Madras Agric. J., 99 (10-12): 794-798, December 2012
https://doi.org/10.29321/MAJ.10.100197

Field Dissipation of Herbicides under Different Crops in Tamil Nadu

P. Janaki*, S. Meena and C. Chinnusamy
DWSR centre, Department of Agronomy
Tamil Nadu Agricultural University, Coimbatore - 641 003

Field experiments were carried out in sandy clay loam and clay loam soils from 2007 to 2009 to study the persistence and degradation of common herbicides applied to rice (butachlor, pretilachlor), maize (atrazine, alachlor) and soybean (pendimethalin, metolachlor) crops at two levels of application. Soil samples at depth of 0-15 cm were collected at periodical intervals from 0 day to harvest for residue analysis. Herbicides residue after their extraction was determined using GC-ECD, except atrazine which was determined using GC-FID. Results showed that the initial deposits of herbicides in soil vary with the concentration applied and a gradual continuous dissipation of all herbicides in soil was observed as a function of time irrespective of the crops grown. Dissipation of all the herbicides in soil followed first order kinetics. The correlation coefficient (r_2) lies between 0.714 and 0.957 and the best fit was observed for acetanilide group of herbicides. Half life of the herbicides increased with the increased concentration with mean half life of 5.88, 12.44, 31.45, 4.78, 14.63 and 22.42 days for butachlor, pretilachlor, atrazine, alachlor, pendimethalin and metolachlor respectively. Within the period of crop harvest more than 98 per cent of herbicides dissipated from the soil, except metolachlor and atrazine.

Key words: Dissipation, half life, herbicides, sandy clay loam, clay loam

Due largely to the soaring cost of laborers caused by the rapid industrial development, chemical weed control practice has become increasingly adopted by the Indian farmers and herbicides consumption occupies 21 per cent share on the agro chemicals use. If herbicides are applied at normal recommended level, they degrade in to safe and non toxic products. However when these herbicides are applied in higher levels it is necessary that residue level in soil and plant has to be monitored as they are prone to leaching (Masse *et al*., 1994) and may contaminate the soil and groundwater also (Kalkhoff *et al*., 1998 and Rivard, 2003). The persistence agrochemicals often cause health hazards to non -target organisms including animals and man. The fate of herbicides applied in soil is governed by various processes such as adsorption and transformation in addition to the influence of factors such as herbicide application rate, crop type, agricultural practices and climatic conditions (Arnold and Briggs, 1990).

Commonly used pre emergence herbicides in wet and garden land crops like rice, soybean and maize grown in Tamil Nadu are butachlor, pretilachlor, atrazine, alachlor, pendimethalin and metolachlor. Chloroacetanilide herbicides have been found to degrade more rapidly in soil than other herbicides, with half-lives from 7 to 50 days (Vencill, 2002), whereas estimated half- life for atrazine was 32 days in topsoil to 83 days in subsoil (Mbuya et al., 2001). Yu *et al*. (2003) reported that the half-lives of butachlor in non-rhizosphere, rhizospere and inoculated rhizosphere soils were measured to be 23.2, 18.0, and 10.8 days, respectively. The dissipation of alachlor in soil was found to follow the first-order kinetics and the half-life in soil varied from 2.6 to 7.8 days (Beestman and Deming, 1974; Ramesh and Maheswari, 2004) under different cropped soils. In soil, alachlor degradation was found to increase with time and also increases with increase in soil pH (Sethi and Chopra, 1975). This indicates that the OH ions from alkali soil were more effective in breaking down alachlor. Metolachlor is considered to be moderately persistent in different soil types and has an average field dissipation half-life of 114 days (Kollman and Segawa, 2000). Since metolachlor is relatively mobile and persistent in soil (Fava *et al.*, 2000), it has a very high potential to contaminate ground water. Extensive leaching can occur in soils with low organic carbon content, and is greater if soil texture is coarse (Rivard, 2003).

While atrazine is triazine group herbicide, pendimethalin is grouped under dinitroaniline family with the field half lives of 60 and 44 days respectively (Vencill, 2002). Winkelmann and Klaine (1991) reported that the rate of dissipation for atrazine followed first-order kinetics and atrazine half-life was

*Corresponding author email: janakibalamurugan@rediffmail.com

approximately 21 days in the microcosm and 14 days in surface field soil. Tsiropoulos and Lolas (2003) reported that the half life of pendimethalin varied from 43 and 62 days in the soil grown with cotton under drip and normal irrigated conditions. Degradation of pendimethalin was faster under anaerobic condition than aerobic condition and so it varies with soil moisture and temperature (Vencill, 2002).

However, little information is published about the dissipation of the above said herbicides under field conditions in South India. Hence this study was carried out to find out the persistence and degradation behavior of above herbicides in sandy clay loam and clay loam soils applied to rice, maize and soybean crops.

Materials and Methods

Field Experiments

Field experiments were carried out at Wet land and Eastern Block Farm of Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India during *Kharif* seasons from 2007 to 2009 in Randomized Block Design with three replications. Field was prepared to fine tilth as needed for each crop and all agronomic and cultural practices were followed as recommended for each crop. Each treatmental plot was of 5 x 4 m_2 in dimension and all four sides of the plots were protected by soil boundaries raised to a level of 40 cm height and 30 cm width. One meter distance was maintained between plots. All the herbicides were applied as pre emergence at two levels (x- Recommended dose; 2x- Double the recommended dose) along with the Control (no herbicide application). Herbicides were sprayed using Knapsack sprayer with the spray volume of 450 lit of water ha^{-1}. Water alone was sprayed in control treatment to maintain the uniformity. Experimental fields soil were sandy clay loam to clay loam (sand 32 - 47%, clay 29 – 31 % and silt 24 -39 % per cent) in texture and having the following chemical properties as: pH – 7.87 - 8.18, EC – 0.08 – 0.29, organic carbon – 0.36 to 0.68 %, low in available nitrogen, medium in available phosphorus and high in available potassium.

Soil Sampling

Soil samples were collected at different intervals from 0 day (2 hr) after herbicide application to harvest of the crop. About 1 kg of soil sample was collected randomly from each plot using a soil auger up to a depth of 15 cm from the surface. Pebbles and other unwanted materials were removed, the soil sample was mixed thoroughly and 250 g was sub sampled for the analysis of herbicide residues. Collected samples were stored at -10 ^{0}C, processed and analyzed within seven days.

Analytical Techniques

Herbicides residue from soil samples collected were subjected the extraction and cleaned up as detailed below.

Extraction and clean up

Butachlor, pretilachlor, alachlor and metolachlor were extracted from soil samples using acetone, methanol, acetonitrile and dichloromethane respectively. Then the residues were eluted using dichloromethane, hexane and ethyl acetate in iso-octane respectively for butachlor, pretilachlor and alachlor. Clean up of all herbicide residues were done using anhydrous sodium sulphate / NaCl and florisil. Dried residues were redissolved in known volume of solvents (hexane for butachlor and pretilachlor, acetone for alachlor and ethyl acetate for metolachlor) to inject in to Gas Chromatograph.

For atrazine analysis, soil samples were extracted with acetonitrile, filtered and cleaned up through anhydrous sodium sulphate in chromatographic column and evaporated over water bath. Finally moistened residue was mixed with known quantity of hexane. The extracted sample was injected in gas chromatograph with flame ionization detector.

Pendimethalin was extracted from the sample with methanol and the extract was filtered and evaporated at 60^{o}C to about 10 ml. The concentrated extract was transferred to separatory funnel and 30 ml of 5% aqueous NaCl was added. The contents were partitioned with n-hexane and passed through anhydrous sodium sulfate. Hexane layer was concentrated on rotary vacuum evaporator at 60^{0}C to approximately 5 ml and quantified by Gas Chromatograph equipped with ^{63}Ni electron capture detector.

Instrumental conditions

Residues of all herbicides were determined using Gas Chromatograph equipped with Electron Capture Detector (ECD) and Flame Ionization Detector (FID). Separation of the compound was done in megabore capillary column of 30 m x 0.53 mm, ID-BP1 0.5 µm. Temperature conditions of the instrument, gas flow rate and retention time of all the herbicides are given in Table 1.

Recovery and Detection limits

Different known concentrations of all herbicides (2.0, 1.0, 0.5, 0.1, 0.01 and 0.001 mg kg^{-1}) studied were prepared in acetone/ hexane / ethyl acetate by diluting the stock solution. 0.5 µl of standard solution was injected and the peak area measured. Validation of the method was performed in terms of recovery studies before analysis of unknown sample. The recovery study was conducted for all herbicides in soil. The average recovery and detection limits of all herbicides are shown in Table 1.

Dissipation Coefficients

Degradation of herbicide was described (Timme *et al*., 1986) using first order kinetics as given below.

$dA/dt = Ka$ '! $A(t) = A_o \exp(kt)$

Where A is herbicide amount, t is time, A_o is the initial amount and k is degradation coefficient. The half life of the herbicide molecules were determined from the equation given below using the highest concentration.

$T_{1/2} = 0.6931 / K$

Results and Discussion

Initial deposition of herbicides

The initial concentrations of applied herbicides in soil (2 hr after their application) was varied with the type and quantity of herbicides applied to the soil (Figure 1). Generally higher rate of deposition was recorded under double the recommended rate of application and varied with the herbicides. Initial deposition of different herbicides in soil was in the order of alachlor > butachlor > metolachlor > pretilachor > atrazine > pendimethalin. The difference in intial deposition could be attributed to the physical and chemical properties of the herbicides such as organic -carbon and mineral-surface sorption coefficients, aqueous solubility, soil dissipation half-life etc., and environment factors such as application rate, herbicide persistence and mobility, rainfall, topography, and climate (Lin *et al*., 1999) besides the type of crop grown.

Table 1. Gas Chromatographic conditions and recovery of herbicides from soil

Herbicide molecules	Detector & N_2 / H_2 flow rate (ml/mi)	Temperature conditons ($_0$C) Oven / Injection / Detector	Retention time (minutes)	Limit of detection (µg/g)	Average Recovery (%)
Butachlor	ECD/50	210/230/250	3.32	0.001	89
Pretilachlor	ECD/40	210/230/250	4.92	0.001	85
Alachlor	ECD/10	240/220/260	2.49	0.001	82
Metolachlor	ECD/40	210/220/240	5.35	0.001	83
Atrazine	FID/40	220/200/250	3.80	0.01	86
Pendimethalin	ECD/40	185 - 220 /240/260	3.47	0.001	81

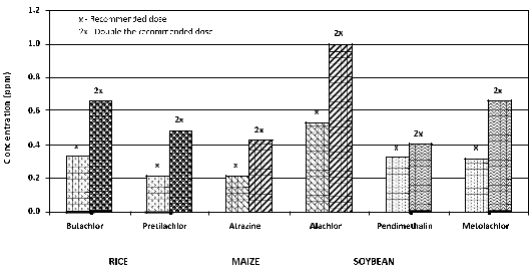

Fig 1. Initial deposits of applied herbicides in soil grown with different crops

In case of rice, more than 100 per cent higher deposition was recorded for both the herbicides (101 and 127 % for butachlor and pretilachlor, respectively). Higher initial deposition of butachlor and pretilachlor in rice soil could be attributed to higher K_{oc} values and minimal volatilization losses. Initial deposition of 101 and 89 percent was recorded for atrazine and alachlor in maize crop grown soil and atrazine had higher deposition as it was not highly mobile in soil (Vencill, 2002). In case of soybean grown soil, the initial depositions at the double dose of application is 24 and 108 per cent higher with respect to pendimethalin and metolachlor respectively. Similar result was reported by Singh et al. (1997) that the application of metolachlor @ 1 and 2 kg a.i. ha^{-1} resulted in the deposits of 6.10 and 9.47 ppm respectively in soil (at a depth of 0-7.5cm).

Persistence of herbicides

Persistence characteristics of herbicides are shown in Fig. 2 and residues of different herbicides decreased consistently with time. Within the period of crop harvest (60 days after herbicide application) more than 98 per cent of herbicides dissipated from the soil, exception that the metolachlor and atrazine.

The degradation of herbicides in soil followed first order kinetics and the corresponding data fitting first order kinetics are given in Table 2. The correlation coefficient (r_2) derived from the regression lines lies between 0.714 and 0.957 and the best fit was observed for butachlor, pretilachlor, pendimethalin and metolachlor. Half life of the herbicides increased with the increase in its applied concentration. The mean half life of initial concentration of herbicides studied in sandy clay loam and clay loam soils is 5.88, 12.44, 31.45, 4.78, 14.63 and 22.42 days for butachlor, pretilachlor, atrazine, alachlor, pendimethalin and metolachlor respectively (Table 2). Degradation of herbicides in soil initially depends on the intrinsic properties of the herbicides, secondly on the soil properties and climatic conditions (Singh *et al*., 1997). Among the acetanilide herbicides, half life for metolachlor was high because of its relatively high water solubility (530 mg/L at 20º C) and low K_{oc} (200 mL/g) as reported by Rivard (2003) and Parker *et al*. (2005). Weber *et al*. (2003) reported that metolachlor sorption, mobility, and soil retention was related to organic matter, clay content, and surface area.

Table 2. Optimized first order field dissipation curves as influenced by quantity of application

Herbicides*	DT_{50}	Predicted equation	Goodness of fit
Rice			
Butachlor – x	5.44	y = -0.007x + 0.271	R^2 = 0.869
Butachlor – 2x	6.28	y = -0.012x + 0.502	R^2 = 0.790
Pretilachlor – x	13.16	y = -0.003x + 0.178	R^2 = 0.886
Pretilachlor – 2 x	11.72	y = -0.007x + 0.425	R^2 = 0.923
Maize			
Atrazine - x	30.81	y = -0.001x + 0.158	R^2 = 0.714
Atrazine – 2 x	32.09	y = -0.003x + 0.333	R^2 = 0.784
Alachlor – x	5.15	y = -0.016x + 0.419	R^2 = 0.771
Alachlor – 2x	4.41	y = -0.031x + 0.810	R^2 = 0.797
Soybean			
Pendimethalin - x	13.24	y = -0.003x + 0.265	R^2 = 0.828
Pendimethalin – 2x	16.02	y = -0.004x + 0.313	R^2 = 0.837
Metolachlor – x	21.13	y = -0.003x + 0.297	R^2 = 0.944
Metolachlor - 2x	24.71	y = -0.003x + 0.333	R^2 = 0.957

* x- Recommended dose; 2x – double the recommended dose

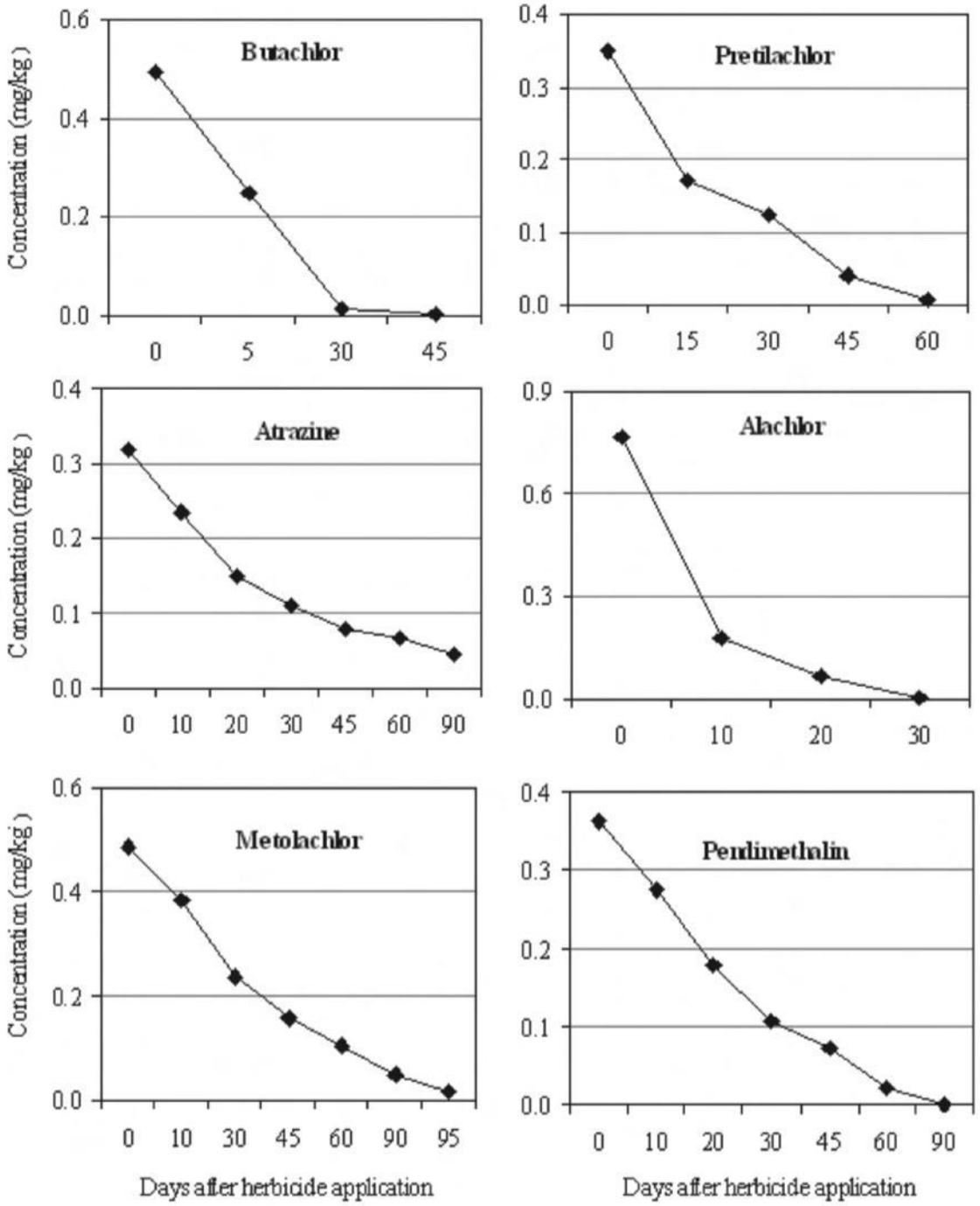

Fig. 2. Field persistence of applied herbicides in sandy clay loam soil

Alachlor and butachlor dissipated at a faster rate than other herbicides which might be due to the faster microbial degradation of these herbicides in soil (Yu *et al*., 2003). Pretilachlor and metolachlor dissipation from soil was biphasic, i.e. initial faster dissipation upto 20 days thereafter; their dissipation becomes slow. This could be attributed to an equilibrium that was reached with these herbicides where soil adsorption had occurred, and then desorption of the parent was observed over time (Patakioutas and Albanis, 2002). Vidotto *et al*. (2004) reported that the half life of pretilachlor in rice soil varied from 15 to 28 days and was influenced by the higher ratio of its low percolation rate and adsorption on the sediment.

Comparing the atrazine and pendimethalin, atrazine persisted in the soil even after harvest of the crop while pendimethalin was below detectable limit. Higher half life of atrazine in soil could be attributed to the non availabilty of required moisture and temperature as they are the primary factors enhancing the degradation of triazine herbicides (Weber and Weed, 1974) by promoting microbial

population. Walker and Zimdahl (1981) reported that the degrdation of atrazine is greater in moist soil than in dry soil. Persistence of atrazine is increased by soil pH as well as by cool, dry soil conditions (Vencill, 2002). Higher half life of pendimethalin when compared to chloracetnilide herbicides is attributed to the bounding of pendimethalin to soil organic matter and slow loss from soil rich in clay or organic matter (Kulshrestha and Yaduraju, 1987) besides it's immobility in soil (Vencill, 2002).

Conclusion

Initial deposition of herbicides was influenced by the quantity of application in this study. Gradual and continuous dissipation was observed as a function of time and all the herbicides dissipation followed first order kinetics. Half life increased with increase in its concentration of application and the mean half life of herbicides studied was in the order of atrazine > metolachlor > pendimethalin > pretilachlor > butachlor > alachlor. Among the chloracetanilide herbicides, metolachlor persisted longer period in soil. The study confirms that the degradation of herbicides in soil depends on the intrinsic properties of the herbicides and soil properties.

References

Arnold, D.J. and Briggs, G.G. 1990. Fate of pesticides in soil: predictive and practical aspects. *In*: Hutson, D.H., Roberts, T.R. (Eds.), *Environmental Fate of Pesticides*. John Wiley and Sons, New York, pp. 101–202.

Beestman, G.B. and Deming, J.M. 1974. Dissipation of acetanilide herbicides from soils. *Agron. J.,* **66**: 308– 311.

Fava, L., Bottoni, P., Crobe, A. and Funari, E. 2000. Leaching properties of some degradation products of alachlor and metolachlor. *Chemosphere.* **41**:1503-1508.

Kalkhoff, S.J., Kolpin, D.W., Thurman, E.M., Ferrer, I. and Barcelo, D. 1998. Degradation of chloroacetanilide herbicides: The prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwater and surface waters. *Environmental Science and Technology.* **32**: 1738-1740.

Kollman, W. and Segawa, R. 2000. Pest Chemistry Database. Environmental Hazards Assessment Program. California Department of Pesticide Regulation. Sacramento, CA.

Kulshrestha, G. and Yaduraju, N.T. 1987. Persistence of pendimethalin in soil following pre-emergence application to wheat. *Indian J. Agron.,* **32**: 271 - 275

Lin, Y.W., Makesh, K., Anugrah, S. and Gupta, G. 1999 Effect of simulated sunlight on atrazine and metolachlor toxicity of surface waters. *Ecotoxicology and Environmental Safety.* **43**:35-37.

Masse, L. Prasher, S.O., Khan, S.U., Arjoon, D.S. and Barrington, S. 1994. Leaching of metolachlor atrazine and atrazine metabolites into ground water. *Transaction of the ASAE.* **37**: 801-806.

Mbuya, O.S., Nkedi-Kizza, P. and Boote, K.J. 2001. Fate of Atrazine in Sandy Soil Cropped with Sorghum. *J. Environ. Quality.* **30**: 71-77

Parker, D.C., Simmons, F.W. and Wax, L.M. 2005. Fall and early preplant application timing effects on persistence and efficacy of acetamide herbicides. *Weed Technology.* **19**: 6-13.

Patakioutas, G. and Albanis, T.A. 2002. Adsorption-desorption studies of alachlor, metolachlor, EPTC, chlorothalonil and pirimiphos-methyl in contrasting soils. *Pest Management Science.* **58**: 352-362.

Ramesh, A. and Maheswari, S.T. 2004. Dissipation of alachlor in cotton plant, soil and water and its bioaccumulation in fish. *Chemosphere.* **54**: 647–652

Rivard, L. 2003. Environmental fate of metolachlor. Environmental Monitoring Branch, Department of Pesticide Regulation, 1001 I Street Sacramento, CA 95812

Sethi, R.K. and Chopra, S.L. 1975. Adsorption, degradation and leaching of alachlor in some soils. *J. Indian Soc. Soil Sci.,* **23**: 184-194.

Singh, S.B., Yaduraju, N.T. and Kulshrestha, G. 1997. Residues of Metolachlor Herbicide in Soil and Potato Tubers Under Indian Tropical Conditions. *Bull. Environ. Contam. Toxicol.,* **59**: 216-221

Timme, G., H. Frehse and Laska, V. 1986. Statistical interpretation and graphic representation of the degradation behavior of pesticide residues. *II. Pflanxenschutz-Nachrichten Bayer.* **39**: 189-203.

Tsiropoulos N.G. and Lolas P.C.2003. Persistence of pendimethalin in cotton fields under sprinkler or drip irrigation in central Greece. *International Journal of Environmental and Analytical Chemistry.* **84**: 199-205

Vencill, W.K. 2002. Herbicide Handbook. 8th edition, Weed Science Society of America, Lawrence, KS, U.S.A. pp 1-440.

Vidotto, F., Ferrero, A., Bertoia, O., Gennari, M. and Cignetti, A. 2004. Dissipation of pretilachlor in paddy water and sediment. *Agronomie.* **24**: 473-479

Walker, A. and Zimdahl, R.L. 1981. Simulation of the persistence of atrazine, linuron and metolachlor in soil at different sites in the USA. *Weed Res*., **21**: 255-265.

Weber, J.B. and Weed, S.B. 1974. Effects of soil on the biological activity of pesticides. *In*: Guenzi WD. (ed). Pesticides in Soil and Water. Soil Science Society of America, Madison, p.223-226.

Weber, J.B., McKinnon, E.J. and Swain, L.R. 2003. Sorption and mobility of 14C-labeled imazaquin and metolachlor in four soils as influenced by soil properties. *J. Agric. Food Chemistry.* **51**: 5752-5759.

Winkelmann, D.A. and Klaine, S.J. 1991. Degradation and bound residue formation of atrazine in a Western Tennessee soil. *Environmental Toxicology and Chemistry.* **10**:335-345.

Yu, Y.L., Chen, Y.X., Luo, Y.M., Pan, X.D., He, Y.F. and Wong, M.H. 2003. Rapid degradation of butachlor in wheat rhizosphere soil. *Chemosphere.* **50**: 771–774

Received: June 20, 2012; Accepted: July 7, 2012