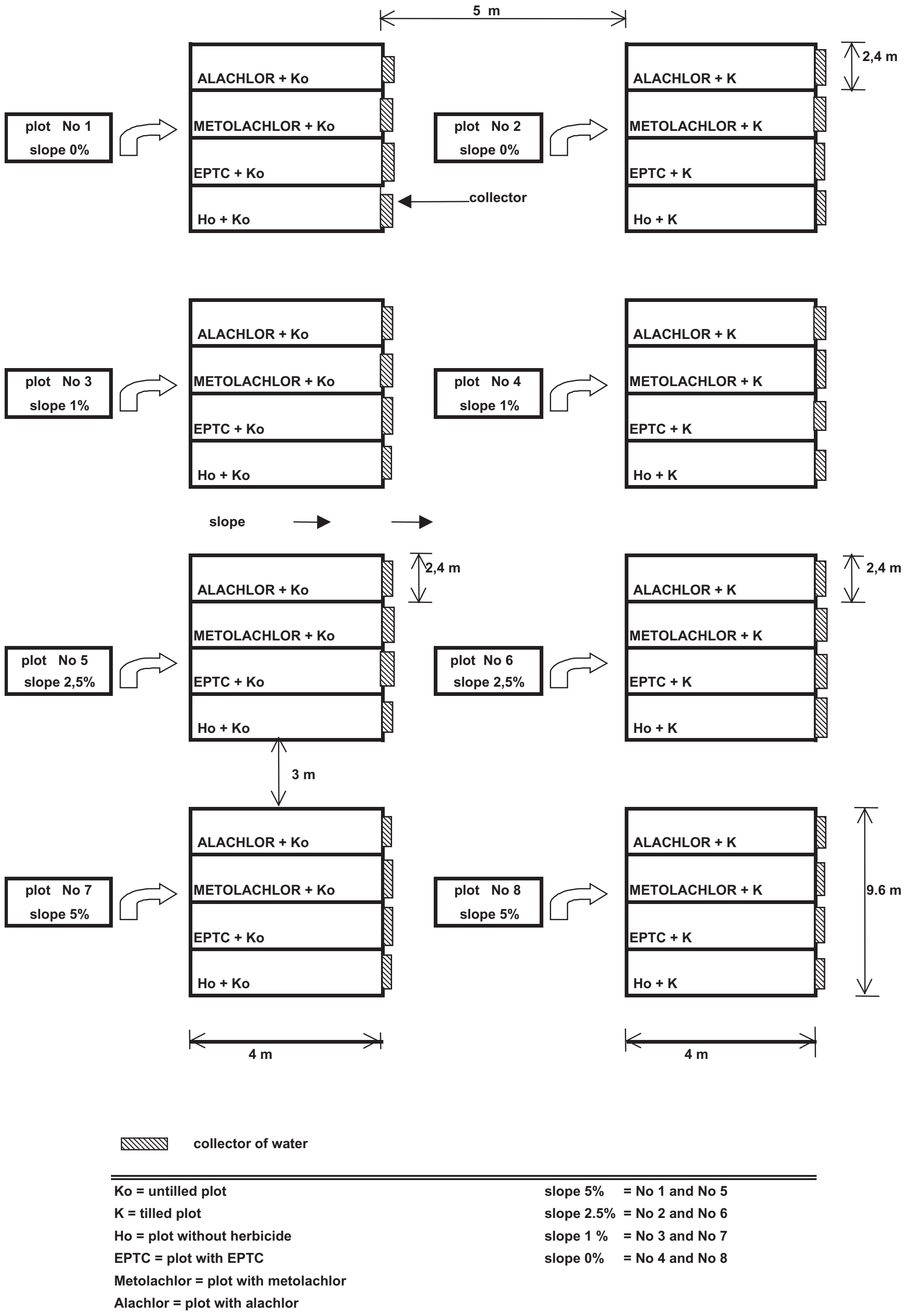


FIGURE 1 The experimental design.

TABLE I Climatological data of the Katsika area and sampling days of runoff events between 9 June and 15 November 1998

Sampling date	*Runoff event*	*Time*[a] (*days*)	*Temperature mean daily* (°C)	*Temperature maximum* (°C)	*Precipitation*[b] (mm)
9 June	Application of EPTC	(0)	24.5	28.2	–
19 June	Application of alachlor, metolachlor	0 (10)	25.7	39.8	–
28 June	Irrigation	9 (29)	26.6	33.4	–
17 July	Irrigation	28 (38)	23.9	26.4	–
27 July	Rainfall	38 (48)	24.9	28.4	6.5
2 August	Rainfall	44 (54)	19.7	20.2	36
11 August	Rainfall	53 (63)	23.1	28.0	2
20 August	Irrigation	62 (72)	21.5	25.4	–
26 August	Rainfall	68 (78)	21.6	24.8	31.5
15 September	Irrigation	88 (98)	23.5	26.4	–
16 September	Rainfall	89 (99)	20.2	23.6	2.5
3 October	Rainfall	107 (117)	17.4	21.2	7
15 October	Rainfall	119 (129)	11.9	12.2	183
25 October	Rainfall	129 (139)	13.7	14.8	38
30 October	Rainfall	134 (144)	7.0	8.0	32.5
9 November	Rainfall	144 (154)	15.5	18.2	80
15 November	Rainfall	150 (160)	10.3	11.2	39
Total					458

[a]Values in parentheses refer to the elapsed days from the application of EPTC; [b]rainfall since previous sampling date.

extracted within 48 h. The moisture content of the soil sample was determined by oven drying at 105 °C.

MATERIAL AND METHODS

Chemicals

The herbicides were applied as EC formulations: alachlor: Lasso, 48% active ingredient – Monsanto Hellas; metolachlor: Dual, 50% active ingredient – Ciba Geigy Hellas; EPTC: Eradicane, 6% active ingredient – Zeneca Hellas. Standard physico-chemical properties of these compounds are shown in Table II. All solvents were purchased from Pestiscan (Labscan Ltd, Dublin, Ireland). Sodium chloride and sodium sulfate were purchased from Merck (Darmstadt, Germany).

Extraction and Analysis

Water Extraction

An aliquot of 800 mL of the collected water was prefiltered through a Whatman filter, and was then extracted with 2×50 mL of *n*-hexane. The organic layer was collected, filtered through 10 g anhydrous Na_2SO_4 and evaporated to 5 mL in a rotary evaporator at 30°C. Finally, the samples were evaporated under a stream of N_2 to 1 mL.

TABLE II Physicochemical properties of alachlor, metolachlor and EPTC

Property	*Alachlor*	*Metolachlor*	*EPTC*
Molecular weight	269.27	283.80	189.32
Solubility in water at 20°C (mg/L)	242	530	375
Vapor pressure at 25°C (mPa)	2.9	1.7	4.7
Log K_{ow}	2.6	2.9	3.2
Log K_{oc}	2.49	2.80	3.11

Soil Extraction

Soil sub-samples of 5 g were extracted with acetone (20 mL) in 20-mL glass test-tubes with shaking (Vortex machine) for 1 min, sonicated in a bath for 15 min and shaken again for 1 min. The soil was allowed to settle for 10 min and the acetone extract was removed. The extraction procedure was repeated twice more with acetone (15 mL). The combined organic extracts were transferred to a 100-mL Erlenmeyer flask, filtered through 10 g anhydrous Na_2SO_4 using fiberglass and evaporated to 5 mL using a vacuum rotary evaporator at 30°C. Finally, the samples were evaporated under a stream of N_2 to 1 mL.

Chromatography Conditions

Analysis of EPTC was performed with a Shimadzu 14A gas chromatograph combined with a flame thermoionic detector (FTD) and a Shimadzu AOC-20i (autoinjector). The chromatograph was fitted with a DB-1 capillary column, 30 m × 0.32 mm i.d., 1-μm film thickness, from J&W Scientific, Folsom, CA. The temperature program was from 130°C (2 min) to 210°C with a rate of 5°C/min, at 210°C for 4 min, 210 to 270°C with a rate of 20°C/min. Helium (1.5 mL/min) and nitrogen (40 mL/min) were used as the carrier and make-up gases, respectively. The detector gases were hydrogen and air, and their flow rates were regulated at 4 mL/min and 120 mL/min, respectively. The ion source of the FTD was an alkali metal salt (Rb_2SO_4) bonded to a 0.2-mm spiral of platinum wire. Splitless injection was carried out at 220°C, the purge valve was on at 1 min after the injection. The detector temperature was 250°C.

Analyses of alachlor and metolachlor were carried out on a Varian-3300 gas chromatograph equipped with a Ni^{63} EC detector. The column used was glass, 180 cm × 2 mm i.d., filled with diverse phase 4% SE-20 + 6% OV-210 coated on chromosorb W, 80–100 mesh. Nitrogen was the carrier gas at a flow rate 60 mL/min. The temperatures of the column, the injector and the detector were 180, 240 and 300°C, respectively.

All samples were run in triplicate and finally their concentrations were analyzed by gas chromatography, quantified after addition of the external standard bromophos-ethyl (1 ppm). Injections were 1 μL for ECD and 1.5 μL for FTD.

Recovery and Detection Limits

The mean recoveries obtained by the above-described analytical procedures were 102.1% in water and 103% in soil samples for alachlor, 72.5% in water and 86.2% in soil samples for metolachlor and 76.1% in water and 95.5% in soil samples for EPTC. The limits of detection achieved in water samples were 0.02 μg/L for alachlor and 0.05 μg/L for metolachlor and EPTC. The detection limits in soil samples were 0.02 μg/g for alachlor and metolachlor and 0.04 μg/g for EPTC.

RESULTS AND DISCUSSION

Runoff Samples

The cumulative amounts of alachlor, metolachlor and EPTC runoff from each plot for the period between 9 June and 15 November 1998, are shown in Figs. 2–4. The water volumes collected after runoff events and the corresponding pesticide concentrations for each plot are given in the Tables III (a,b) and IV(a,b).

The rainfall amount required for runoff events depended on the season, the time lapse between the events and the slope of the sub-plots. The amounts of runoff from rainfall were between 6.5 and 26.4% of the rainfall amounts. A rainfall event of 36 mm was required for the first runoff event on 2 August 1998 and the collected amount of water was 9.2–39.2 L from plots with slope 0–5% respectively. During the winter, smaller amounts of rainfall were required for runoff events, with higher amounts of collected water because of the antecedent moisture effect.

From Table III (a,b) and Figs. 2–4, it is clear that the runoff levels of herbicides were higher at the first and second runoff events due to irrigation, 9 and 28 days for alachlor and metolachlor, and 19 and 38 days for EPTC after their applications, respectively. The concentration level was related to the time lapse between herbicide application and the date of the runoff event. The detected runoff concentration was also high

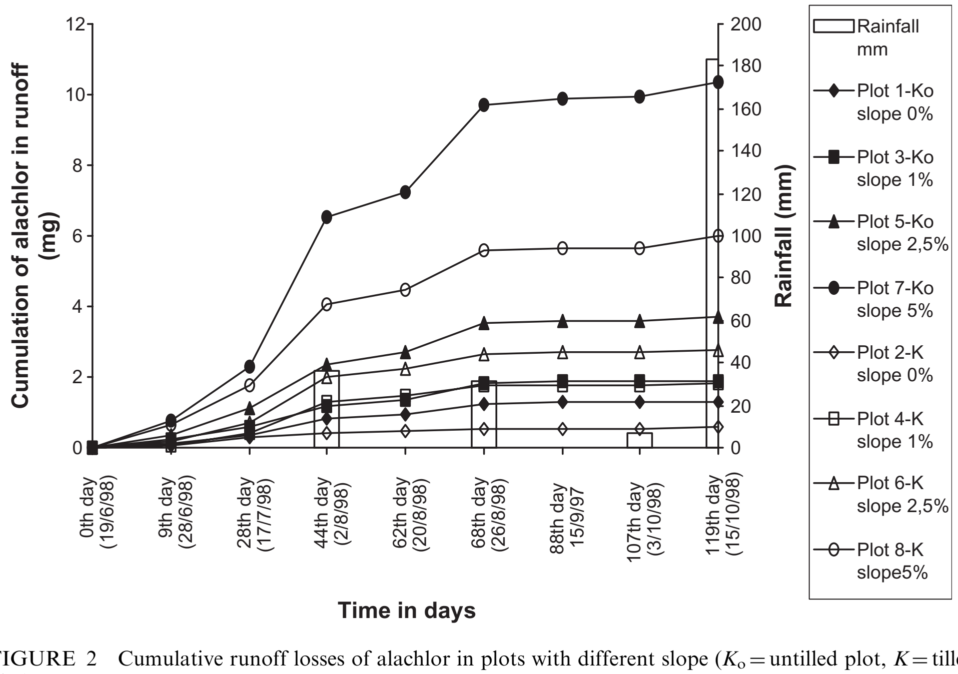


FIGURE 2 Cumulative runoff losses of alachlor in plots with different slope (K_o = untilled plot, K = tilled plot).

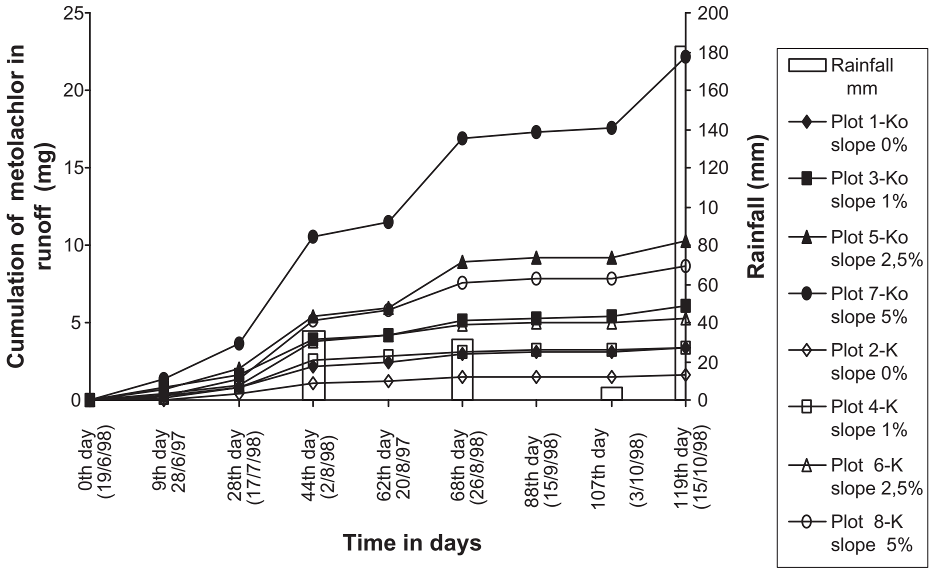


FIGURE 3 Cumulative runoff losses of metolachlor in plots with different slope (K_o = untilled plot, K = tilled plot).

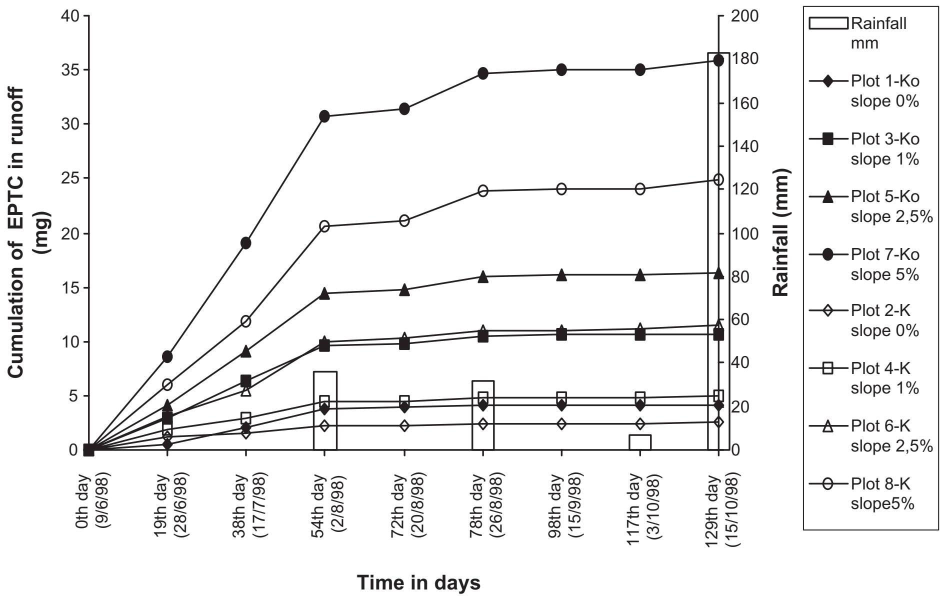


FIGURE 4 Cumulative runoff losses of EPTC in plots with different slope (K_o = untilled plot, K = tilled plot).

after the first major rainfall event, 44 days for alachlor and metolachlor, and 54 days for EPTC after the first herbicide application.

The presence of the applied pesticides was evident 119 days and 129 days for alachlor, metolachlor and EPTC respectively, in the runoff water for the tilled and the untilled plots and for all the different slopes. The detected concentrations were higher for the

TABLE IIIa Water volume collected from tilled plots with corn after runoff events for the period between June 1998 and November 1998

Sampling date	*Time*[a] (*days*)	*Water volume* (mm)											
		Alachlor				*Metolachlor*				*EPTC*			
	Plot slope (%)	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*
9 June	Initial application of EPTC												
19 June	Initial application of alachlor, metolachlor												
28 June	9 (19)	0.28	0.43	0.59	1.08	0.27	0.43	0.55	1.03	0.32	0.33	0.44	0.82
17 July	28 (38)	0.22	0.33	0.44	0.82	0.23	0.34	0.45	0.84	0.22	0.32	0.43	0.80
27 July	38 (48)	–	–	–	–	–	–	–	–	–	–	–	–
2 August	44 (54)	1.02	1.56	2.04	3.82	1.00	1.53	2.00	3.75	1.08	1.71	2.48	4.08
11 August	53 (63)	–	–	–	–	–	–	–	–	–	–	–	–
20 August	62 (72)	0.50	0.59	0.72	1.19	0.54	0.64	0.75	1.20	0.60	0.81	0.84	1.30
26 August	68 (78)	1.94	2.97	3.89	7.28	1.90	2.90	3.78	7.09	2.39	3.22	4.24	7.89
15 September	88 (98)	0.58	0.77	0.89	1.32	0.68	0.91	1.06	1.49	0.65	0.77	0.93	1.29
16 September	89 (99)	–	–	–	–	–	–	–	–	–	–	–	–
3 October	107 (117)	0.32	0.49	0.65	1.21	0.28	0.43	0.56	1.05	0.36	0.51	0.64	1.09
15 October	119 (129)	6.17	9.44	12.33	23.14	5.82	8.91	11.64	21.82	5.85	8.93	11.70	21.47
25 October	129 (139)	1.43	2.18	2.86	5.34	1.22	1.86	2.44	4.57	1.55	2.36	3.00	5.45
30 October	134 (144)	1.60	2.46	3.21	6.01	1.67	2.55	3.33	6.25	2.04	2.79	3.24	6.70
9 November	144 (154)	2.82	4.33	5.67	10.61	2.51	3.84	5.03	9.43	2.62	4.01	5.46	10.1
15 November	150 (160)	1.91	2.94	3.84	7.21	1.83	2.79	3.76	6.84	2.32	3.49	4.23	8.17
Total		**18.79**	**28.49**	**37.13**	**69.03**	**17.95**	**27.13**	**35.35**	**65.36**	**20.00**	**29.25**	**37.63**	**69.16**
Total percentage of rainfall		**4.10**	**6.22**	**8.10**	**15.07**	**3.91**	**5.92**	**7.71**	**14.27**	**4.37**	**6.39**	**8.22**	**15.10**

[a]Values in parentheses refer to the elapsed days from the application of EPTC.

TABLE IIIb Water volume collected from untilled plots without corn after runoff events for the period between June 1998 and November 1998

Sampling date	*Time*[a] *(days)*	*Water volume* (mm)											
		Alachlor				*Metolachlor*				*EPTC*			
	Plot slope (%)	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*
9 June	Initial application of EPTC												
19 June	Initial application of alachlor, metolachlor												
28 June	9 (19)	0.23	0.34	0.46	0.85	0.25	0.38	0.49	0.92	0.25	0.39	0.51	0.96
17 July	28 (38)	0.27	0.43	0.55	1.03	0.28	0.43	0.56	1.05	0.27	0.42	0.55	1.03
27 July	38 (48)	–	–	–	–	–	–	–	–	–	–	–	–
2 August	44 (54)	0.98	1.50	1.97	3.69	0.96	1.47	1.92	3.59	1.01	1.54	2.01	3.77
11 August	53 (63)	–	–	–	–	–	–	–	–	–	–	–	–
20 August	62 (72)	0.45	0.51	0.74	1.09	0.48	0.56	0.71	1.09	0.36	0.46	0.61	0.90
26 August	68 (78)	1.94	2.96	3.86	7.25	1.80	2.76	3.60	6.76	1.86	2.86	3.75	7.02
15 September	88 (98)	0.47	0.60	0.71	1.08	0.56	0.71	0.74	1.23	0.30	0.53	0.70	0.99
16 September	89 (99)	–	–	–	–	–	–	–	–	–	–	–	–
3 October	107 (117)	0.25	0.38	0.50	0.93	0.30	0.47	0.61	1.16	0.22	0.33	0.44	0.82
15 October	119 (129)	5.49	8.40	10.98	20.58	5.08	7.78	10.17	19.06	5.49	8.39	10.98	20.58
25 October	129 (139)	1.26	1.93	2.52	4.73	1.29	1.97	2.57	4.82	1.26	1.92	2.51	4.71
30 October	134 (144)	1.58	2.43	3.17	5.95	1.61	2.46	3.22	6.03	1.69	2.58	3.38	6.33
9 November	144 (154)	2.68	4.08	5.34	10.02	2.69	4.13	5.39	10.10	2.59	3.97	5.19	9.72
15 November	150 (160)	1.72	2.64	3.45	6.45	1.68	2.56	3.34	6.27	1.86	2.86	3.74	7.01
Total		**17.32**	**26.20**	**34.25**	**63.65**	**16.98**	**25.68**	**33.32**	**62.08**	**17.16**	**26.25**	**34.37**	**63.84**
Total percentage of rainfall		**3.78**	**5.72**	**7.48**	**13.90**	**3.71**	**5.61**	**7.28**	**13.55**	**3.75**	**5.73**	**7.50**	**13.94**

[a]Values in parentheses refer to the elapsed days from the application of EPTC.

TABLE IVa Detected concentrations of herbicides in water collected from tilled plots with corn after runoff events for the period between June 1998 and November 1998

Sampling date	*Time*[a] *(days)*	*Concentration* (μg/L)											
		Alachlor				*Metolachlor*				*EPTC*			
	Plot slope (%)	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*
9 June	Initial application of EPTC												
19 June	Initial application of alachlor, metolachlor												
28 June	9 (19)	19.6	20.4	32.8	64.2	19.5	46.8	81.2	26.6	364.0	584.5	715.2	762.1
17 July	28 (38)	102.5	109.3	130.9	142.6	181.1	175.4	116.9	135.7	188.8	319.6	620.9	765.4
27 July	38 (48)	–	–	–	–	–	–	–	–	–	–	–	–
2 August	44 (54)	15.4	58.3	65.9	62.0	65.3	126.3	151.8	104.1	62.6	93.3	187.9	221.3
11 August	53 (63)	–	–	–	–	–	–	–	–	–	–	–	–
20 August	62 (72)	8.6	26.3	29.4	34.9	35.1	42.3	51.9	66.5	10.1	12.0	30.6	42.6
26 August	68 (78)	4.2	10.2	11.4	15.8	11.6	9.2	18.9	25.0	8.7	8.8	16.9	35.2
15 September	88 (98)	1.9	3.5	4.2	5.6	7.0	8.5	11.7	15.2	3.0	3.5	8.7	15.1
16 September	89 (99)	–	–	–	–	–	–	–	–	–	–	–	–
3 October	107 (117)	0.6	0.8	1.2	2.8	3.8	4.5	4.6	5.8	1.3	2.3	4.5	7.0
15 October	119 (129)	0.3	0.5	0.6	1.4	2.2	1.1	1.9	3.7	0.8	1.5	3.3	4.3
25 October	129 (139)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30 October	134 (144)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9 November	144 (154)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15 November	150 (160)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a]Values in parentheses refer to the elapsed days from the application of EPTC; n.d. = not detected.

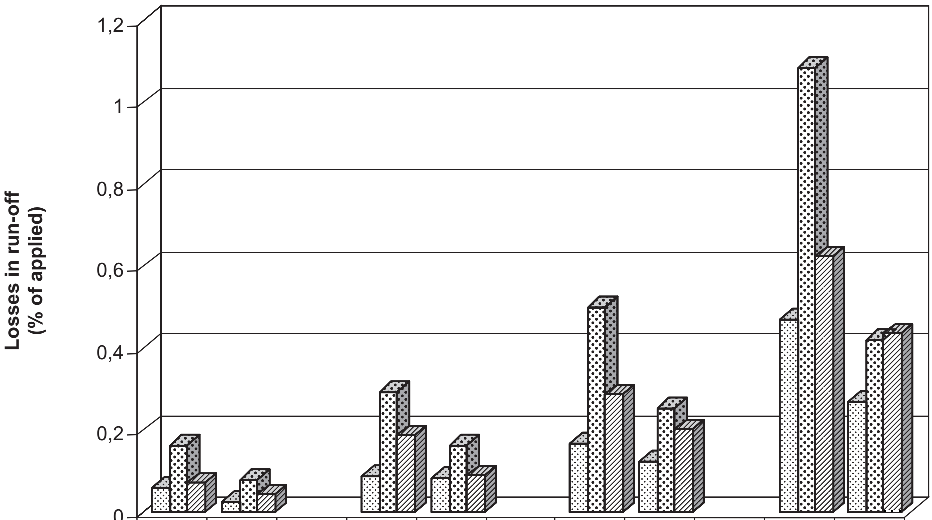
TABLE IVb Detected concentrations of herbicides in water collected from untilled plots without corn after runoff events for the period between June 1998 and November 1998

Sampling date	*Time*[a] (*days*)	*Concentration* (μg/L)											
		Alachlor				*Metolachlor*				*EPTC*			
	Plot slope (%)	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*	*0*	*1*	*2.5*	*5*
9 June	Initial application of EPTC												
19 June	Initial application of alachlor, metolachlor												
28 June	9 (19)	54.8	63.3	84.9	92	94.5	222.8	153.3	154.3	183.5	802.4	855.6	931.0
17 July	28 (38)	97.3	99.3	141.6	154.2	195.7	201.2	231.3	221.1	614.9	829.3	947.4	1071.1
27 July	38 (48)	–	–	–	–	–	–	–	–	–	–	–	–
2 August	44 (54)	47.9	40.9	66.6	120.2	157.9	162.2	188.3	201.5	185.1	225.0	274.5	323.8
11 August	53 (63)	–	–	–	–	–	–	–	–	–	–	–	–
20 August	62 (72)	31.1	25.9	43.3	66.2	42.6	53.1	70.1	94.5	12.1	34.3	48.0	63.3
26 August	68 (78)	16.3	17.9	23.1	35.7	35.9	34.9	86.8	82.5	10.9	26.3	33.5	49.9
15 September	88 (98)	6.5	5.3	7.9	19.8	13.5	20.5	31.1	39.2	3.9	12.7	15.5	23.6
16 September	89 (99)	–	–	–	–	–	–	–	–	–	–	–	–
3 October	107 (117)	0.9	1.9	3.2	4.6	12.4	16.1	16.1	20.1	0.8	3.1	6.4	12.5
15 October	119 (129)	0.5	0.6	0.9	1.9	4.3	9.6	10.4	25.2	0.2	0.3	2.9	4.1
25 October	129 (139)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30 October	134 (144)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9 November	144 (154)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15 November	150 (160)	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.	n.d.

[a]Values in parentheses refer to the elapsed days from the application of EPTC; n.d. = not detected.

TABLE V Mean values of soil erosion from plots with different slope ($N = 8$)

Plot slope (%)	*Sediment collection*	
	Tilled plot (kg/ha)	*Untilled plot without corn* (kg/ha)
0	470 ± 36	350 ± 19
1	680 ± 63	520 ± 44
2.5	950 ± 105	810 ± 78
5	1350 ± 162	1020 ± 106



	plot 1 0%+Ko	plot 2 0%+K	plot 3 1%+Ko	plot 4 1%+K	plot 5 2,5%+Ko	plot 6 2,5%+K	plot 7 5%+Ko	plot 8 5%+K
alachlor	0,059	0,026	0,087	0,082	0,168	0,125	0,469	0,272
metolachlor	0,163	0,08	0,297	0,163	0,501	0,257	1,088	0,423
EPTC	0,072	0,043	0,185	0,086	0,286	0,2	0,626	0,436

FIGURE 5 Percent losses of initial applied active ingredient of alachlor, metolachlor and EPTC in surface runoff with different slope (K_o = untilled plot, K = tilled plot).

untilled plots, and ranged from 4.3 to 25.2 μg/L for metolachlor, from 0.5 to 1.9 μg/L for alachlor and from 0.2 to 4.1 μg/L for EPTC. For the next four determinations in the water samples until the 160th day after the first application, the concentrations were below detection limits.

The reduction of dissolved herbicide residues in waterways is mainly a result of water loss by infiltration and sorption on vegetative and organic matter [24]. At the same time, sediment erosion due to the plot slope (Table V) increases the pesticide pollution of waterways.

A large difference was observed in the concentration levels among the different slopes both in tilled and untilled plots in the same runoff event, for all the events. The effect of slope on the runoff concentration can be derived from the calculated cumulative runoff losses shown in Figs. 2–5. The same can be concluded from the raw concentration results for all herbicides. For the major runoff event of the 44th day the concentration of alachlor in tilled plots ranged from 15 to 62 μg/L for 0 and 5% slope, respectively, while for the untilled plots the corresponding concentrations were 47 and 120 μg/L. For metolachlor, the corresponding values for 0 and 5% slopes were 66 and 104 μg/L (tilled plots) and 157 and 201 μg/L (untilled plots). Finally, for EPTC the corresponding values were 62 and 221 μg/L (tilled plots) and 185 and 324 μg/L (untilled plots).

The maximum herbicide concentrations in runoff were observed for the soil plots with the greatest slope (5%) during the second runoff event, 17 July 1998, reaching 142 and 154 μg/L for alachlor, 135 and 221 μg/L for metolachlor and 765 and 1071 μg/L for EPTC, in tilled and untilled plots, respectively. The low runoff losses in this study are due to a large extent to the delayed application of water in irrigation after chemical application, which simulate the environmental conditions and agricultural practices in the Mediterranean region.

The overall results from these watershed studies under natural rainfall and irrigation conditions indicated that there was little movement of alachlor, metolachlor and EPTC in surface flow. Losses of alachlor in surface runoff, resulting from tilled and untilled plots with a slope 5%, were estimated at only 0.27 and 0.47% of the initially applied active ingredient, respectively, while for plots with a slope of 0% the percentages were 0.03 and 0.06%. For metolachlor the corresponding values from tilled and untilled plots were 0.42 and 1.09% (slope 5%), and 0.08 and 0.16% (slope 0%), and for EPTC the corresponding values from tilled and untilled plots were 0.44 and 0.63% (slope 5%), and 0.04 and 0.07% (slope 0%). From the above results (Fig. 5) the highest percentage loss was observed for metolachlor.

The differences in the solubilities of the herbicides (242, 530 and 375 mg/L for alachlor, metolachlor and EPTC, respectively) and their movement capacity indicated by their leaching potential, can explain to a certain extent the differences in the observed losses. Alachlor and metolachlor were reported as of large and medium runoff potential [25], respectively. The results are also consistent with estimations for percentage fluxes of the above herbicides reported for watersheds with similar soil composition and climatological conditions [6].

Soil Samples

The results obtained from the soil samples for alachlor, metolachlor and EPTC are shown in Figs. 6–8. These figures summarize the changes in the residual concentrations of the three herbicides detected in the corresponding soil plots up to a depth of 15 cm for the period between 19 June 1998 and 28 November 1998.

The herbicide dissipation in soil was over 50% in a period of 15 days for alachlor and metolachlor and 25 days for EPTC after the first (19 June 1998) and second (4 July 1998) compound application. The two main rainfall events that took place on 3 and 28 August with 43.1 and 76.5-mm precipitation have not significantly influenced the herbicide residue concentrations in the top layer of soil. The higher rainfall events that took place between 15 October and 15 November 1998 (372-mm precipitation), seem to have contributed to herbicide residue decrease to non-detectable levels.

From the analyses of soil samples the following quantitative facts are observed:

- There is a gradual drop in the concentration of the three herbicides detected in the soil as a function of time, except for the soil sampling that followed the second application of herbicides on 9 July 1998.

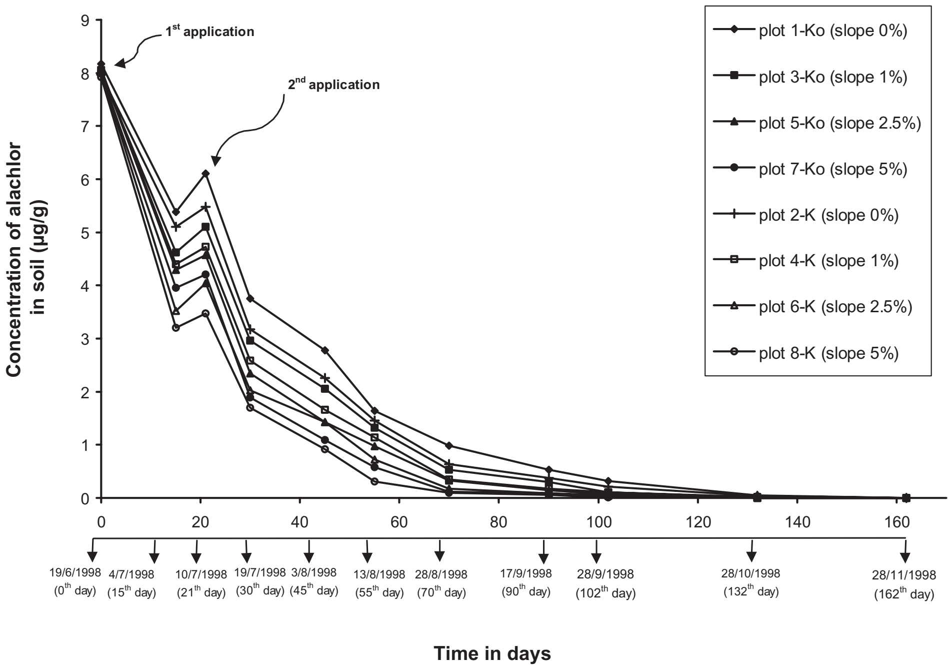


FIGURE 6 Residual concentrations of alachlor in tilled plots (2, 4, 6, 8) and untilled plots (1, 3, 5, 7) with different slopes.

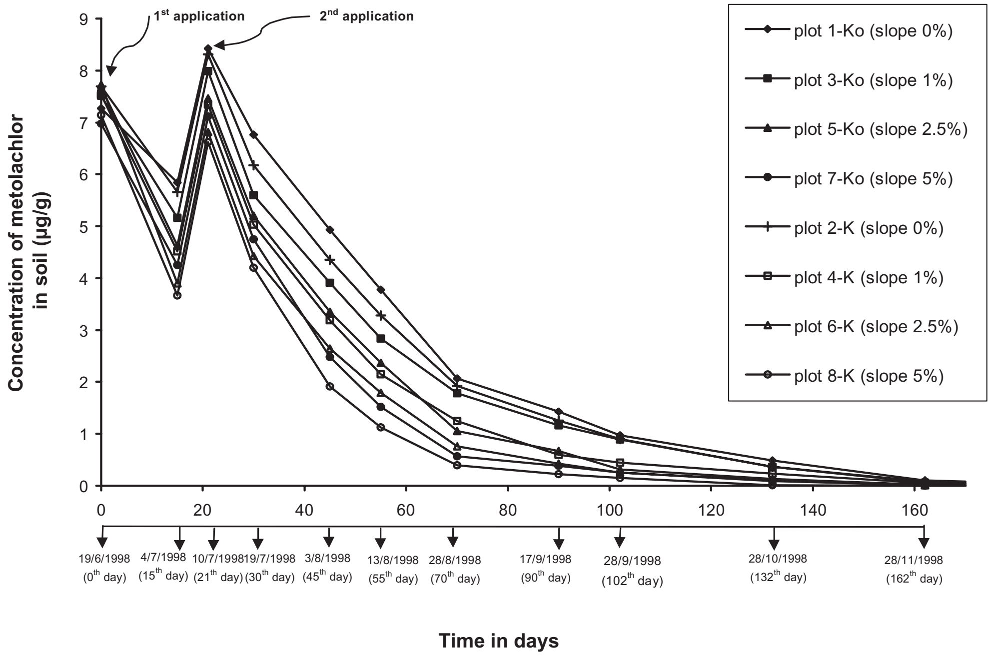


FIGURE 7 Residual concentrations of metolachlor in tilled plots (2, 4, 6, 8) and untilled plots (1, 3, 5, 7) with different slopes.

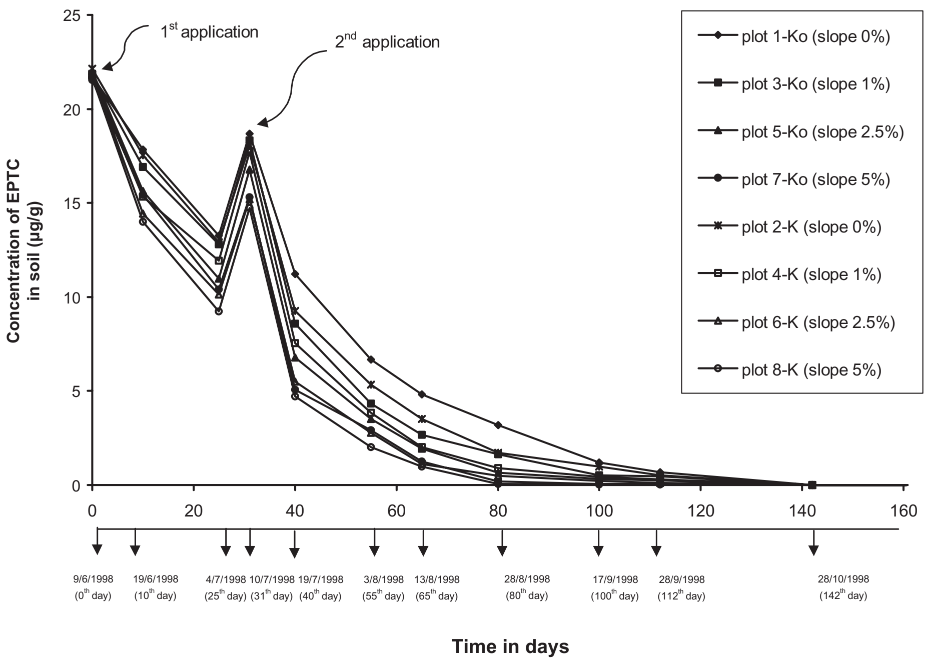


FIGURE 8 Residual concentrations of EPTC in tilled plots (2, 4, 6, 8) and untilled plots (1, 3, 5, 7) with different slopes.

- The dissipation is faster in tilled plots than in untilled plots;
- Increasing slopes accelerate the dissipation of herbicides in soil, but the half-life depends on the physicochemical properties of each compound and the soil properties.

Batch studies have been performed with alachlor, metolachlor and EPTC on clay soil from experimental plots. The results showed that the isotherms were linear over the range of concentrations studied (0.1–20 mg/L). Slopes of the log-transformed Freundlich isotherms were 1.32 for alachlor, 0.91 for metolachlor and 1.07 for EPTC, with correlation coefficients 0.98, 0.92 and 0.99 respectively [26, 27]. The highest sorption capacity was obtained for alachlor; K_d was 16.84 for alachlor, 4.81 for metolachlor and 1.04 for EPTC. The estimated K_{oc} values from the log-transformed Freundlich equation,

$$\log S = \log K_d + 1/n \log C_e, \tag{1}$$

where S = mg of compound adsorbed per kg soil and C_e = mg of compound per liter of supernatant, were 682 for alachlor, 506 for metolachlor and 1608 for EPTC [26, 27].

The gradual drop of the herbicide concentration might be due to various reasons. The first is of physical origin and relates to the transport of herbicide molecules through the soil by rainfall or irrigation water. The second might be of chemical origin, related to hydrolysis of herbicides and destructive reaction with certain soil components. A third might be the microbiological decomposition of herbicides by various micro-organisms existing in the soil. Finally, a fourth mechanism might be photochemical

TABLE VI Fitting parameters k ($R^2 = 0.9664$–0.9929) for the first-order decomposition of alachlor, metolachlor and EPTC in the tilled and untilled plots with different slopes and half-life ($t_{1/2}$)

Plot	*Slope* (%)	*Crop*	*Equation*	*k*	$t_{1/2}$ (*days*)
1	0	–	$C = 17.938 \cdot e^{-0.0296t}$	0.0296	23.4
2	0	Corn	$C = 17.668 \cdot e^{-0.0311t}$	0.0311	22.3
3	1	–	$C = 16.458 \cdot e^{-0.0313t}$	0.0313	22.1
4	1	Corn	$C = 14.464 \cdot e^{-0.0342t}$	0.0342	20.3
5	2.5	–	$C = 18.555 \cdot e^{-0.0393t}$	0.0393	17.6
6	2.5	Corn	$C = 21.585 \cdot e^{-0.0464t}$	0.0464	14.9
7	5	–	$C = 15.334 \cdot e^{-0.0411t}$	0.0411	16.9
8	5	Corn	$C = 20.177 \cdot e^{-0.0522t}$	0.0522	13.3
1	0	–	$C = 16.347 \cdot e^{-0.0415t}$	0.0415	16.7
2	0	Corn	$C = 14.301 \cdot e^{-0.0432t}$	0.0432	16.0
3	1	–	$C = 15.926 \cdot e^{-0.0484t}$	0.0484	14.3
4	1	Corn	$C = 16.678 \cdot e^{-0.0534t}$	0.0534	13.0
5	2.5	–	$C = 12.640 \cdot e^{-0.0502t}$	0.0502	13.8
6	2.5	Corn	$C = 13.968 \cdot e^{-0.0576t}$	0.0576	12.0
7	5	–	$C = 11.483 \cdot e^{-0.0561t}$	0.0561	12.4
8	5	Corn	$C = 13.929 \cdot e^{-0.0669t}$	0.0669	10.4
1	0		$C = 59.809 \cdot e^{-0.039t}$	0.039	17.8
2	0	Corn	$C = 54.798 \cdot e^{-0.0417t}$	0.0417	16.6
3	1	–	$C = 58.134 \cdot e^{-0.0453t}$	0.0453	15.3
4	1	Corn	$C = 59.827 \cdot e^{-0.0493t}$	0.0493	14.1
5	2.5	–	$C = 63.507 \cdot e^{-0.0527t}$	0.0527	13.2
6	2.5	Corn	$C = 64.228 \cdot e^{-0.0578t}$	0.0578	12.0
7	5	–	$C = 132.66 \cdot e^{-0.0749t}$	0.0749	9.3
8	5	Corn	$C = 183.04 \cdot e^{-0.0865t}$	0.0865	8.0

in nature, and this will clearly be operative at the surface of the soil. Evaporation is also especially important for EPTC because of its high volatility.

The gradual dissipation of alachlor, metolachlor and EPTC from field soil under natural cultivation conditions can be described by first-order kinetics. In Table VI (a–c) the data are fitted to the first-order kinetic equation shown.

$$C = C_0 \cdot \exp(-kt) \tag{2}$$

Then the total rate of dissipation R_{total} will be the sum of the particular rates resulting in a final first-order equation:

$$\begin{aligned} R_{\text{total}} &= R_{\text{physical}} + R_{\text{chemical}} + R_{\text{biochemical}} + R_{\text{photochemical}} \\ &= (k_{\text{physical}} + k_{\text{chemical}} + k_{\text{biochemical}} + k_{\text{photochemical}}) \cdot C = kC \end{aligned} \tag{3}$$

Averaged over all the plots, corn cultivation decreased the half-lives compared to the untilled fields as follows: for metolachlor from 22.3 to 13.3 days, for alachlor from 16.7 to 10 days and for EPTC from 17.8 to 8 days.

Metolachlor is the compound with the highest solubility and the lowest K_d values and presents the highest percentage decrease of the half-life in soil compared to the other two herbicides. This change was much higher in plots with higher slope. The more soluble molecules of metolachlor in the water are more readily adsorbed by the root system of the plants together with the adsorbed water. In addition, the high solubility of metolachlor contributes greatly to the rapid disappearance of its residues from the soil, owing to the large runoff and soil erosion with surface flow.

CONCLUSIONS

The slope of the soil surface, the solubilities of the compounds and their different sorption capacities are the main parameters influencing the transportation of the studied herbicides, alachlor, metolachlor and EPTC residues via surface water in soil–water systems. A large difference was observed in the concentration levels among the different slopes in both tilled and untilled plots with corn in the same runoff events. The calculated cumulative runoff loss from experimental tilled and untilled plots can demonstrate the effect of slope, on the amount of runoff concentration. For the major runoff event of the 44th day the concentration of alachlor in tilled plots ranged from 15–62 μg/L for 0 and 5% slope, respectively, while for the untilled plots the corresponding concentrations were 47 and 120 μg/L. For metolachlor, the values for 0 and 5% slopes, were 66 and 104 μg/L (tilled plots) and 157 and 201 μg/L (untilled plots). Finally, for EPTC the corresponding values were 62 and 221 μg/L (tilled plots) and 185 and 324 μg/L (untilled plots).

The disappearance rates indicate that corn plantation decreased the half-life of herbicides as compared to the control fields as follows: for alachlor from 16.7 to 10 days, for metolachlor from 22.3 to 13.3 days and for EPTC from 17.8 to 8 days.

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