Monitoring of acetochlor residues in soil and maize grain supported by the laboratory study

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ABSTRACT

The purpose of this work was to evaluate the acetochlor degradation rate in soils and investigate acetochlor contamination of maize grains and soil. Two kinds of soil: medium silty loam (soil A) and heavy loamy sand (soil B) were collected for the laboratory experiment. The degradation data were plotted. Good linearity was found between logarithmic concentration of acetochlor residues and time, indicating first-order rates of degradation. The $t_{1/2}$ values varied from 10.5 days for soil A to 15.1 days for soil B. The degradation rate depends on the soil properties. In the soil A (higher content of clay and organic carbon) the $t_{1/2}$ value was shorter than in the soil B. Monitoring tests were carried out during the 2010–2012 time period on maize fields located in the south-western Poland. Soil and maize grain samples were collected at harvest time. The determination of acetochlor residues was conducted using gas chromatography with electron capture detection. Based on the analysis of a total of 124 environmental samples, acetochlor residues were detected in 17.4% of soil and 8.1% of maize grain samples. None of the examined samples showed a herbicide concentration exceeding the maximum residue level.

Keywords: herbicide; plant; degradation; chloroacetamide; gas chromatography

Maize belongs to the most important crops in Poland. All parts of the crop can be used for food and non-food products. Maize is largely used as livestock feed and as a raw material for industrial products. Protection of maize against weeds is equally important (Gołębiowska 2008). The chloroacetamide herbicide acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)-acetamide] is used for pre-emergence control of annual grasses and broadleaf weeds in maize and soybean. Acetochlor is a common herbicide used worldwide. Previous studies based on sorption and degradation experiments showed that acetochlor presents a risk of soil contamination (Zhou et al. 2006, Chao et al. 2007).

The pollution of plant, soil, surface and groundwater 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 substance and its degradation products in the environment as well as their effects on ecologically sensitive areas close to agricultural fields (Triantafyllidis et al. 2009, Łozowicka et al. 2012).

Processes like chemical degradation, degradation by soil microorganisms, sorption and binding by organic and mineral components, uptake by plant roots and volatilization determine pesticide behavior in soil. Evaluation of the persistence in topsoil is fundamental in the assessment of the fate and behavior of all chemical substances, including active ingredients in plant protection products. The $t_{1/2}$ (dissipation time; time required for 50% of the initial pesticide concentration to dissipate) under field conditions should be less than 3 months unless there are no unacceptable effects on terrestrial organisms and plants (Boesten 2000).

The purpose of this work was to evaluate the acetochlor degradation rate in soils in the laboratory conditions and to investigate contamination of maize grains and soil with acetochlor, based on the monitoring tests done on maize fields located in the south-western Poland.

MATERIAL AND METHODS

Laboratory studies. The influence of soil type on degradation rate of acetochlor was studied under controlled laboratory conditions. Two kinds of soil (medium silty loam (soil A) and heavy loamy sand (soil B)) were collected for the laboratory experiments from the upper soil layer (0–15 cm depth). Soil was free from acetochlor residues (not detected) and is representative for the maize-growing regions of Lower Silesia (south-western Poland). The soil properties are presented in Table 1.

After passing the soil through a 2-mm sieve, it was stored in covered trays in greenhouse for 10 days and regularly mixed. Soil moisture was measured before the start of the trials by heating to dryness for 24 h at 105°C and determining the difference in weight. Soil moisture was set at 60% of field capacity, checked at regular intervals and adjusted with distilled water to the initial level.

Soil samples were transferred into 90 mm diameter and 85 mm height pots that were placed in growth chambers; each variant had three replicates. Day/night temperature regimes were 20°C/10°C (average temperatures recorded at the end of April and May – typical term of acetochlor application on the field in Poland) and light intensity was 320 ± 10 μmol/m^2/s photosynthetic photon flux, with 15 h day length. Two days after placing the pots into the growth chambers, the commercial formulation of acetochlor (herbicide Guardian Max 840 EC; Monsanto®, Antwerp, Belgium) at a dose 1680 g of active substance per hectare was applied. Application of herbicide was done using a stationary chamber sprayer equipped with a mobile nozzle TeeJet XR 11003-VS. The nozzle was operated at pressure of 200 kPa and speed 3.6 km/h producing a spray volume 250 L/ha. Herbicide doses and spraying conditions were the same as for field conditions.

Soil samples (one pot containing ca. 250 g of soil = one sample and one replication) were taken for analysis 1 h after herbicide application and 2, 4, 8, 16, 32, 48 and 64 days after treatment. Samples taken from the experiment were well mixed and stored in polyethylene bags at –20°C until sample extraction.

Residues monitoring in soil and maize grain. Monitoring research was conducted in the years 2010–2012 on maize fields. In three growing periods, shortly before harvest, the soil samples (from the 0–20 cm soil layer) and maize grain were collected from different 62 cultivated fields (62 samples of soil and 62 samples of maize grain). Interviews were conducted among the field owners, who stated that in most cases, the previous crops were cereals (mainly wheat and winter barley). The fields were established on different soils (pH = 5.5–6.4, C_{org} = 0.92–2.14%). The size of the controlled maize fields was diverse and ranged from 4 to 15 ha. Herbicide containing acetochlor (1680 g/ha) was applied on the selected fields. Herbicide treatments and introduced amounts were done according to instructions regarding the terms and the doses set up by herbicide producers. Herbicides were applied before and shortly after maize emergence. Maize was sown at the end of April to the end of the first decade of May. The harvest took place from the middle of October to the first days of the third decade of November. Soil and maize grain were collected as eight random subsamples from each field. The eight subsamples of each field were pooled to obtain one composite sample and they were kept frozen (–20°C) until the analysis.

Acetochlor determination – analytical method. Soil samples were homogenized and then passed through a 2-mm sieve. The maize grain was ground in a blender. Soil or grain portions (3 × 10 g) were mixed with 3 × 2.5 g of Diatomaceous Earth (Dionex®, Sunnyvale, USA) and transferred into stainless steel cells. Extraction was done using accelerated solvent extractor Dionex ASE 350 (Dionex®) [extraction solvent – acetone (33 mL per cell for two cycles of extraction), temperature 40°C, extraction time – 20 min and pressure – 0.2 MPa)]. The combined extracts (from three cells) were then slowly evaporated under a nitrogen stream until dry.

Dry residues were dissolved in 30 mL of water and subjected to SPE (solid phase extraction). 3 mL-capacity cartridges and sorbent bed – 0.5 g of octadecyl, 40 μm particle size (Bakerbond®, J.T.Baker®, Phillipsburg, USA) were used. Sorbent was preconditioned with water (3 mL) and then methanol (3 mL). 30 mL of extract solution was loaded with small portions onto the cartridge and the eluate was discarded. Analytes were eluted with 3 mL of acetone.

A gas chromatograph Varian CP 3800 equipped with the electron capture detector (Varian®,

Table 1. Properties of the soils used in the laboratory test

Soil	pH_{KCl}	C_{org}	Sand	Silt	Clay
		(%)			
Soil A – medium silty loam	6.4	2.14	15	33	52
Soil B – heavy loamy sand	5.5	0.92	64	20	16

Middelburg, Netherlands) was used to carry out the final determination. Throughout the entire experiment, a VF-5 ms capillary column (30 m × 0.25 mm × 0.25 μm film thickness) (Varian®) was used. Nitrogen was used as carrier gas at a flow rate of 1.5 mL/min. Chromatographic separation was performed at the column oven where the initial temperature was held at 120°C for 7 min. Then, the temperature ramped at a rate of 10°C/min to 200°C and was held for 2 min. Finally, the second ramp was continued at 5°C/min to 230°C, which was held for 20 min. Injector and detector temperatures were set at 230°C and 300°C, respectively. Aliquots of 1 μL of the samples were injected.

The recovery of acetochlor from soil and maize grain was determined by analyzing fortified samples. Analysis was carried out at four concentration levels [0.0005 (0.0008 for maize grain), 0.001, 0.01 and 0.1 mg/kg] in three replicates. The average recovery for all concentration was 93.2% for soil and 86.4% for maize grain. The quantification limit of the method was 0.0005 and 0.0008 mg/kg for soil and grain samples, respectively.

All soil and grain samples were analyzed three times. Repeatability of the analytical results was satisfactory, with relative standard deviation (RSD) not exceeding 8.3% of the mean values. All experimental data were calculated using the statistical program Statgraphics Centurion, version XV (Herndon, USA).

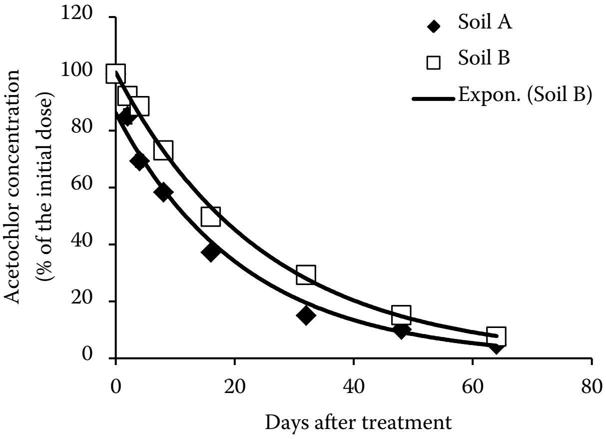

Figure 1. Degradation of acetochlor in soils (laboratory test). Vertical bars represent ± standard errors of means (for 3 replicates). Soil A – medium silty loam soil; soil B – heavy loamy sand soil

RESULTS AND DISCUSSION

Degradation in soil. The results of the acetochlor degradation rate in surface soils are shown in Figure 1. The initial acetochlor concentration (analysed 1 h after application) amounted to 1.785 ± 0.143 mg/kg for all samples. The degradation rates of acetochlor differed significantly between the two soils, being faster in the medium silty loam soil and slower in the heavy loamy sand soil. After about 48 days of herbicide application, the residue levels for both soils were similar. At 64 DAT (days after treatment), acetochlor residues amounted to 7.6% of initial dose for the soil A and 5.8% for the soil B.

The degradation data were plotted. Good linearity was found between logarithmic concentration of acetochlor residues and time, indicating first-order rates of degradation with correlation coefficients (R^2) about 0.97–0.99 for both soils. The $t_{1/2}$ values (graphically derived by interpolating the values between successive residue measurements) varied from 10.5 days for soil A to 15.1 days for soil B. The $t_{1/2}$ values obtained after fitting the curves to first-order kinetics were similar (Table 2). The same model of kinetics equation was noticed for acetochlor and other herbicides (Ma et al. 2004, Cuevas et al. 2007, Hu et al. 2011, Kucharski and Sadowski 2011). Significant differences in degradation rate of the herbicide in soil in the first period after treatment influenced the $t_{1/2}$ indicator. The $t_{1/2}$ values for both soils in this experiment are consistent with the data compiled by EFSA (European Food Safety Authority). The $t_{1/2}$ found for acetochlor varied from 3 up to 29 days (EFSA Journal 2011). $t_{1/2}$ values for acetochlor obtained from field experiments were similar and

Table 2. Equations for acetochlor degradation curves and values of $t_{1/2}$

Soil	Equation of degradation curve (for average values)	$t_{1/2}$ (days)	
		graphically determined	calculated from equation
A	$C_t = 1.684e^{-0.056t}$; $R^2 = 0.974$	10.5 ± 1.1	12.4
B	$C_t = 1.862e^{-0.045t}$; $R^2 = 0.989$	15.1 ± 1.3	15.4

$t_{1/2}$ – dissipation time; time required for 50% of the initial pesticide concentration to dissipate; C_t – acetochlor concentration at time t; R^2 – correlation coefficient ranged from 2 to 18 days (Yu et al. 1998, Mills et al. 2001, Coroi et al. 2012).

The acetochlor degradation rate depends on soil properties. In the soil A (higher content of silt, clay and C_{org}) the $t_{1/2}$ value was shorter than in the soil B, but residues determined 64 DAT in both soils were similar. Soil texture (content of sand, silt, clay) and the content of C_{org} influenced degradation rate of herbicide and retention. Results of this study showed that the type of soil (especially clay and C_{org} content) could influence speed, run and final residues of acetochlor in soils. Priya et al. (2006) proved that the degradation of herbicide was influenced by the clay content and the persistence was longer in soils with higher clay content. After 60 days of incubation, the residues were below detectable level in soils with low clay content, while traces were detected in soils having higher clay percentage. In soils with high content of clay and organic matter, the decomposition process in the initial period is fast (short $t_{1/2}$), but due to sorption and herbicide binding by organic and mineral components the second period is significantly longer and determines the persistence of the herbicide in the soil (Forouzangohar et al. 2005, Bedmar et al. 2006, Chaabane et al. 2008, Kucharski and Sadowski 2009).

Residues monitoring. Within the three-year research period, 62 soil and 62 maize grain samples were subjected to analysis. Acetochlor residues were detected in 17.4% of soil and 8.1% of maize grain samples. Detected residues ranged from 0.0010 to 0.0032 mg/kg for soil and 0.0008–0.0016 mg/kg for maize grain. Comprehensive results are shown in Table 3.

Fields, from which the soil and grain samples containing residues were collected can be described as having diverse soil properties (pH, content of C_{org}, silt and clay). Gained results were subjected to statistical analysis (discriminant function analysis), showing lack of significant differences among the paramenters group, which resulted in hindering the influence evaluation.

In most cases, if residues were detected in maize grains, they were present in soil too. The highest acetochlor residues in soil and in grain were reported in 2012.

None of the examined samples showed herbicide residue concentration of a similar value or one exceeding the permissible level (MRL). For acetochlor, MRL amount is 0.1 mg/kg (Regulation 396/2005), while maximum values obtained in this research did not exceed 0.0016 mg/kg for maize grain. Hu et al. (2011) and Coroi et al. (2012) described, that acetochlor residues level determined at harvest time in soil and maize grain samples was low and did not exceed 0.01 mg/kg.

The residues level detected in soil and maize grain was different in each vegetation season. All soil and grain samples containing residues were detected in 2011 and 2012 only. During the whole research period the residues level was strongly affected by rainfall occurring after the herbicide application. In 2010, rainfall from May to July amounted 312.7 mm and was higher than for long-term observations (219.3 mm). The next two years were dryer – the rainfall amounted to 222.9 mm and 198.9 mm, respectively. An increase of rainfall influenced the leaching of herbicide into soil profile (substance moves to deeper soil layer) and residues detected in the top

Table 3. Number of tested samples and level of detected residues

	Soil	Maize grain
2010		
Number of tested samples	20	20
Samples with residue	0*	0*
2011		
Number of tested samples	20	20
Samples with residue	4	2
Location and residue level (mg/kg)		
Lubiechowa (LS)	0.0010	ND
Borek (OP)	0.0019	0.0008
Bukowice (LS)	0.0023	0.0011
Gliniany (LS)	0.0017	ND
2012		
Number of tested samples	22	22
Samples with residue	7	3
Location and residue level** (mg/kg)		
Gierczyn (LS)	0.0016	ND
Jugowa (LS)	0.0032	0.0014
Gola (OP)	0.0029	0.0016
Szybowice (OP)	0.0015	ND
Zalesie (LS)	ND	0.0009
Ludwinowo (SW)	0.0012	ND
Dubin (SW)	0.0018	ND
Chynowa (SW)	0.0011	ND

*all soil and maize grain samples without detectable acetochlor residues; **location of field: city/village (region of Poland); LS – Lower Silesia; OP – Opole province; SW – Southern Wielkopolska; ND – residue not detected soil layer as well as grain were lower (undetectable). This effect was more evident when intensive rainfall occurred at first weeks after treatment (year 2010). Similar results were presented by Cuevas et al. (2007).

The research results involving acetochlor residues in maize grain and soil, prove that the use of herbicides could not result as a threat to humans or the agricultural environment. Nevertheless, it should be stressed that all the samples originated from the fields were along with requirements, where herbicide application was controlled and the instructions given by the producer were followed. It is not possible to exclude sporadic incidents exceeding permissible values. Such cases are usually caused by a lack of farmers' knowledge, spraying devices which are in bad conditions, exceeding the recommended dosage or the use of fake herbicides (Sadowski and Kucharski 2005).

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