DISSIPATION OF ACETOCHLOR AND RESIDUE ANALYSIS IN PLANTS AND SOIL UNDER FIELD CONDITIONS

Irina COROI[1], Mihai CARA [1], Gerard JITAREANU[1]

e-mail: coroirina@yahoo.com

Abstract

The present study was undertaken to determine the persistence of acetochlor under real field conditions at maize crop. The chloroacetanilide herbicide acetochlor was applied as a pre-emergent spray on maize crop at 3 days after sowing in the experimental field in Didactical Station Ezăreni. The herbicide acetochlor was identified and quantified from soil and maize plants based on accelerated solvent extraction (ASE) followed by GC-MS analysis. Since the herbicide was applied to the soil surface, its dissipation and degradation will vary depending on the concentration, soil type, pH, organic matter and environmental conditions. 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 from 14 to 17 days. Dissipation followed first order kinetics. The higher concentration of herbicide was found to be safe, as the residues of acetochlor were below maximum residue limits (MRL) at the end of maize crop season.

Key words: acetochlor, herbicide, persistence

The protection of the crops being cultivated is a priority for the improvement of agricultural productivity to sustain the growing population. There are a large number of pesticides currently in use, with a wide range of physic-chemical properties and belonging to a wide variety of chemical classes. Once incorporate in soil a pesticide enters a dynamic ecosystem in which it can move, degrade *in situ* move from the initial system to other systems or remain in place with its original structure intact or degraded to a greater or lesser degree for a variable length of time (Sheng et al., 2001; Kong et al., 2005). The pesticide acetochlor (*2-chloro-N-ethoxymethyl-6′-ethylaceto-o-toluidide*) is a selective herbicide used pre-emergence or preplant to control mainly annual grasses and broadleaf weeds. It has been shown that acetochlor could induce metamorphosis of ranid species and accelerated T-3-induced metamorphosis in amphibians (Crump et al., 2002; Li et al., 2009). Despite of its high ecological risk and wide application, there are little data available concerning acetochlor environmental fate and persistence under field conditions. Previous studies based on sorption and degradations experiments have shown that acetochlor presents a risk of soil contamination, especially in phaeozem (Chao et al., 2007; Xiao et al., 2005; Zhou et al., 2006) whereas there is no report about its presence in chernozem soil under Romanian temperate conditions. Therefore, a field experiment was undertaken to investigate the fate of acetochlor in soil and plants of maize fields. Gas chromatographic mass spectrometer was standardized for the quantitative determination of acetochlor from soil and plants, and on the residues level.

MATERIAL AND METHOD

An automated ASE 300 system with 34 mL stainless steel extraction cells was from Dionex, UK. The GC-MS equipment consisted of an Agilent 7832 GC equipped with a mass spectrometer detector, an auto-sampler, a split-splitless injector and a HP-5, fused silica capillary column.

Gas chromatographic conditions: The column oven temperature program was used as follows: initial temperature 50^{o}C, increased to 200^{o}C at a rate of 30^{o}C/min, increased to 280^{o}C at 10^{o}C/min and held for 1 min, and then increased to 310^{o}C and held for 3 min. The injector temperature was set to 250^{o}C in splitless mode (volume injected 1.00 µL) and MS temperature was 280^{o}C. The carrier helium (99.999%) with a flow rate of 0.8 mL/min was selected based on the instrument optimization results provided by the manufacturer's identification of peak and compared with the retention time of the compound with the standard solution. Extraction procedure: Soil and plant

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[1] Universitatea de Ştiinţe Agricole şi Medicină Veterinară. Iaşi

samples were solvent extracted using accelerated solvent extraction (ASE) following the Environmental Protection Agency (EPA) method 3545 for the analysis of organic compounds in solid matrices. The dried samples were ground into powder and sieved through a 40 mesh sieve and then stored at room temperature before their analysis. A total of 10 g of each sample was mixed in a mortar with 3 g of Diatomaceous earth and the mixture was added directly to the extraction cell containing cellulose extraction filters. The extraction was performed under the optimized conditions: extraction solvent acetone-hexane (1:1, v/v); temperature: 140^{o}C; pressure: 1500 psi; heat-up time: 5 min; flush volume: 60%; purge: N_2 60 s; number of cycles: 1. Finally, elutes were evaporated in a rotary evaporator and dissolved in 100 µL of n-hexane for the determination by GC-MS. Experimental layout: Field experiments on the persistence of acetochlor in soil and plants were conducted at the Agricultural Research Institute Ezareni, belonging to ''Ion Ionescu de la Brad'' University of Agriculture and Veterinary Medicine Iasi, Romania using a split plot design. Maize (*Pioneer PR38V91*) was sown in field plots and the size of each plot was 18m x 7m. Phoenix (960 g L^{-1} a.i. acetochlor) was applied at three different dosages, 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 maize crop at 3 days after sowing with the help of a knapsack sprayer. Soil samples for acetochlor persistence were randomly collected from 0-25 cm depth using a tube auger from 7-8 spots in each plot. Approximately 500 g of soil was collected from each plot. The samples were collected at 5, 10, 15 and 30 day time intervals after the herbicide treatment and at the crop harvest time from all the treated plots. Plant samples from each plot were collected 30 days after application and at the crop harvest time. Samples were mixed thoroughly, air dried, ground and passed through a 2 mm sieve and stored in sterile glass bottles in the dark at 4^{o}C until analysis.

Residues from soil and plants were performed on three replicates for each treatment and the significance of the differences was determined by one-way analysis of variance (ANOVA) using the SPSS program.

RESULTS AND DISCUSSION

Evaluation of recovery: The average recoveries of acetochlor from the soil are shown in Table 1. The recoveries of acetochlor from soil ranged from 80.9% to 96.04% with a relative standard deviation (RSD) less than 1.4%. The limits of detection and quantification were found to be 0.2 ng g^{-1} and 0.67 ng g^{-1} of dry soil, respectively. This data indicated that the extraction method is satisfactory for the analysis of residual acetochlor from soil.

Persistence under field conditions: One application of acetochlor was giving residues to maize crop at all three rates of application.

Residues were monitored up to 30 days after pplication and at harvest time.

Table1

Recoveries of acetochlor from spiked soil

Fortification level (mg kg^{-1})	**Mean recovery (%)**	**Relative standard deviation (%)**
0.01	81.6	1.4
0.5	94.1	0.4

The concentrations of acetochlor (mg kg^{-1} dry soil) in different soil layers as a function of time after herbicide application are shown in Fig 1.

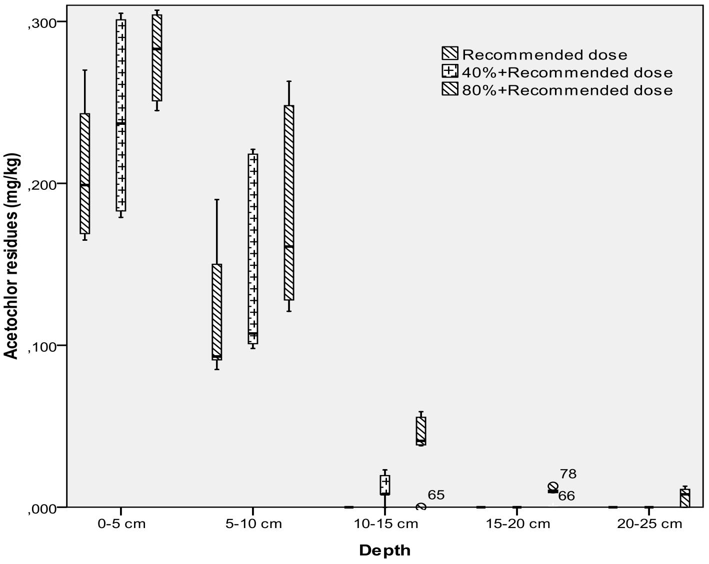

Figure 1 **Soil residues after acetochlor treatments**

For all three rates of application and sampling times, the highest amounts of acetochlor were found in the top 0-10 cm soil layer. It should also be noted that the concentrations on day 5, were 0.243, 0.301 and 0.304 mg kg^{-1} in 0-5 cm depth at RD, 40%+RD and 80%+RD respectively. However the concentrations detected indicate less sorption strength at increasing concentration. As pointed out by sorption isotherms (laboratory experiments), 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). According to this and taking into account the physicochemical properties, acetochlor is more likely to be levigated particularly at high concentration. The residual acetochlor detected in depth of 5-10 cm were between 0.169-0.259 mg kg^{-1} but lower than those from the depth of 0-5 cm soil.

Despite acetochlor accumulates within the 0-10 cm surface layer, the amounts of acetochlor present at deeper layers indicated that the herbicide moved deeper. At recommended dose (RD) the acetochlor residues were below calibration curves at the depth of 10-15 cm and not detectable at the depth 15-25 cm. While at 40% + recommended dose (40% + RD) herbicide residues reached up to 20 cm after 30 days but no residues were after 25 cm. However after 30 days of acetochlor application at 80% + recommended dose (80% + RD), leads to herbicide dispersion to lower depths. 53.73% of the initially applied concentration was detected at 0-15 cm depth and traceable herbicide concentration also reached the depth 20-25 cm but no higher than 0.01 mg kg^{-1}.

At the end of crop period only traceable concentrations were reached and were otherwise completely degraded. At the applied dose of 80%+RD the residual acetochlor remaining at the harvest time were higher in surface soil 0-10 cm and was in order of 0.002 mg kg^{-1}. Similarly at RD and 40%+RD variants, concentrations persist but were mainly limited to 0.001 mg kg^{-1} at the end of crop period.

Residues in maize: The acetochlor residues, measured 30 days after application on maize plant, was in the range 0.0029-0.0032 mg kg^{-1} and 0.0047-0.0073 mg kg^{-1} for the lowest and highest dosage respectively. At harvest the active ingredient acetochlor was below calibration curves at recommended dose and 40% + recommended dose whereas at higher field rate was 0.0011 mg kg^{-1}. These relatively low residue levels for acetochlor could be related to conjugation with GSH and cysteine, which has been observed in some plants as a mechanism of resistance to the herbicidal activity of the compound.

Degradation: Concerning the chloroacetanilide herbicide effect on soil microbial activity to its persistence in soil it was necessary to establish the degradation kinetics of this molecule. The dissipation patterns of acetochlor in chernozem soil are presented in Fig. 2. The degradation followed first order kinetics for all three doses. In soil, dissipation was quick during the first week and then slowed down from third week onwards. The dissipation rate was lowest at RD and 40%+RD and highest in 80%+RD. The half-lives of acetochlor were calculated as 13.86 and 17.32 days respectively with r^2 values of 0.967 and 0.978 respectively.

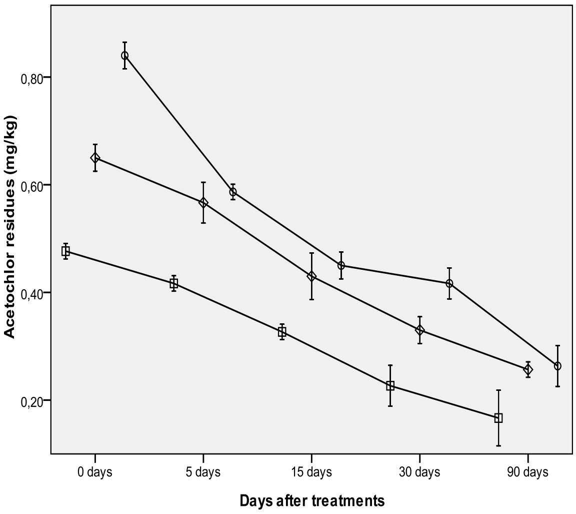

Figure 2 **Degradation curves of acetochlor in soil. All values represent mean±standard deviation of triplicate samples**

Our results are in agreement with the reports of Xiao et al. (2006), where it was reported that the degradation rates may be influenced by the initial concentrations, because in soil the degradation rate of acetochlor is faster at the lowest concentration (5 mg kg^{-1}) that at highest (80 mg kg^{-1}). Mills et al. (2001) reported that half-life of acetochlor in surface soils was 18 days, whilst in subsurface soils down to 4.6 mbs, range from 2 to 88 days.

CONCLUSIONS

The results obtained in this study indicated that that increased dose of acetochlor to soil exbibited a concentration dependent impact on the persistence of acetochlor. The persistence of acetochlor in soil was increased with increasing dose of acetochlor. No maximum residue limits (MRL) have been set in plants and other agricultural products.

REFERENCES

Acetochlor Registration Agreement and Addendums. [Online]. USEPA document type: Supporting and Related Materials; document ID: EPA-HQ-OPP-2007-0725-0005, USEPA, Washington, DC (1994). Available: www.regulations.gov/fdmspublic/component/main?main=DocketDetail&d=EPA-HQ-OPP-2007-0725 [30 July 2010]

Chao L, Zhou Q X, Chen S, Cui S, Wang M, 2007 - *Single and joint stress of acetochlor and Pb on three agricultural crops in northeast China*. Journal of environmental Sciences 19(6):719-724.

Crump D, Werry K, Veldhoen N, Van Aggelen G, Helbing C, 2002 - *Exposure to the herbicide acetochlor alters thyroid hormone dependent gene expression and methamorphosis in Xenopus Laevis.* Environmental health Perspectives, 110(12):1199-1205.

Giles C.H., MacEwan TH, Nakhwa SN, and Smith D. Studies in adsorption. Part XI, 1960 - *A system of classification of solution adsorption isotherm, and its use in diagnosis of adsorption mechanism and in measurement of specific surface area of solids*. Journal of Chemical Society 111: 3973-3993.

Hiller E., Krascsenits Z., Cernanky S., 2008-*Sorption of acetochlor, atrazine, 2,4-D, chlorotoluron, MCPA and trifluralin in six soil from Slovakia*. Bull. Environ. Contam. Toxicol. 80: 412-416.

Kong K., Cheung K., Wong C., Wong M., 2005 – *The residual dynamic of polycyclic aromatic hydrocarbons and organochlorine pesticide in fishponds of the Pearl River delta, South China.* Water resources 39, 1831-1843.

Li W, Zha J M, Li Z L, Yang L H, Wang Z L, 2009 - *Effects of exposure to acetochlor on the expression of thyroid hormone related genes in larval and adult rare minnow* (*Gobioscypris rarus*). Aquatic Toxicology, 94: 87-93.

Mills MS, Hill IR, Newcombe AC, Simmoms ND, Vaughan PC, Verity AA, 2001 - *Quantification of acetochlor degradation in the unsaturated zone using two novel in situ field techniques: comparisons with laboratory generated data and implications for groundwater risk assessments*. Pest Manac Sci 57:351-359.

Nadin P., 2009 - *The use of Plant Protection Products in the European Union, Data 1992-2003*. European Comission, Luxembourg.

Xiao H, Zhou Q X, Ma L Q, 2005. - *Joint effects of acetochlor and urea on germinating characteristics of crops seeds.* Science in China Series C-Life Sciences, 48(S1): 1-6.

Zhou Q X, Zhang Q R, Liang J D, 2006 - *Toxic effects of acetochlor and methamidophos on earthworms Eisenia fetida in Phaeozem, Northeast China*. Journal of Environmental Scinces, 18(4): 741-745.

Sheng G., Johnson C.T., Teppen B.J., Boyd S.A., 2001 – *Potential contribution of smectite clays and organic matter to pesticide retention in soil.* Journal oj Agricultural Food Chemistry 49, 2899-2907.

Supradip Saha, Deashis Dutta, Rajib Karmakar, Deb Prasad Ray, 2012 - *Structure toxicity relationship of chlororacetanilide herbicide: Relative impact on soil microorganisms.* Environmental Toxicology and Pharmacology 34(2012) 307-314.

Xiao N, Jing B., Ge F, Liu X, 2006 - *The fate of herbicide acetochlor and its toxicity to Eisenia Fetida under laboratory conditions*. Chemosphere 62:1366-1373.

Xiaoyin Sun, Qixing Zhou, Wenjie Ren, Xuhui Li, Liping Ren, 2011 - *Spatial and temporal dsitribution of acetochlor in sediments and riparian soils of the Songhua River Basin in northeastern China.* Journal of Environmental Sciences, 23(10):1684-1690.

Weber J.B., Miller C.T., 1989 -*Organic chemical movement over and through soil*. In Sawhney B.L., Brown K., Reaction and Movement of Organic chemicals in soil. Special publication 22. Soil Science Society of America, Madison WI, pp. 305-334.

Tomlin CDS, **2009** - *The Pesticide Manual, 15th edition.* British Crop Protection Council, Alton, Hants, UK.