AgroLife Scientific Journal - Volume 6, Number 1, 2017
ISSN 2285-5718; ISSN CD-ROM 2285-5726; ISSN ONLINE 2286-0126; ISSN-L 2285-5718

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

Irina Gabriela CARA[1], Florin Daniel LIPŞA[1], Mihai Sorin CARA[1], Lavinia BURTAN[2], Denis ŢOPA[1], Gerard JITĂREANU[1]

[1]Ion Ionescu de la Brad University of Agricultural Sciences and Veterinary Medicine of Iasi, 3 Mihail Sadoveanu Alley, Iaşi, 700490, Romania, Phone: +40232.407.430, Email: coroirina@yahoo.com
[2]National Research and Development Institute for Soil Science, Agrochemistry and Environment Protection – ICPA Bucharest, 61 Mărăşti Blvd., District 1, Bucharest, Romania, Phone: +4021.318.44.63, Fax: +4021.318.43.48, Email: lavinia.parvan@yahoo.com

Corresponding author email: topadennis@yahoo.com

Abstract

Acetochlor is a widespread used herbicide in maize crops; however, the environmental risk of its residues in the soil-plant system remains unknown. There was assessed the dissipation dynamics of acetochlor doses and its impact on residue level and microbial activity in soil over a season of vegetation. Since the herbicide was applied to the soil surface, its degradation varies as a dependence of concentration, soil type, pH, organic matter and environmental conditions. The field soil samples extraction in different imposed conditions of depths, time and herbicide application revealed a moving deeper of doses. The increased dose (80%+Rd) affects the persistence of acetochlor in the top layer by increasing its half-life from 14 to 17 days. Dissipation followed a first order kinetics. The diversity of soil microbial community changed after the introduction of acetochlor doses. An evident increase of bacteria and soil microorganisms was observed; however, fungal growth was prone to be inhibited. The higher concentration of herbicide was found to be safe, as well as the residues of acetochlor below maximum residue limits (MRL) at the end of maize crop season.

Key words*: adsorption, degradation, microorganisms, residues.*

INTRODUCTION

Environmental contamination with pesticides and heavy metals as a result of agricultural and industrial activities represents an ongoing concern (Gavrilescu, 2010). The protection of crops is a top priority for the agricultural productivity improvement to sustain an exponential growing population (Gupta et al., 2012). Sustainability of agricultural technologies, including intensive agriculture, integrated pest management and ecological farming is focused on soil quality, the relation between its use and management and the environment (Székács et al., 2014).

The widespread use of pesticide in agriculture leads to soil contamination, surface water and groundwater. These pesticides are broadly applied to crops in different stages of cultivation (preemergence, postemergence) to provide protection against pests and thus to prevent/reduce agricultural losses and to improve the production yield (Zhang et al., 2011). There are studies that organochlorine compounds are toxic, bioaccumulative and tend to persist due to the lipophilic characteristics (Gavrilescu, 2010; Miclean et al., 2011). Herbicides are the main type of pesticide causing public concern because of their implied short and long term risks for ecosystems and for human health (Pogăcean et al., 2009). However, many of these compounds have been proved a mutagenic and carcinogenic character.

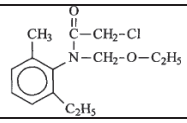
Acetochlor (2-chloro-N-ethoxymethyl-6′-ethylaceto-o-toluidide) is a selective herbicide used in conditions of pre-emergence or preplant to control mainly annual grasses and broadleaf weeds; its physical properties are given in Table 1. Acetochlor possessed the capability to be adsorbed by shoots and germinating plants roots and inhibits cell division by blocking protein synthesis (Tomlin et al., 2009). As a member of acetanilide herbicide family, it was widely detected as a pollutant in soil and surface water at concentrations values higher than the European Union accepted limit for

drinking water of 0.1 µg L^{-1}. It has become a special concern due to its large quantity of use and potential for transport and accumulation. In 1997, acetochlor was already the fourth most used herbicide in US agriculture, with an annual use of approximately 14800 tons, which increased up to 16400 tons in 2002. The use of it in EU and also in Romania is in a lesser extend; it was ranked as the seventh most used herbicide in the EU in 2003, with an annual use of 2300 tons (Nadin et al., 2009).

Acetochlor is a B-2 carcinogen and may be removed in conditions that exceeds the limits of 0.10 µg L^{-1} in groundwater or 2.00 µg·L^{-1} as an annual average in surface water (Xiaoyin et al., 2011). Also 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 risks and wide range applications, there are only a few available data concerning acetochlor in environmental protection and its persistence under field conditions. Previous studies (Chao et al., 2007; Xiao et al., 2005; Zhou et al., 2006,) based on adsorption and degradations experiments have been demonstrated a high/medium risk of soil contamination, especially in phaeozem soil type.

Table 1. Physical chemistry data for acetochlor

Chemical structure	
Molecular formula	$C_{14}H_{20}ClNO_2$
Molecular weight	269.77 g mol^{-1}
Vapor pressure	3.4 x 10^{-8} mm Hg at 25°C
K_{ow}	300
Water solubility	233 mg L^{-1}

There is no report about its presence in cheornozem soil type from Romanian in temperate climate conditions. In this paper, the research was focused on the investigation of acetochlor evolution 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. Persistence studies were also carried out under field conditions to evaluate the impact of acetochlor on the soil microbial communities in the rhizosphere soil zone.

MATERIALS AND METHODS

Reagents

Acetochlor (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.

Field experiments

The area for field experiments on microbial activity and on the persistence of acetochlor in soil and plants was located at Ezăreni – The Experimental Farm of the Agricultural University Iasi (47°07′ N latitude, 27°30′ E longitude), Romania using a split plot design. The geographic location of the sampling site is depicted on Figure 1.

The soil is a cambic chernozem (SRTS, 2012) (haplic chernozem WRB-SR, 2006), with a clay-loamy texture, 6.96 pH, 3.06% humus content and a medium level of fertilization, without irrigation (Table 2).

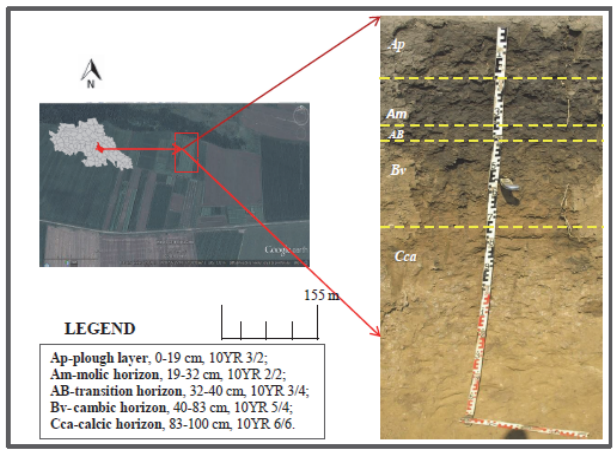


Figure 1. Spatial distribution of sampling and soil profile in Ezăreni area (Iași County)

Maize (variety Pioneer PR38V91) was sown in field plots and the size of each plot was 18 m x 7 m. 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 maize crop at 3 days after sowing with the help of a knapsack sprayer. The high concentration (80%+Recommended dose) simulates a spill during the filling, while 40%+Recommended dose was to imitate overlap application of the herbicide.

Table 2. Main properties of the soil

Measurements	Amount
Bulk density (g cm^{-3})	1.33
pH (1:2.5)	6.96
Clay (g kg^{-1})	41.8
C_{oc} (%)	1.30
Ca+Mg+Na+K	17.47 meq 100 g^{-1}
Humus	3.06
Texture class	clay-loamy

Data collection

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 1000 g of soil was collected from each plot. The samples were taken at intervals of 0, 5, 10, 15 and 30 day after the initial herbicide treatment and after the crop harvest time from all the treated plots.

Plant samples from each plot 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.

In order to assess the effect of acetochlor on soil microbiology, soil samples were collected before and after the treatment considering an interval of 7, 14 and 21 days. The procedure of samples collection included samples at a depth of 10 cm. After this step, they were processed by grinding and homogenization in a sterile mortar.

Pesticide extraction and residue analysis

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.

Gas chromatographic analysis of acetochlor was performed on Agilent 7832 GC 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. The carrier helium (99.999%) with a flow rate of 0.8 mL·min^{-1} 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.

Determination of soil microorganisms

The total numbers of microorganism and colony forming units (CFUs) of fungi and bacteria were determined by serial dilution and plating into selective media methods.

One gram of soil was mixed with 9 mL sterile water (dilution 10-1) and then 1 mL of the dilution 10-1 was poured into 9 mL sterile water (dilution 10-2). After a successive tenfold dilution series, 10-2 to 10-6 dilution were prepared. Aliquots (0.1 mL) of 10-2 to 10-6 dilution were spread on simple PDA (potato-dextrose-agar) medium for the total number of microorganisms. Similarly, aliquots (0.1 mL) of 10-2 to 10-6 dilution were spread on PDA with streptomycin (35 mg·kg^{-1}) medium for the number of bacteria. The numbers of bacteria or fungi were counted using the plate counting method after 24 hours for the bacteria colonies and 5 days for the fungi colonies. The experiments were performed in triplicates.

Recovery assay

A recovery assay was conducted to confirm the validity of the method described above. Known amounts of acetochlor were added to 10 g soil samples to give final spiked concentrations of

0.01 and 0.5 mg·kg^{-1} of dry soil. Extraction procedure and analysis were performed in triplicate as described previously.

RESULTS AND DISCUSSIONS

Evaluation of recovery

The average recoveries of acetochlor from the soil are shown in Table 3. The recoveries of acetochlor from soil ranged from 80.9% to 96.04% with a relative standard deviation (RSD) of 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.

Table 3. Average recovery and relative standard deviation of different samples

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

Persistence and mobility of acetochlor

One application of acetochlor was giving residues to maize crop at all three doses applied. In the case of all three rates of application the highest amounts of acetochlor were always found in the top 0-10 cm soil layer (Figure 2).

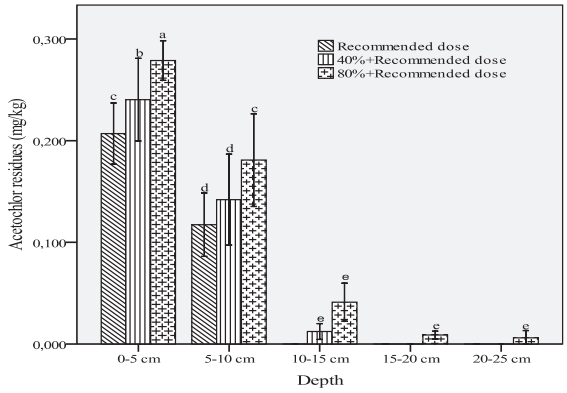


Figure 2. Distribution of acetochlor residues under field conditions. All values represent means ± standard deviation of triplicate samples. Means with different letters are significantly different ($p<0.05$) by Duncan test

This fact reflected a medium potential leaching of acetochlor herbicide, most like due to concentrations applied and rainfall events. It should be also noticed a variation for concentration values between 0.301 and 0.304 mg·kg^{-1} acetochlor, after 5 days after application of 40 and 80% + Rd in the top 0-5 cm. This case 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).

According to these circumstances and taking into account the physicochemical properties, acetochlor seems to be more likely levigated particularly at high concentration. Also, the low adsorption and the rainfall event three hours after pesticide application lead to a dispersion to lower depths, especially at 80%+Rd followed by 40%+Rd. The residual acetochlor detected in depth of 5-10 cm were in the range of 0.169-0.259 mg·kg^{-1} but lower than in the case belonging to the depth of 0-5 cm soil. Baran et al. (2004) reported that the residual acetochlor had been detected at 60-70 cm depth of a Luvisol 7 days after being directly sprayed onto the soil surface.

In the experimental measurements (Figure 3) after 30 days of pesticide application it was shown that only 53.75% of the initially applied pesticide remained in 0-10 cm depth at 80%+Rd against, 49.15% in 40%+Rd and 44.89% in Rd. It can be observed a decreasing of acetochlor concentration value as a dependence of the increasing of time.

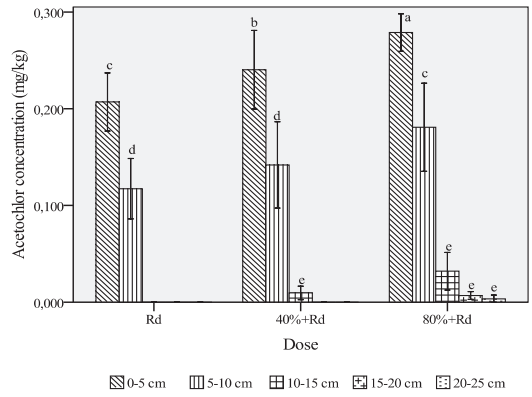


Figure 3. Soil residues after 30 days. All values represent means ± standard deviation of triplicate samples. Means with different letters are significantly different ($p<0.05$) by Duncan test

This fact is attributed to the combined effect between acetochlor degradation and its dispersion to a lower depth level. As the tested soil had relatively high humus content (3.06%) and proportion of clay-sand (22.9-41.8%), which probably caused the acetochlor molecules to be absorbed and therefore quickly degradated, as the acetochlor in the surface soil was prone to undergo highly chemical and biological loss and volatilization (Jablonkai 2000; Ma et al., 2004; Dictor et al., 2008; Hiller et al., 2009; Zhen et al., 2012).

In the case of recommended dose (Rd) after 30 days, it was observed the acetochlor residues were below calibration curves at the depth of 10-15 cm and no residue below 15 cm depth. While at 40%+Rd, herbicide residues reached up to 20 cm but no residues were after 25 cm. However, at values of 80%+Rd, in 10-15 cm depth, 9% of the initially applied concentration was reached after 30 days of acetochlor application. The traceable herbicide concentration also reached the depth 20-25 cm but no higher than 0.01 $mg \cdot kg^{-1}$. Possible routes of acetochlor dissipation in the environment include plant species, climatic conditions, photo conversion and biotransformation via soil microorganisms and soil.

The moment corresponding to the end of crop period suggests that traceable concentrations were reached and otherwise completely degraded. 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 0.0027 $mg \cdot kg^{-1}$. Similarly, at Rd and 40%+Rd variants, concentrations persist but were mainly limited to 0.001 $mg \cdot kg^{-1}$ 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).

Residues in maize

The active ingredient acetochlor was below calibration curves at recommended dose and 40%+Rd whereas at higher field rate (80%+Rd) was 0.0011 $mg \cdot kg^{-1}$ at harvest time. These residue levels for acetochlor could be related to the conjugation with GSH and cysteine, which has been observed in some plants as a mechanism of resistance to the herbicidal activity of the compound. 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.

Taken into account the final residues of acetochlor in maize were below the EPAs MRL (0.01 $mg \cdot kg^{-1}$), it could be considered as safe for human beings and environment.

Microbial activity

Many of the pesticide used in modern agriculture present a high potential to influence the number and functions of a diverse range of soil microorganisms that contribute to soil microbiological processes and thus to soil fertility (Saha et al., 2012).

The effect of acetochlor doses on the total number of microorganisms is shown in Figure 4. Significant increase of soil biological activity was observed in all the variants where acetochlor was applied.

The number of microorganism g^{-1} in 40%+Rd variant was significantly increased compared to Rd and 80%+Rd variants, on 7 and 14 day and much greater than the level of control (before herbicide application) on day 21. Furthermore, the Rd and 80%+Rd biological activity, was almost equal and some lower compare to first variant. As it was noticed in our research and many other studies, the soil microorganisms generally react to herbicide molecule by increasing their biomass and activity although inhibitory (at 80%+Rd) effects have also been noted. This observation was in agreement with previously published studies (Zhen et al., 2012).

Compared to the number of microorganism g^{-1}, the ratio between the mains group of microorganism not only were significantly higher but also present a difference derived from the doses applied. The log values of fungal biomass at 40%+Rd ranged from 3.9 to 4.6 and were significantly increased from day 7 to day 21; in the case of Rd and 80%+Rd, their log values varied between 3.8 and 4.2 and were decreased to 0.465-0.477 log units from day 14 to day 21. The increase in fungal diversity may have resulted from the release of

additional organic carbon as the acetochlor degraded, because the degradation half-life of acetochlor in soil is between 3 and 6 days (Zheng et al., 2001). Guo et al. (2009) reported that the soil fungi population increased at day 7 after application of 25 and 75 $mg \cdot kg^{-1}$ acetochlor, decreased at day 14, and recovered thereafter. Le et al., (2010) reported that the diversity indices changed rapidly after application of 250 $mg \cdot kg^{-1}$ and were lower than those from 50 and 150 $mg \cdot kg^{-1}$ acetochlor treatment. Comparing with these results, our research is more consistent.

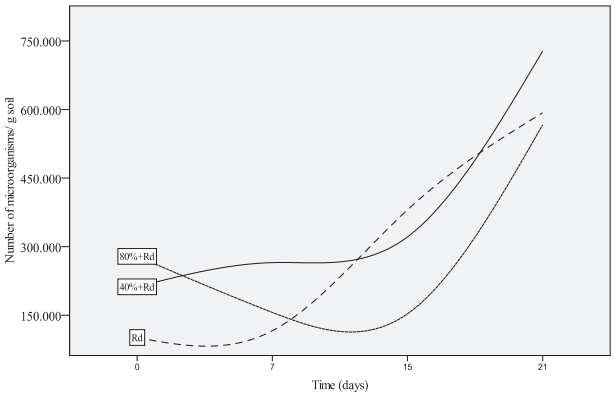


Figure 4. The effect of acetochlor doses on the total number of microorganisms

For the bacterial biomass completely reverse trends responding to acetochlor doses were observed: at 80%+Rd their log values were significantly decreased by 0.270 units on day 7 and 0.424 on day 14 respectively; thereafter, increased in day 21 and were almost equal to Rd variant. An increase in bacterial CFUs was observed in Rd and 40%+Rd from 7 to 21 day. Feng et al. (2008) studied the effects of acetochlor on soil microbiology and showed that acetochlor decreased the biomass of bacteria soon after application, but the biomass of bacteria recovered to a level similar to that of the control over time.

The increase in fungal diversity after acetochlor application may be explained due to the negative effect of acetochlor on bacterial population. This fact could result in a decrease in competition for nutrients among the remaining soil microbes (Le et al., 2010).

The soil fungal composition was altered after increased acetochlor treatment. As a consequence of the control soil (before acetochlor application) displayed no changes in the number of fungus, all changes in soil on the frequency were in response to acetochlor application. The results showed that acetochlor application led to an increase in the proportion of some common fungi such Penicillium, Fusarium and Aspergillus. In spite of a high dose, only one genus proliferated, while identical species in all three variants were obtained. Our results showed that the most significant shift appeared in day 7, whereas the drastic change in the Penicillium abundance occurred in day 14 and 21.

The temporal alteration of soil microbial might be due to different responses of microbial groups to the applied acetochlor: bacteria, affect in early stage the metabolism of soluble compounds whiles fungi degraded resistant complexes in the later decomposition phase.

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 Figure 5.

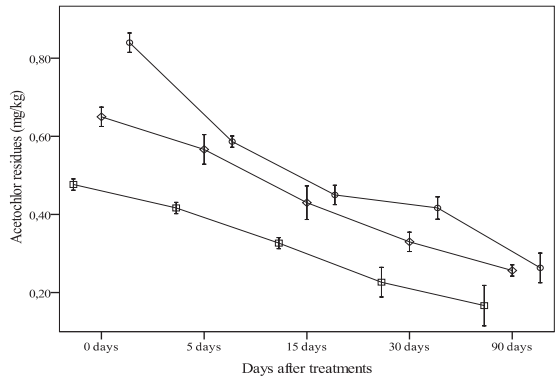


Figure 5. Degradation curves of acetochlor in soil. All values represent mean ± standard deviation of triplicate samples

The degradation followed a 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 recommended dose and 40%+Rd and highest in 80%+Rd. The half-lives of acetochlor were calculated as 13.86 and 17.32 days respectively with r2 values of 0.967 and 0.978 respectively.

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 $mg \cdot kg^{-1}$) than at a highest one (80 $mg \cdot kg^{-1}$).
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. These data shows a relatively fast decline of residues in field soil due to environmental conditions that control soil temperature and moisture content.

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.
All three doses applied caused changes in soil microbial diversity with enhancement of bacteria and microorganisms at a higher concentration.

ACKNOWLEDGEMENTS

This paper was accomplished with the support of European Social Fund, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/132765.

REFERENCES

Andras Szekacs, Maria Mortl, Gábor Fekete, Ágnes Fejes, Béla Darvas, Miklós Dombos, Orsolya Szecsy, Attila Anton, 2014. Monitoring and biological evaluation of surface water and soil micropollutants in Hungary. Carpathian Journal of Earth and Environmental Sciences, 9(3), p. 47-60.

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), p. 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), p. 1199-1205.

Gavrilescu M., 2010. Behaviour of persistent pollutants and risks associated with their presence in the environment - integrated studies. Environmental Engineering and Management Jou., 9, p. 157-1531.

Gupta Manika, Garg N.K., Himanshu Joshi, Sharma M.P., 2012. Persistence and mobility of 2.4-D in unsaturated soil zone under winter wheat crop in sub-tropical region of India. Agriculture, Ecosystems and Environment, 146, p. 60-72.

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, p. 87-93.

Miclean Mirela, Oana Cadar, Cecilia Roman, Claudiu Tănăselia, Lucrina Ștefănescu, Codruța Ileana Stezar, Ioan Ștefan Groza, 2011. The influence of environmental contamination of heavy metals and organochlorine compounds levels in milk. Environmental Engineering and Management Journal, 10(1), p. 37-42.

Mills M.S., Hill I.R., Newcombe A.C., Simmoms N.D., Vaughan P.C., Verity A.A., 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 Management Science, 57, p. 351-359.

Nadin P., 2009. The use of Plant Protection Products in the European Union, European Comission, Luxembourg.

Pogăcean Manuela Olga, Maria Gavrilescu, 2009. Plant protection products and their sustainable and environmentally friendly use, Environmental Engineering and Management Jou., 8(3), p. 607-627.

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, p. 307-314.

Tomlin C.D.S., 2009. The Pesticide Manual, 15th edition, British Crop Protection Council, Alton, Hants, UK.

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), p. 1-6.

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, p. 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), p. 1684-1690.

Yaping Zang, Jun Yang, Ronghua Shi, Qingde Su, Li Yao, Panpan Li, 2011. Determination of acetanilide herbicides in cereals crops using accelerate solvent extraction, solid-phase extraction and gas chromatography-electron capture detector. Journal of Separation Science, 34, p. 1675-1682.

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), p. 741-745.

***SRTS, 2012. Romanian System of Soil Taxonomy, Sitech, Craiova, 157.

***WRB-SR, 2006. World Reference Base for Soil Resources, World Soil Report No. 103 FAO, Rome, 60 p.