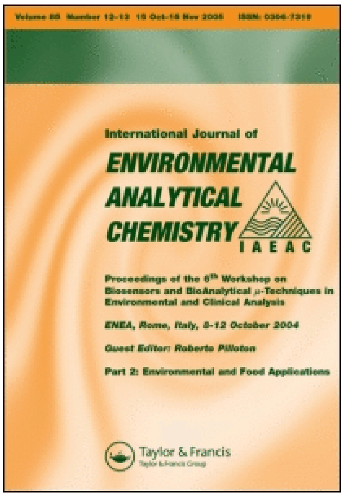

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Imidacloprid losses in surface runoff from plots cultivated with tobacco

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Imidacloprid losses in surface runoff from plots cultivated with tobacco

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The loss of imidacloprid, a systemic insecticide, was determined in runoff water from loamy soil plots of various surface slopes cultivated with tobacco over a period of 174 days. Conditions were selected to simulate agricultural practices employed in the Mediterranean region. The surface slopes of plots were 0, 2.5, 5, 7.5, and 10%, and both cultivated and uncultivated (control) areas were monitored simultaneously. The cumulative losses of imidacloprid in surface runoff from tilled and untilled plots with a slope of 10% were estimated at 0.076% and 0.131% of the initial applied active ingredient, respectively, while for the plots with a slope of 0%, they were 0.003% and 0.005%. Analyses of soil samples for a 110 day period made it possible to study the kinetics of pesticide residue decrease. The average half-life was 17.8 days in bare soil and 16.9 days in tobacco-cultivated plots.

Keywords: Insecticide; Imidacloprid; Runoff; Tobacco cultivation

1. Introduction

The pollution of soil, ground, and surface water by pesticides involves a serious risk to the environment and also to human health due to direct exposure or through residues in food and drinking water. The use of agricultural chemicals inevitably raises questions about the fate of the active ingredient and its degradation products in the environment as well as their effects on ecologically sensitive areas close to agricultural fields. In order to provide information on the fate of an active ingredient under typical environmental and use conditions, field dissipation studies are conducted. Terrestrial field dissipation studies are useful for determining the rate of dissipation of parent compounds under actual use conditions as well as providing an indication of accumulation of residues in soil along with leaching and runoff potential [1].

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Imidacloprid [1-(6-chloro-3-pyridymethyl)-*N*-nitro-2-imidazoli-diamine] is a systemic chloronicotinoid insecticide, first introduced in Europe in the 1990s. It acts as an inhibitor at nicotinic acetylcholine receptors in the nervous system of an insect pest. Imidacloprid controls sucking insects, soil insects, termites, and some chewing insects, and is effective against adult and larval stages. By virtue of its good contact properties and powerful systemic action after uptake through the root system, imidacloprid can be applied to soil and used as a seed dressing or foliar treatment in different crop [2].

Imidacloprid has a low mammalian toxicity [2], and *in vivo* experiments on the blood of tobacco-growing farmers have revealed no cytotoxic effects [3]. The reported analytical methods for imidacloprid in water, soil, and vegetable samples include the use of HPLC–DAD [4–7] owing to its low volatility and, after hydrolysis in a basic medium, the use of GC-MS [8]. The sorption–desorption of imidacloprid and its metabolites has been studied [9–12], and its persistence as affected by pH and type of formulation has been reported [13]. Little is known about the dissipation of imidacloprid in soil and its runoff from the fields.

This work presents the results of a field study concerning the dissipation of imidacloprid, with an emphasis on runoff. The aim was to investigate runoff losses of imidacloprid in soil along with the effect of soil surface inclination and soil cultivation. The study was performed under real field conditions of tobacco cultivation and rainfall, including tilled and untilled plots with different slopes.

2. Experimental

2.1 *Experimental design and sampling*

The experimental field was located in the Agrinio area and in a site with no history of pesticide use for the last 10 years. The field soil consists of loam (46.6% sand, 34.1% loam, and 19.3% clay) with 1.68% organic matter and a pH of 6.24. The total area of the field was approximately 1000 m^2 and the field was divided into two groups of five plots each (approximately 40 m^2). One group of plots was used for the cultivation of tobacco, and the other was the group of control plots where the pesticide was applied without cultivation. Five different slopes (0, 2.5, 5, 7.5, and 10%) were formed in each group. At the end of each plot, a stainless steel collector was attached to collect runoff samples (see figure 1). Tobacco plants were planted in five rows (100 plants per plot) on 8 June 2001. The plots were first irrigated on 7 June 2001 using a Tichelmann irrigation system. The first application of imidacloprid took place 18 days after planting, with an application dose of 5.5 $mg\,m^{-2}$ and a second at the same dose after 45 days, as recommended in tobacco cultivation.

Soil samples were collected as eight random cores in two depths (0–5 cm and 5–10 cm). The samples of each depth were mixed and kept frozen (−20°C) until analysis. The moisture content of the soil sample was determined by oven drying at 105°C. Samples were taken seven times within the cultivation period (June–October 2001).

Water samples from the collectors were collected in amber glass bottles after each irrigation or rainfall event. These were then kept frozen (4°C) until analysis, i.e. within 48 h. The sampling dates and time after the first herbicide application, as well as the climatology data of the area, are listed in table 1. Six samples were collected after irrigation or rainfall events, within the period of June–December 2001.

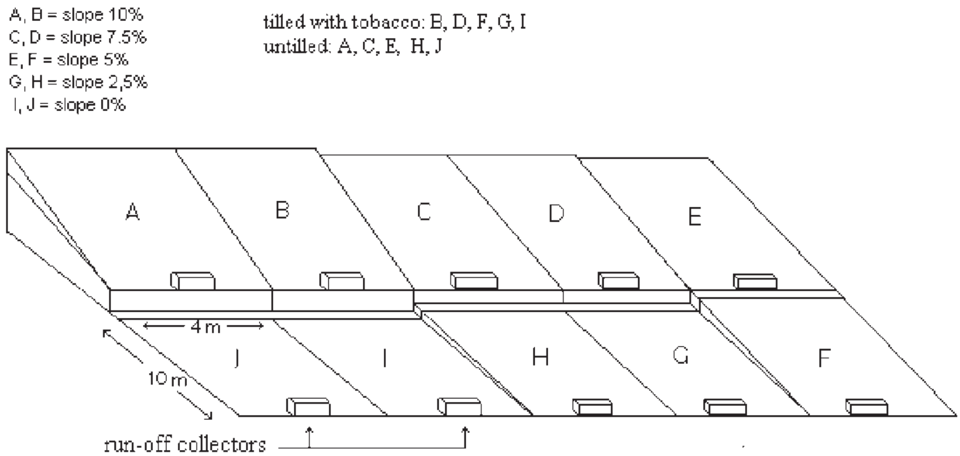


Figure 1. Experimental field diagram.

Table 1. Climatology data of the Agrinio area and sampling days of runoff events between 22 June and 20 December 2001.

Sampling date	Runoff event	Time (days)[a]	Solar radiation (W/m^2)	Relative humidity (%)	Mean daily temperature (°C)	Precipitation plus irrigation (mm)[b]
26 June	First application of imidacloprid	(0)	364.8	72.1	20.2	–
23 July	Second application of imidacloprid	0 (28)	350.2	65.5	23.1	17.5
24 July	Irrigation	1 (29)	344.0	67.5	24.1	74.8
2 August	Irrigation	10 (38)	318.9	62.1	26.3	27.3
6 September	Irrigation	45 (74)	237.6	69.5	21.1	91.0
9 October	Irrigation	78 (106)	183.3	75.1	20.9	54.5
23 November	Rainfall	122 (153)	16.5	88.9	9.5	69.2
16 December	Rainfall	146 (177)	12.5	92.9	9.3	31.6

[a]Numbers indicate time elapsed since the second application, and the days elapsed since the first application are shown in parentheses.
[b]Total amount since the last sampling.

2.2 *Chemicals*

The insecticide was applied as SL formulation: Confidor, 20.6% active ingredient (Bayer, Hellas). All solvents were HPLC-grade from Merck (Darmstadt, Germany), imidacloprid standard was obtained from Riedel-de Haen (Germany), and Empore C18 extraction disks and Empore 400 filter aid glass beads were from Varian (St. Paul, MN).

2.3 *Sample extraction and analysis*

2.3.1. Water extraction. One litre of runoff water sample was extracted using C18 extraction disks. The disks were conditioned with acetone and then with acetonitrile. Methanol was used as extraction solvent (10 mL) and acetonitrile as elution solvent

(1 × 10 mL). One gram of filter aid (Empore 400 filter aid glass beads) was also used. After elution, the collected eluents were passed through funnels filled with sodium sulphate, rotary-evaporated to 5 mL, and then concentrated to 1 mL in a nitrogen stream.

2.3.2. Soil extraction. Soil samples were homogenized, passed through a 2 mm sieve, and 5 g transferred into a glass tube. Twenty millilitres of acetonitrile was added and the mixture mixed in a vortex for 1 min. The samples were put into a sonication bath, left for 10 min, and the solvent phase collected. The extraction was repeated twice with 15 mL of acetonitrile. The extracts were then centrifuged, passed through funnels filled with sodium sulphate, rotary-evaporated to 5 mL, and concentrated to 0.5 mL in a nitrogen stream.

2.3.3. Determination. An HPLC–DAD system (Shimadzu) equipped with a C18 column (25 cm × 4.6 mm × 5 μm, Supelco) and a C18 pre-column (2 cm × 4.6 mm × 5 μm, Supelco) was used for the analysis of samples under the following conditions: mobile phase gradient of acetonitrile–water (AcN: 0–2 min 25%, 7 min 50%, 15 min 90%, 25 min 25%). The injection volume was 20 μL, and the mobile flow rate was 1 mL min^{-1}. Gradient elution was used to separate imidacloprid from other herbicides also applied in the field. A UV detector response was obtained at 270 nm by injecting triplicate standard solutions ranging from 0.1 to 10 mg L^{-1}. All chromatographic runs were performed in duplicate, and the reproducibility of the retention times was ±0.5% or better. The minimum detection concentration was 0.01 mg L^{-1}. The recovery of imidacloprid from a spiked soil sample was 83% (at 5 μg kg^{-1}) and that from water was 86% (at 0.5 μg L^{-1}). The corresponding limits of detection were 2 μg kg^{-1} and 0.01 μg L^{-1}, respectively.

3. Results and discussion

3.1 *Soil samples*

The results obtained from the analysis of soil samples at two depths for the period June–October 2001 are illustrated in figures 2 and 3. There was a gradual drop in residual concentrations of imidacloprid for the topsoil layer as a function of time. A vertical movement was also observed as the concentrations in depth increased within the first and second spraying and up to 24 days thereafter. Low residual concentrations were found in the samples 74 days and after the first application at both levels for all plots. The residues of imidacloprid were detected up to 109 days after the first treatment in all plots at the topsoil layer except for the untilled plot with 10% slope and the tilled plots with slopes of 10, 7.5, and 2.5%, for which the concentration was below the detection limit.

The rate of dissipation was accelerated in the plots planted with tobacco in comparison with untilled plots. The percentage of dissipation, 23 days after the first pesticide application, ranged from 60–70% (slopes 0–10%) of the amount applied for the tilled plots, while it was 54–62% (slopes 0–10%) of the amount applied for the untilled plots.

The dissipation of imidacloprid in soil can be described by first-order kinetics, and the equations and fitting parameters are summarized in the table 2. The half-life for

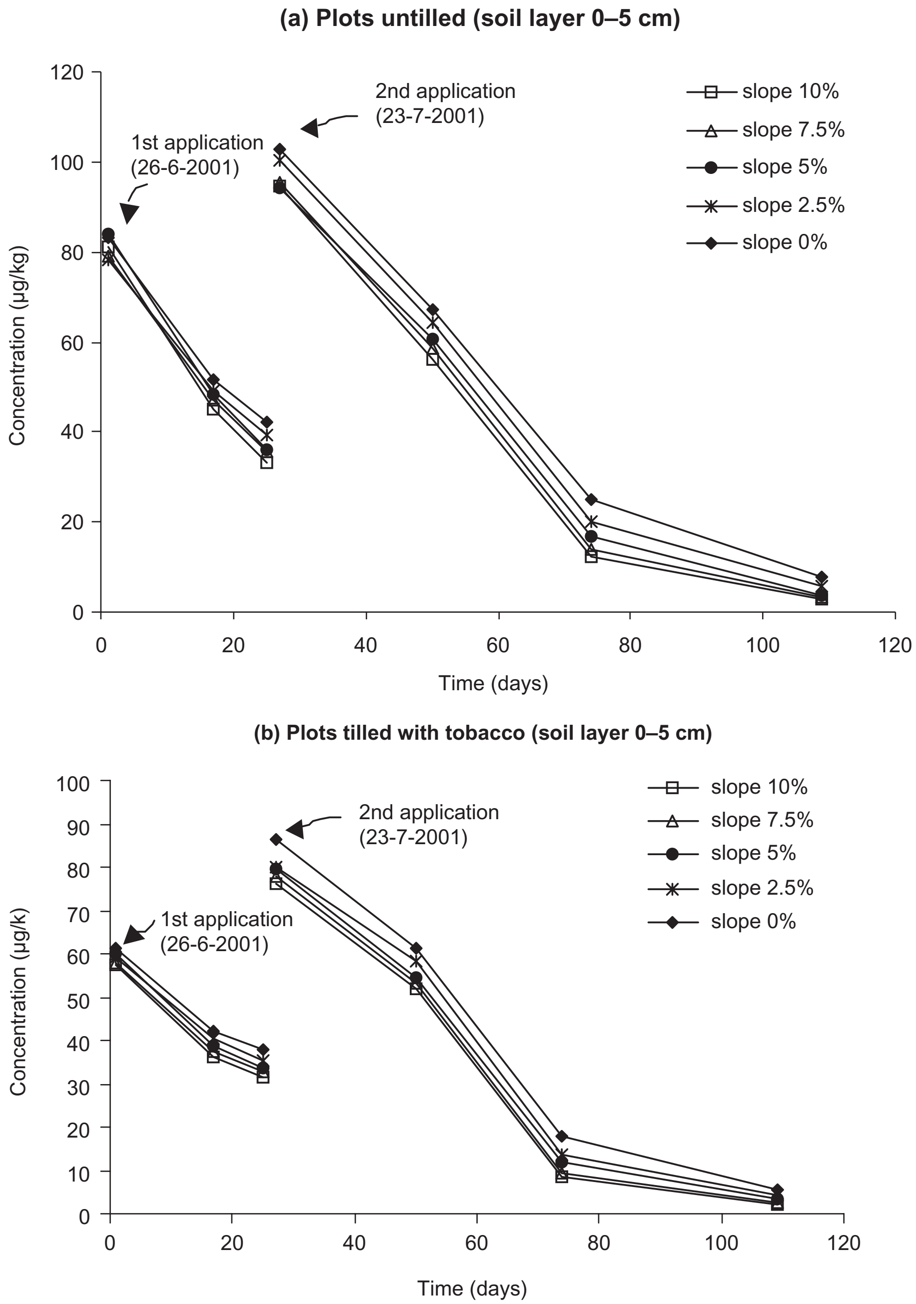


Figure 2. Residual concentrations of imidacloprid in the topsoil (0–5 cm) of experimental plots with different slopes: (a) untilled plots and (b) plots tilled with tobacco.

the different slopes ranged from 15.7 days for a 10% slope to 21.3 for a 0% slope in the untilled plots, while for the plots cultivated with tobacco, the results were lower, ranging from 14.7 days for a 10% slope and 19.6 days for a 0% slope. As expected, soil inclination increased the rate of dissipation in both tilled and untilled plots,

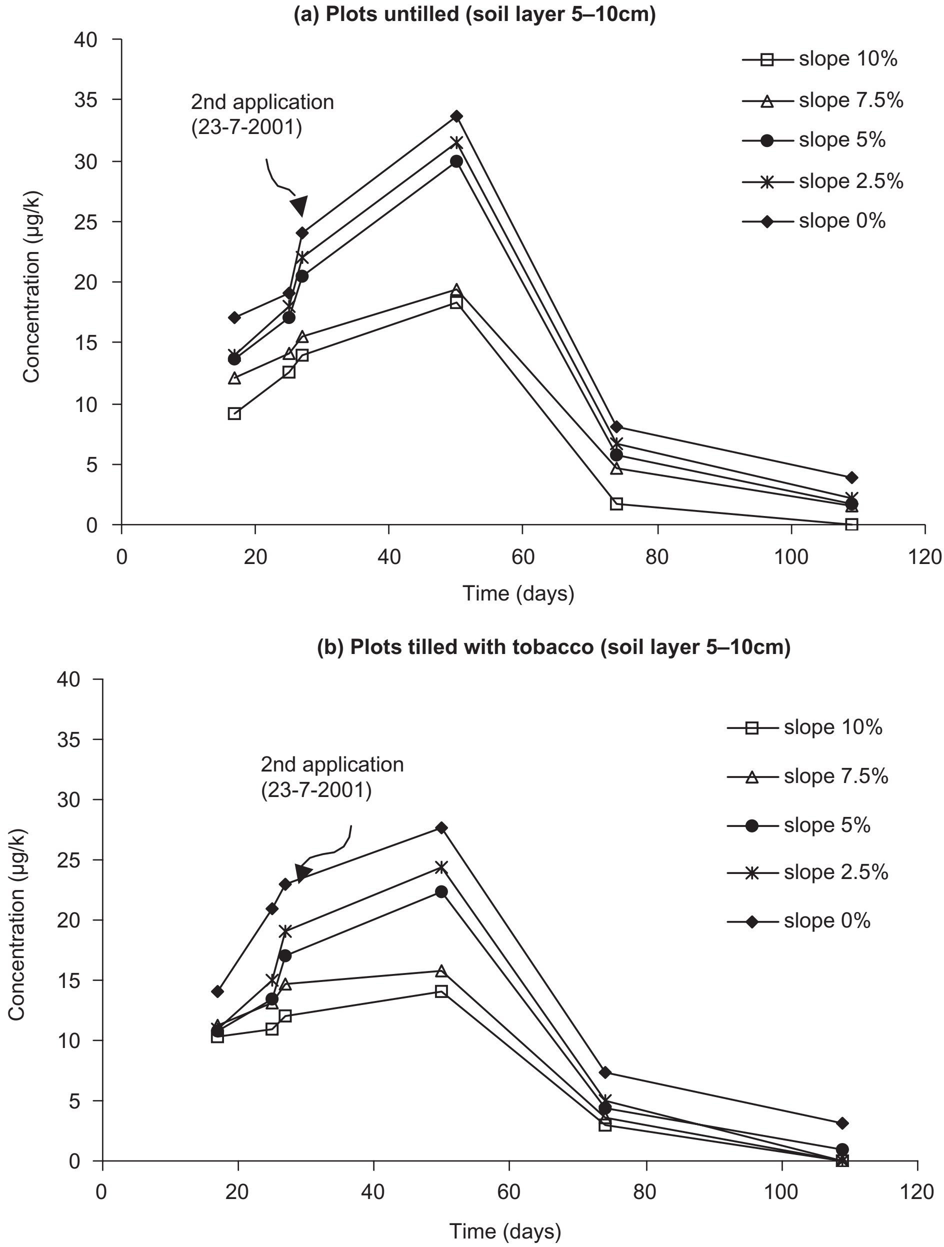


Figure 3. Residual concentrations of imidacloprid in the soil layer of 5–10 cm of experimental plots with different slopes: (a) untilled plots and (b) plots tilled with tobacco.

and this was observed for other field studies for different compounds [14, 15]. Averaged over all the plots, tobacco cultivation decreased the half-life from 17.8 to 16.9. This influence of tobacco plants growth was much lower than that of vegetation in other reported studies [16]. The half-life of imidacloprid in soil reported by Bayer was 7–146 days in field studies in the USA and on average 96 days in Europe [17].

Table 2. Fitting parameters k ($R^2 = 0.9627–0.9857$) for the first-order decomposition of imidacloprid in tilled and untilled plots with different slopes and half-life ($t_{1/2}$).

Slope (%)	Crop	Equation	k	$t_{1/2}$ (days)
0	Untilled	$C = 281.89\,e^{-0.0325t}$	0.0325	21.3
0	Tobacco	$C = 268.5\,e^{-0.0354t}$	0.0354	19.6
2.5	Untilled	$C = 308.9\,e^{-0.0361t}$	0.0361	19.2
2.5	Tobacco	$C = 267.56\,e^{-0.0378t}$	0.0378	18.3
5	Untilled	$C = 348.31\,e^{-0.0408t}$	0.0408	17.0
5	Tobacco	$C = 298.8\,e^{-0.0414t}$	0.0414	16.7
7.5	Untilled	$C = 395.06\,e^{-0.0436t}$	0.0436	15.9
7.5	Tobacco	$C = 329\,e^{-0.0451t}$	0.0451	15.4
10	Untilled	$C = 370.48\,e^{-0.0442t}$	0.0442	15.7
10	Tobacco	$C = 346.83\,e^{-0.0473t}$	0.0473	14.7

The disappearance of pesticides depends on many factors—physical, chemical, biochemical, photochemical—and each one contributes to the total rate of dissipation. Sorption on soil components is one of the governing factors. Batch studies on different soils from the area of the field experiment have shown an adsorption constant K_{oc} value of 300, thus indicating a relatively low adsorption on soil, and so imidacloprid is not expected to show a long persistence in the soil of the field experiment (unpublished data). On the other hand, Cox *et al.* have reported that the sorption of imidacloprid increases with residence time in the soil, which would make it more resistant to leaching [9]. A similar K_{oc} was reported elsewhere for brown forest soil [10] and for different sandy loam soils values, ranging between 109 and 256 [17]. In other studies, imidacloprid sorption was concentration-dependent, and organic matter and minerals were the most important soil properties affecting its sorption on soils [9, 11]. The rate of imidacloprid degradation on soil was shown to be enhanced under the influence of sunlight [17], and this is probably one of the reasons for the disappearance of the pesticide under the field conditions of this experiment, which was conducted in an area of high solar radiation during the summer period (see table 1).

3.2 *Runoff samples*

Residues of imidacloprid were detected in the water samples that were collected in the collectors at each experimental plot after runoff events that were due mainly to irrigation water. Because the period after the first pesticide application (26 June) was dry, the plots were irrigated as described in section 2. Water sampling dates as well as the water amount collected from plots with different plots expressed as millimetres of water that had fallen in the area of the experimental field due to irrigation and/or rainfall are given in table 3. The residual detected concentrations of imidacloprid in the water of the collectors are given in table 4. Runoff water was collected for the first time on 24 July, one day after the second application of the pesticide. Imidacloprid concentrations were at a ppb level and higher in the collectors from the untilled plots in comparison with the cultivated plots for all the slopes. Maximum concentrations were measured in the first runoff event, from 1.5 to 7.61 $\mu g\,L^{-1}$ in tilled plots, and from 1.99 to 11.98 $\mu g\,L^{-1}$ in the untilled plots, beginning with the plot of lower inclination. A gradual drop in residual

Table 3. Water volume collected from plots tilled with tobacco after runoff events for the period between June 2001 and November 2001.

		Water volume (mm)									
		Tobacco cultivation					Untilled				
Sampling date[a]	Time (days)[b]	0%	2.5%	5%	7.5%	10%	0%	2.5%	5%	7.5%	10%
24 July	1 (28)	0.06	0.08	0.19	0.20	0.23	0.05	0.11	0.20	0.21	0.27
2 August	10 (37)	0.05	0.05	0.16	0.20	0.25	0.07	0.09	0.14	0.20	0.26
6 September	45 (76)	0.06	0.09	0.14	0.18	0.20	0.07	0.09	0.16	0.18	0.30
9 October	78 (106)	0.06	0.08	0.11	0.14	0.16	0.07	0.08	0.13	0.14	0.16
23 November	122 (150)	0.40	0.45	0.50	0.64	0.68	0.41	0.45	0.58	0.64	0.73
16 December	146 (174)	0.45	0.50	0.55	0.66	0.73	0.48	0.55	0.61	0.68	0.82
Total water amount		1.09	1.26	1.64	2.02	2.25	1.15	1.38	1.81	2.05	2.53
Water amount as a percentage of rainfall or irrigation		0.94	1.09	1.43	1.76	1.96	1.00	1.20	1.58	1.78	2.20

[a]26 June was the date of the first application and 23 July was the date of the second application of imidacloprid.
[b]The days since the first application are shown in parentheses.

Table 4. Detected concentrations of imidacloprid in water collected from tobacco-tilled and untilled plots after runoff events for the period between June 2001 and December 2001.

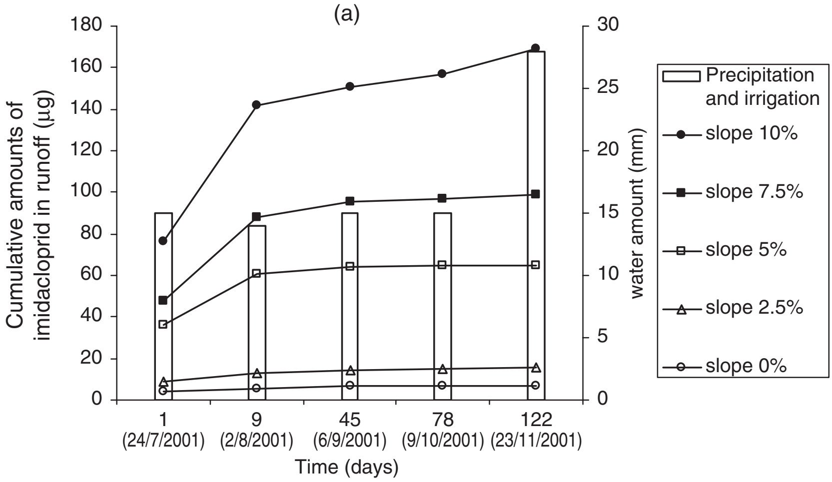
		Concentration (μg/L)									
		Tobacco cultivation					Untilled				
Sampling date[a]	Time (days)[b]	0%	2.5%	5%	7.5%	10%	0%	2.5%	5%	7.5%	10%
24 July	1 (28)	1.50	2.53	4.31	5.37	7.61	1.99	3.16	6.13	7.06	11.98
2 August	10 (37)	0.92	1.84	3.50	4.45	5.99	0.93	2.14	5.10	5.00	9.70
6 September	45 (73)	0.27	0.37	0.57	0.96	0.97	0.57	0.59	1.50	1.08	1.49
9 October	78 (106)	0.16	0.18	0.20	0.19	0.83	0.12	0.08	0.22	0.63	1.09
23 November	122 (150)	nd[c]	0.03	nd	0.07	0.41	0.04	0.15	0.16	0.05	0.29
16 December	146 (174)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a]26 June was the date of the first application and 23 July was the date of the second application of imidacloprid.
[b]The days since the first application are shown in parentheses.
[c]nd: not detected.

concentrations was observed until they reached levels below the detection limit in the samples collected 146 days after the second pesticide application.

The slope of the soil surface and the plant coverage influence the levels of the pesticide transported with runoff. As the inclination increases, the residual concentrations increase, whereas they are generally lower in runoff water from the cultivated plots. This is illustrated better in figure 4 where the cumulative amounts of imidacloprid in runoff for a period of 122 days after the second application are shown for tilled and untilled plots, respectively, along with the rainfall or irrigation amounts.

The cumulative losses of imidacloprid in surface runoff from tilled and untilled plots with a slope of 10% were estimated at 0.076% and 0.131% of the initial applied active ingredient, respectively, while for the plots with a 0% slope, they were 0.003% and 0.005% (see figure 5).



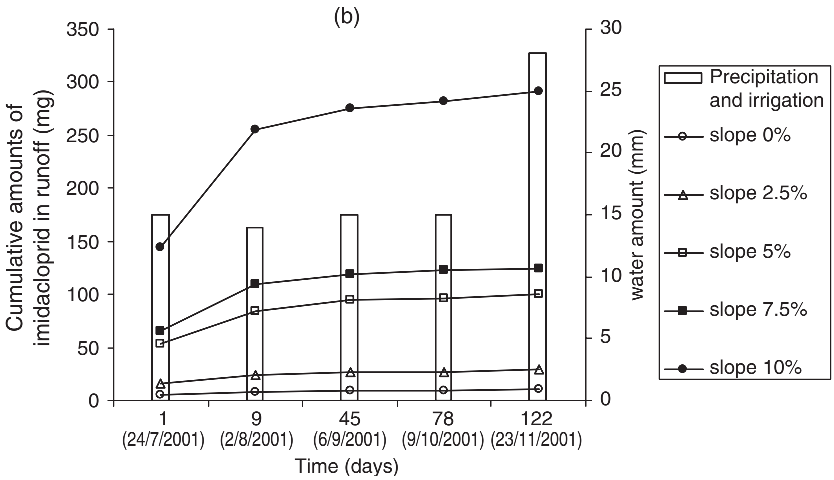


Figure 4. Cumulative amount of imidacloprid (μg) in runoff water: (a) in plots tilled with tobacco and (b) in untilled plots.

4. Conclusions

The dissipation of imidacloprid in the field conditions studied followed first-order kinetics, with an average half-life of 17.8 days in bare soil with an inclination from 0 to 10%. Imidacloprid degradation in soil was enhanced under the influence of tobacco-plant growth in the field experiment conducted, showing a half-life of 16.9 days averaged over all the soil slopes. The measured residual concentrations in runoff water were up to 11.98 $\mu g\,L^{-1}$ for the greatest slope of 10% in the untilled plots and dropped to undetectable levels 146 days after the final pesticide application. Under the conditions of the experiment that were similar to those of typical tobacco cultivation in Greece, less than 0.01% of the initial applied imidacloprid active ingredient was lost with surface runoff.

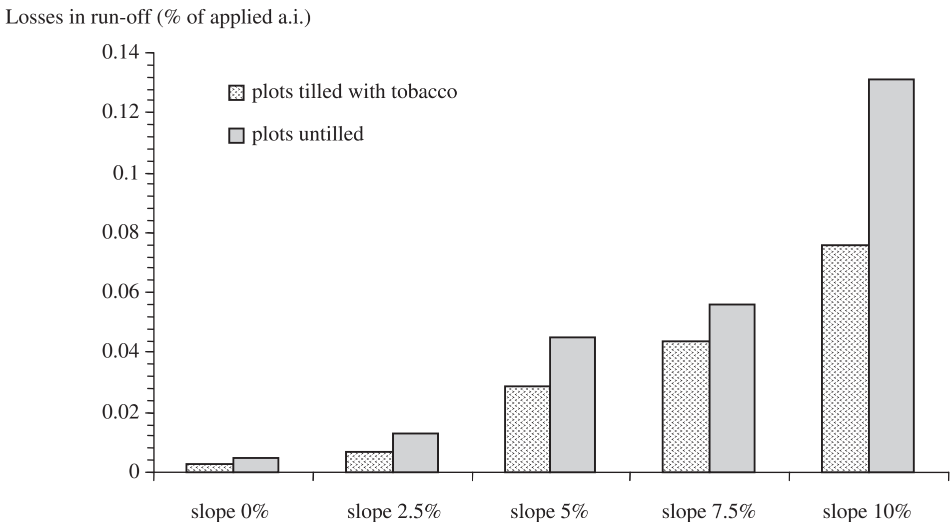


Figure 5. Losses of imidacloprid in runoff as a percentage of applied active ingredient (a.i).

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