

RESIDUES OF ACETOCHLOR HERBICIDE IN SOYBEAN AND SOIL IN MOLDAVIAN FIELD

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Abstract

Herein, we report the results of a study aimed at estimating the potential of acetochlor for translocation into soybean plants and groundwater and its retention in one of the most common soil in Romania. The chloroacetanilide herbicide acetochlor was applied at three different dosages, i.e. 2.2 L ha⁻¹ (Recommended dose), 3.1 L ha⁻¹ (40%+Recommended dose) and 3.96 L ha⁻¹ (80%+Recommended dose) as a pre-emergent spray on soybean crop at 3 days after sowing in the experimental field of Ezăreni – The Experimental Farm of the Agricultural University Iasi. Analyses were performed using Gas chromatography mass spectrometry (GC-MS). Extraction of field soil samples taken from different depths (0-5, 5-10, 10-15 and 15-20 cm) at different times after herbicide application, showed that all applied doses moved deeper and increased dose (80%+Rd) affected the persistence of acetochlor in the top layer increasing its half-life to 5 days. Dissipation followed a first order kinetics. At harvest, soil and plant samples were found to contain acetochlor below maximum residue limits (MRL) following the 80%+ recommended dosage.

Key words: acetochlor, adsorption, residues.

The major processes that determine the retention of pesticide in soil profile and their translocation into groundwater are adsorption and degradation. Understanding the effects of the physicochemical and biological properties of soil and pesticide is important because it allows for the prediction of the environmental fate of pesticides (Paszko T., 2014).

The fate of herbicides applied to soil is governed by herbicide transformation in addition to the influence of factors such as herbicide application rate, crop type, agricultural practices and climatic conditions.

Acetochlor is a selective herbicide with a log K_{ow} of 3.03, which has been used in agriculture on a large scale worldwide (Zhang et al., 2011). Its retention in soil is relatively low, and the phenomenon is highly correlated with soil organic matter and clay minerals. Nevertheless, soil pH influences both the adsorption mechanisms and the contribution of the soil components in the total sorption.

Acetochlor exhibits moderate persistence in soil with half-lives (DT₅₀) in the range of 1- 63 days in topsoil and subsurface with natural moisture (Janniche G.S. et al., 2010). This indicates the presence of bacteria with genes coding for acetochlor degradation in many environments. Microbial degradation is the

primary route of acetochlor dissipation in soil. Factors that influence microbial activity, especially soil temperature and moisture content, in turn influence the persistence of acetochlor.

Adsorption and degradation are often correlated with each other because sorption process affects biodegradation by modifying the chemical bioavailability of the adsorbed species.

It was widely detected as a pollutant in soil and surface water at concentration values higher than the European Union accepted limit for drinking water of 0.1 μg L⁻¹. In European Union, acetochlor, alachlor and metolachlor are currently no longer authorised for use because the residues exceed specified levels in ground or surface water.

The first aim of the current study was to investigate the residues of acetochlor from soil and soybean plants. The second objective was to estimate the adsorption and degradation processes of acetochlor in one of the most common type of Romanian soil.

MATERIAL AND METHODS

Experimental site and sample collection

The study was conducted on a cambic chernozem soil from the southeast region of Romania at Ezăreni – The Experimental Farm of the Agricultural University Iasi (47°07' N latitude, 27°30' E longitude), using a split plot design.

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Soybean was sown in field plots and the size of each plot was 18m x 7m. Guardian (820-860 g L⁻¹ a.i. acetochlor) was applied at three different dosages, i.e. 2.2 L ha⁻¹ (Recommended dose), 3.1 L ha⁻¹ (40%+Recommended dose) and 3.96 L ha⁻¹ (80%+Recommended dose) as a pre-emergent spray on soybean crop at 3 days after sowing with the help of a knapsack sprayer.

Soil samples for acetochlor residues were randomly collected from 0-25 cm depth using a tube auger from 7-8 spots in each plot. Approximately 1000 g of soil was collected from each plot. The samples were taken at intervals of 5, 10, 15 and 30 day after the initial herbicide treatment and after the crop harvest time from all the treated plots.

Soybean samples were collected (500 g) at the crop harvest time. The samples were then subjected to different treatments: mixed thoroughly, air dried ground and passed through a 2 mm sieve and stored in sterile glass bottles in the dark at 4°C until analysis.

Soil and plant sample extraction

The soil and plant samples were used in a solvent extraction procedure using accelerated solvent extraction (ASE) according with the Environmental Protection Agency (EPA) method 3545 for the analysis of organic compounds in solid matrices. A total quantity of 10 g from each sample was mixed in a mortar with 3 g Diatomaceous earth and the mixture was added directly to the extraction cell containing cellulose extraction filters. The extraction was performed under optimized conditions: extraction solvent acetone-hexane (1:1, v/v); temperature: 140°C; pressure: 1500 psi; heat-up time: 5 min; flush volume: 60%; purge: N₂ 60 s; number of cycles: 1.

Acetochlor standard (95%purity) was supplied by Dr. Ehrenstorfer GmbH, Augsburg, Germany. The commercial formulation of acetochlor (Guardian 820-860 g L⁻¹ active ingredient, Monsanto) was used for soil treatment. Analytical reagents including acetone, n-hexane and dichloromethane were bought from Merck, Germany and used for sample processing and extraction.

A stock solution of 1000 µg mL⁻¹ of acetochlor was prepared in n-hexane. Working standard solutions (0.01, 0.05, 0.1 și 0.5 µg mL⁻¹) used for preparation of standard curve were obtained from stock solution by volumetric serial dilution.

GC analyses were carried out on Agilent 7832 gas chromatograph equipped with a mass spectrometer detector an auto-sampler, a split-splitless injector and a HP-5, fused silica capillary column. The column oven temperature program was used in different steps as follows: initial temperature 50°C, increased to 200°C at a rate of 30°C/min, increased to 280°C at 10°C/min and held for 1 min, and then increased to 310°C and held for 3 min. The injector temperature was set to 250°C in splitless mode (volume injected 1.00 µL) and MS temperature was 280°C. Helium (99.999%) was used as a carrier gas with a flow rate of 0.8 mL min⁻¹.

RESULTS AND DISCUSSION

Residues under field conditions

The residue levels of acetochlor in soil during the 30 days after treatment are presented in table 1. There was a decrease in the residue content and by the end of crop period they were detected even in 20-25 cm depth but at concentrations below calibration curves. Among all factors, temperature played an important role in degradation of acetochlor.

Table 1
Dynamics of acetochlor residues at soybean crop

Dose	Depth (cm)	Sampling interval (days)		
		5	15	30
Recommended dose	0-5	0.473	0.398	0.188
	5-10	N.D ^a	N.D	N.D
40%+Recommended dose	0-5	0.621	0.442	0.371
	5-10	N.D	0.018	0.001
80%+Recommended dose	0-5	0.645	0.487	0.369
	5-10	N.D	0.027	B.C ^b

^a not detectable; ^b below calibration curves

On day 5, initial deposits of acetochlor were observed as 0.473, 0.621 and 0.645 mg kg⁻¹ of soil in 0-5 cm depth at recommended dose, 40%+recommended dose and 80%+recommended dose respectively. *Figure 1* shows the chromatograms of acetochlor 5 days after the administration of experimental variants.

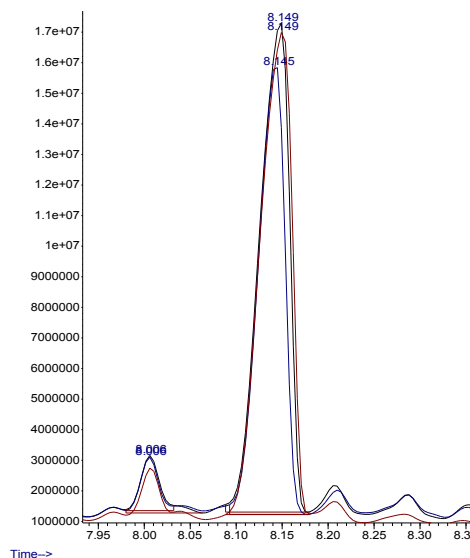


Figure 1 Chromatograms of acetochlor obtained after 5 days

This variation of concentration values between 0.621 and 0.645 mg kg⁻¹ acetochlor indicates a lesser adsorption strength in the conditions of increasing of herbicide concentration. As pointed out by adsorption isotherms (data not shown), the affinity of the acetochlor molecules and soil particles decreases with increases in

acetochlor concentration. Several authors have reported L-type isotherms for acetochlor (Giles et al. 1974; Weber et al. 1989; Hiller et al. 2008).

At a dose of 80%+Rd, residues of acetochlor reached 5-10 cm depth within 15 days, and no detectable residues were found on recommended dose on day 30 of application.

At the two increased rates of application after 30 days, traceable concentration of acetochlor and around of 0.02 mg kg⁻¹ were detected in 5-10 cm depth.

The moment corresponding to the end of crop period suggests that traceable concentrations were reached in 15-25 cm and otherwise completely degraded (table 2).

Table 2
The residues of acetochlor in 0-25 cm depth

Concentration mg kg ⁻¹	Depth cm	D ₁	D ₂	D ₃
		0 - 5	0.07	0.089
	5 - 10	0.06	0.067	0.101
	10 - 15	B.C ^b	0.04	0.04
	15 - 20	N.D ^a	B.C ^b	0.01
	20 - 25	N.D ^a	N.D ^a	B.C ^b

^anot detectable; ^bbelow calibration curves

In the conditions of the applied dose of 80%+Rd the residual acetochlor remaining at the harvest time were higher in surface soil 0-10 cm and around of 0.112 mg kg⁻¹. Similarly, at Rd and 40%+Rd variants, concentrations persist but were mainly limited to 0.06-0.09 mg kg⁻¹ at the end of crop period. The differences between the residual concentrations of acetochlor were mainly caused by leaching, the changes of microbial structure and function and the correlated specific metabolic pathways (Baudoin et al., 2001; Marchand et al., 2002).

Degradation

Figure 2 shows the degradation curves of acetochlor in soil. In Am horizon of the examined soil, acetochlor degradation could be modeled by a first order kinetics with a half-life of 5.3 days.

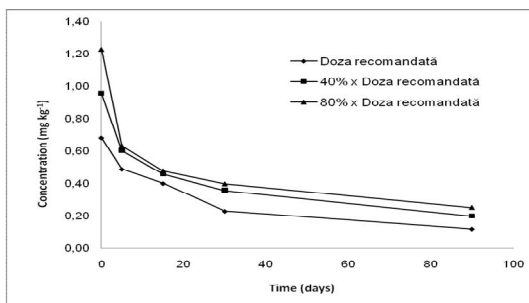


Figure 2 Dissipation rate of acetochlor in soil
Acetochlor degradation occurred at all doses and was more rapid at recommended dose than at

80%+recommended dose. Rates of dissipation are influenced by physicochemical properties of the soil (pH and organic carbon content) biological properties (activity and distribution of microorganisms), the doses applied and environmental conditions that control soil temperature and moisture content.

Residues in soybean

The active ingredient acetochlor was not detectable at harvest time.

The possible ways of acetochlor degradation and dissipation in environment and plants include plant and soil uptake and biotransformation via soil microorganism on soil and conversion to simpler products on plant surfaces.

CONCLUSIONS

Acetochlor was found in the Am horizon of the examined soil and it dissipated faster with concentration that not exceeds the EU contamination limits. The residue trends of all three doses are in the same pattern but at different concentration levels.

Studies have shown that a fraction of acetochlor was retaining by cation exchange mechanism and therefore, the compound was available for plants and microorganisms.

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