

SORPTION AND LEACHING OF S-METOLACHLOR IN SURFACE HORIZONS OF ROMANIA

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Abstract

Sorption is the major process that determines the fate and behavior of most herbicides in soil. Understanding herbicide sorption within soil profile is the first step to predict groundwater contamination. Laboratory studies were conducted to determine the influence of surface soil properties on s-metolachlor sorption. Sorption isotherms were determined from soil plough layer (0-25 cm) using the batch equilibrium method and six concentration (0, 1, 5, 10, 20 and 50 mg L⁻¹). Sorption affinity of herbicide was approximated by the Freundlich equation. The environmental behavior of s-metolachlor was studied at the Didactical and Experimental Research Station Ezareni belonging to "Ion Ionescu de la Brad" University of Agriculture and Veterinary Medicine Iasi, Romania. A randomized complete block design with three replications was used in the experiment. S-metolachlor EC (96% v/v) was applied as a pre-emergence at dosages of 1500, 2100 and 2700 mL ha⁻¹ 1 day before sowing the soybean seeds in the field. The soil was collected at different layers and the residues of s-metolachlor were analyzed by GC-MS. Maximum concentration of s-metolachlor was recovered from 0-15 cm depth in all three doses. Results indicated high mobility of s-metolachlor under field conditions that may be significant in terms of ground water contamination.

Key words: Degradation, Leaching, S-Metolachlor, Sorption

Chloroacetanilide herbicides are among the most commonly used pesticides in agriculture for pre-emergence control of annual grasses and broadleaf weeds in corn, soybean and many other crops. About 15.900 metric tons of acetochlor were used in the United States in 2001, followed by 10.900 metric tons of s-metolachlor (Haitao et al., 2004). Due to the normal agricultural use the herbicide has been detected in groundwater and concentrations have ranged from 0.08 to 4.5 µg L⁻¹ in Wisconsin, Iowa and Pennsylvania (Chesters G., 1989; Philips et al., 1999). S-metolachlor is viewed as a class C human carcinogen (Haitao et al., 2004) and also some metabolites such as 2-ethyl-6-methylalaniline (EMA) show significant toxicological properties (Kimmel et al., 1986; Fava et al., 2000). S-metolachlor is more persistent than other acetanilide herbicides in the soil environment. It has the potential to leach into the groundwater because of its relatively high water solubility (530 mg L⁻¹) and low sorption to soil particles (Bowmna et al., 1989).

Several authors report s-metolachlor degradation (Kause et al., 1985, Liu et al., 1991) and mobility in field conditions or in soil columns (Braverman et al., 1986). S-metolachlor is considered moderately persistent in most soils, with slow microbial and anaerobic degradations and stable in water under regular sunlight. The rate

of leaching in soil columns was increased with increasing dose and with increasing rainfall or irrigation rate following herbicide application (Zheng S. Q. et al., 1993). Herbicide leaching through soil is particularly important in a number of environmental and agronomic problems. Leaching is considered as the main cause of groundwater contamination by pesticide which is determined by its physical and chemical properties. To assess the pollution potential and the mobility of pesticides, the adsorption coefficient (K_d) and the degradation half-life ($t_{1/2}$) are two key parameters. Adsorption of pesticides to soil particles is beneficial as it reduces their leaching potential to groundwater, however it might limit microbial degradation by limiting its bioavailability. While the adsorption of pesticides onto soil particles reduce their leaching potential to groundwater and simultaneously limits their bioavailability to microorganism, degradation effects the concentration of pesticides residues in soils, thereby controlling their persistence in soil. All these parameters were useful to evaluate pesticide persistence and mobility through the soil profile and to improve pesticide fate models that either provide predicted environmental concentrations or simulate environmental fate of pesticides (Vischetti et al., 2010).

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The objectives of the present study were to evaluate the adsorption and leaching characteristics and to determine degradation rates of s-metolachlor in surface soil samples in temperate conditions.

MATERIAL AND METHOD

Chemicals

Metolachlor (96.0%) standard was purchased from Labor Dr. Ehrenstorfer-Schäfers, Germany and 96% s-metolachlor emulsifiable formulation was supplied by Syngenta (Switzerland). Solvents used were of analytical grade and were obtained from Merck, Germany.

Field study

The field study was carried out to measure the sorption and leaching of s-metolachlor on a medium loamy soil from the Didactical Research Station Ezareni belonging to "Ion Ionescu de la Brad" University of Agriculture and Veterinary Medicine Iasi, Romania. A randomized complete block design with three replications was used in the experiment and each plot was 126 m². The pre-emergence herbicide s-metolachlor was applied using a commercial product such Dual Gold (960 g L⁻¹ a.i. s-metolachlor) in three doses, 144 mL m⁻² which is the recommended dosage, 201.6 mL m⁻² and 259.2 mL m⁻² corresponded to 40 and 80% of the recommended doses. In order to determine pesticide residues, representative soil samples were randomly collected in triplicate at 0, 5, 7, 10, 14, 25 and 90 days after treatment. Soil samples were collected from different depths ranging from 0 to 25 cm (0-5, 5-10, 10-15, 15-20, 20-25 cm). The samples were aseptically removed from the inner cores and stored in sterile glass bottles in the dark at 4°C until the start of the experiments. All the soil samples were air dried at room temperature, ground and passed through a 2 mm sieve. The characteristics of the soil are given in Table 1.

Table 1

Main physical and chemical characteristics of soil

Parameter	Value - % -	Parameter	Value - % -
Clay (< 2 μm)	41.8	pH	6.95
Silt (2-20 μm)	30.3	Organic carbon	1.30
Fine sand (50-200 μm)	22.9	Humus	2.94
		Ca+Mg+Na+K	17.47 meq 100 g ⁻¹

Soil extraction was performed with a Dionex ASE 300, accelerated solvent extractor. About 10 g soil was filled into 34 mL stainless-steel extraction cell. The solvent used was acetone-hexane (1:1 v/v). An oven heat-up time of 5 min and an oven temperature of 140°C were chosen. The flush volume amounted to 60% of the

extraction cell volume. The solvent used for each sample was about 60 mL and the time consumption was 15 min. The collected extracts were partitioned in dichloromethane, evaporated to dryness in rotary evaporator and the residue was dissolved in 1.0 mL of hexane and directly injected into gas chromatograph.

Herbicide residues in soil were determined by an Agilent 6890N Gas Chromatograph with 5975C-Mass Spectrometry (GS-MS). A HP-5MS (30mx0.250mmx0.25μm) column was used for the elution of the compound. The injector was operated at 250°C and the oven temperature was held at 50°C, ramped to 200°C at 30°C min⁻¹, ramped to 280°C at 10°C and held for 1 min. The carrier gas was Helium. A selected ion mode (SIM) was used in the analysis and the selected ions of s-metolachlor were: m/z 162, 238 and 240. The sample (1.0 μL) was injected in the splitless mode and the approximate retention time of s-metolachlor was at 8.78 min.

Laboratory procedures

Sorption isotherms were performed at Laboratory of Crop Protection Chemistry at Ghent University, Belgium on medium loamy soil using the conventional batch equilibrium technique according to the OECD guideline 106. Pesticide stock solutions contained 0, 1, 5, 10, 20 and 50 mg L⁻¹ s-metolachlor were prepared in 0.01M calcium chloride (CaCl₂) (Merk, Darmstadt Germany) and 200 mg L⁻¹ sodium azide (NaN₃) in distilled water. CaCl₂ was used as a background electrolyte to simulate an ionic strength similar to that of a natural soil solution, while NaN₃ was added to minimize biological activity (De Wilde et al., 2008).

In triplicate, 2±0.005 g of air dried soil sample was equilibrated with 20 mL s-metolachlor in 50 mL flat bottom flask and the mixture was shaken for 48h on an orbital shaker at 150 rpm at room temperature. After equilibration, samples were filtered using 0.22 μm pore size PVDF membranes.

The aliquots were analyzed using a Finnigan Surveyor HPLC (Thermo Electron Corporation; Waltham, MA, USA) with a gradient pump system, autosampler and diode array detector using a 150 mm x 3.0 mm EPS C18 (Alltech Associates Inc. Deerfield, IL, USA) analytical column. The mobile phase consisted of an acetonitrile and water (65/35, v/v) – which was acidified with 0.1% H₃PO₄. The flow rate was 0.7 mL min⁻¹ and the volume injected was 10 μL. The retention time for s-metolachlor was 2.352 min.

Data analysis

The Freundlich isotherm was used to describe herbicide sorption because is the most frequently model used to describe sorption processes. Sorption data of s-metolachlor was calculated using the following equation:

$$C_s = (C_{i,ini} - C_i)$$

where C_s is the amount of pesticide adsorbed (mg kg⁻¹), V (L) is the volume of pesticides solution

added, M (kg) is the weight of the soil, $C_{i,ini}$ (mg kg^{-1}) the initial pesticide concentration and C_i (mg kg^{-1}) is the concentration in the liquid phase after equilibrium.

The s-metolachlor degradation rate constants were calculated using first-order kinetics:

$$C_t = C_0 e^{-kt}$$

where C_t is the amount of s-metolachlor at time t (mg Kg^{-1} soil) C_0 is the amount of s-metolachlor at time 0 (mg Kg^{-1} soil) and k is the rate constant (week^{-1}).

The half-life for degradation (DT_{50} or $t_{1/2}$) at each soil depth was calculated using the equation:

$$DT_{50} = 0.693/k$$

RESULTS AND DISCUSSIONS

Herbicide sorption in laboratory conditions

Sorption isotherms of pesticides in soil have been described by different equations. Freundlich, Langmuir and linear isotherms are commonly used to describe the pesticide distribution and have been widely applied to study sorption to soil surfaces (Lengyel et al., 2003; Ma et al., 2004). S-metolachlor sorption is often described with the Freundlich equation (Youbin Si et. al., 2009; Gry et al., 2010; Bedmar et al., 2011):

$$C_s = K_f C_l^n$$

where C_s is the amount of pesticides adsorbed (mg kg^{-1}), C_l is the equilibrium concentration in solution (mg kg^{-1}) and K_f and n are empirical constants that reflect the affinity of the adsorbent for the adsorbate and the degree of the linearity between the amount sorbed and the solution concentration respectively. The Freundlich constants K_f , n and the corresponding coefficient of determination (r^2) are presented in Table 2. From the r^2 value, it could be concluded that the Freundlich isotherm fits the observed data well. The K_f value of s-metolachlor indicates that the chernozem soil had a moderate affinity for this herbicide (Table 2). This could be expected as the sorption strength is closely related to the hydrophobicity of herbicides expressed as K_{ow} (octanol-water partition coefficient) and while s-metolachlor is highly soluble in water (488 mg L^{-1}). The value of K_f is positively correlated with OC content and negatively correlated with soil pH. These results agree with those reported by several investigators for s-metolachlor sorption at different soil depth (Bedmar et al., 2011; Johnson et al., 1993; Huang et al., 1989).

The n value of s-metolachlor was lower than 1.0 (Giles et al., 1960), which indicates that as the initial concentration in the soil water increase, adsorption will decrease or the mobility of the s-

metolachlor will increase at higher concentrations (fig. 1).

Table 2

Value of the Freundlich parameters (K_f and n) and the determination coefficient for metolachlor adsorption on chernozem soil

S-metolachlor	
K_f	1.84 (± 0.26) ^a
n	0.95 (± 0.07)
r^2	0.95

^a \pm Standard deviation

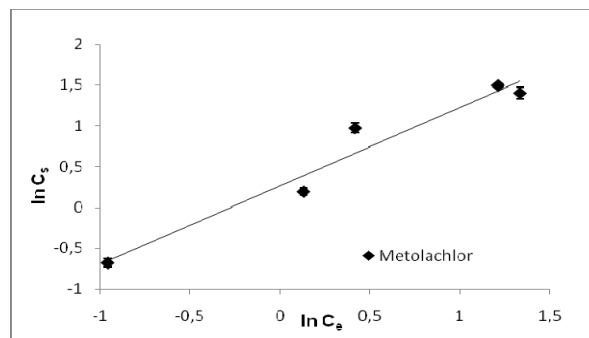


Figure 1 **Metolachlor sorption isotherm on Romanian chernozem soil**

According to the scheme proposed by Giles et al., (1974) isotherms of s-metolachlor were classified as L-type. The former type implies a higher affinity of the adsorbate for the surface at low than at high concentrations (Sparks et al., 2003). The L-type isotherms are indicative of sorption by heterogeneous media, in which high-energy sites are occupied first (Weber et al., 1996). According to Bedmar et. al., 2011 s-metolachlor is more likely to be lixiviated than atrazine, particularly if concentrations greater than those used in this study were applied or if it would accumulate in soil.

Field leaching studies

Field leaching studies following applications of Dual Gold on chernozem soil indicate that s-metolachlor leaches to subsoil and the concentrations below 10-15 cm depth are lower than 0.1 mg kg^{-1} .

Herbicide leaching from the zone of the soil treatment depends on the amount of rainfall or irrigation received and the applied dosage. The concentrations of s-metolachlor recovered from soil at three doses, at various depths are presented in table 3. At recommended dose (1500 mL ha^{-1}), s-metolachlor, is sorbed on organic and inorganic particles and the risk for leaching is minimal. After 25 days and exposure to 115 mm rain, s-metolachlor leached to 10-15 cm depth but nearly 45% of the applied pesticides were retained in the 0-5 cm layer. Samples from 15-20 cm depth indicated, that s-metolachlor residues were below calibration curves. The rate of leaching was found

to be higher and faster at 40% and 80% of the recommended dose. Application of Dual Gold at 2100 mL ha⁻¹ and 2700 mL ha⁻¹ doses increased the mobility of s-metolachlor. As s-metolachlor has low affinity to soil particles at high concentrations, is more susceptible to leaching this might have added further on movement of s-metolachlor under field conditions.

After 25 days, s-metolachlor leach down to 15-20 cm as the adsorption percentage of s-metolachlor decreased with the increasing concentration of s-metolachlor applied to the soil. The herbicide leach down to 15-20 cm soil depth and a major portion of the soil applied s-metolachlor (35 %) moved down to the 5-10 cm soil section. The amount of water moved a significant portion of the surface-applied s-metolachlor to the lower soil profiles, but s-metolachlor still remained in the 0-15 cm profile (93 %). Preferential flow through soil macropores and high concentration reduces the retention of the herbicides in the surface soil and thus may increase the hazards of groundwater contamination. After 90 days, (table 3) s-metolachlor applied at recommended dose, 40 and 80% + recommended dose was found distributed in all the depths. It can be concluded that because of high water solubility and poor soil adsorption characteristics, s-metolachlor has a potential for movement. This could result in contamination of ground water.

Table 3

Vertical distribution of s-metolachlor in chernozem soil

Soil depth (cm)	Residues ^a (mg kg ⁻¹)		
	Dose		
	1500 mL ha ⁻¹	2100 mL ha ⁻¹	2700 mL ha ⁻¹
0-5	0.09±0.03 ^b	0.12±0.04	0.11±0.02
5-10	0.07±0.09	0.1±0.08	0.09±0.06
10-15	0.04±0.05	0.04±0.06	0.1±0.06
15-20	B.C ^c	0.01±0.01	0.02±0.01
20-25	B.C	B.C	0.01±0.01

^a Average of three replication

^b ±Standard deviation

^c Below calibration curves

Degradation dynamics of s-metolachlor in field conditions

Degradation trends of s-metolachlor in soil are presented in Fig. 2. Pesticide degradation followed first order kinetics and half-life values were the same demonstrating a biodegradation activity of this herbicide. The half-life of s-metolachlor in soil was 69.3 days.

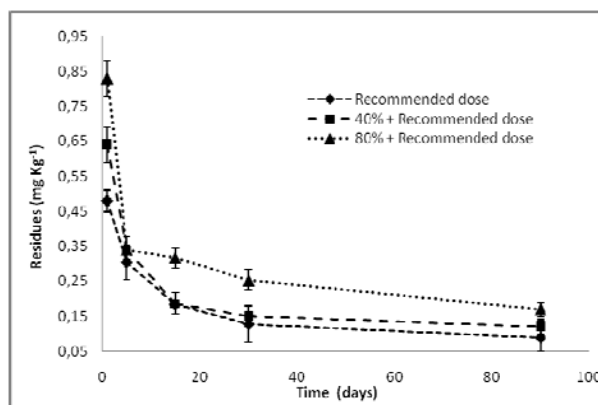


Figure 2 The degradation curves of s-metolachlor in the surface soil

The faster dissipation of s-metolachlor at 80% + recommended dose could be explained probably by leaching or by the strong influence of soil community. The presence of an amount of organic carbon and a particular microbial biomass could explain the results obtained in pesticide degradation. Our hypothesis was that the microbial community had a high metabolic efficiency in the degradation of the organic substrates on which it has been adapted.

CONCLUSIONS

The field study provided useful information on s-metolachlor sorption and leaching, helping in the disappearance of this chemical from the plough layer. The persistence of s-metolachlor has been shown to be quite variable depending on an array of environmental factors and concentrations.

S-metolachlor sorption was moderate and the herbicide leached relatively easily even at low doses. These results show that s-metolachlor might leach into the subsurface soil where it will dissipate slowly and be more available for transport to groundwater.

Further studies are needed to characterize the microbial component of the soil and to evaluate the degradation potential upon a number of pesticides.

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