Bull. Environ. Contam. Toxicol. (2005) 75:1086–1093

DOI: 10.1007/s00128-005-0860-3

Bulletin of Environmental Contamination and Toxicology

Behavior of Acetanilide Herbicides in Soils and the Possibility of Groundwater Contamination

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Received: 25 June 2005/Accepted: 6 October 2005

Acetanilide herbicides are soil-applied herbicides used worldwide. Of these, alachlor [2-chloro-*N*-(methoxymethyl)-*N*-(2,6-diethyl- phenyl) acetamide], butachlor [2-chloro-*N*- (butoxymethyl)-*N*-(2,6-diethylphenyl) acetamide], metolachlor [2-chloro-*N*-(2-methoxy-1-methylethyl)-*N*-(2-ethyl-6- methylphenyl) acetamide] and propachlor [2-chloro-*N*-(1-methylethyl)-*N*-phenyl- acetamide] were introduced to control weeds occurring in soybean, peanut, corn, onion, garlic, cabbage and vegetable fields in Taiwan since 1969 (alachlor and propachlor), 1971 (butachlor) and 1984 (metolachlor). Peter and Weber (1985) reported that adsorption of alachlor and metolachlor was related to the contents of the soil organic matter and the contents of the clay minerals. Beestman and Deming (1974) reported that the main pathway for dissipation of the acetanilide herbicides was microbial degradation. Somasundaram et al. (1991) reported slower movement of pesticides with higher amounts of organic matter and clay in the soil. Two models, the behavior assessment model (BAM) and the groundwater pollution-potential model (GWP) have been studied to evaluate the potential of a chemical to contaminate groundwater (Jury et al. 1983; 1987). BAM is used to assess the relative dynamics of multiple compounds under the same circumstances, and GWP is used to assess the possibility of organic compounds to contaminate groundwater through leaching into the soils. Both the BAM and GWP models belong to the screening models type. In our previous report (Chen et al. 1993; Chang et al. 1993; Wang et al. 1994; Yen et al. 1997; 2000; 2003), the evaluation was useful in predicting the behavior of chemicals in the environment. The present study was designed to investigate the adsorption, movement and dissipation of acetanilide herbicides in the subtropical soils of Taiwan at different temperatures and soil moisture contents. The possibility of the herbicides contaminating the groundwater was assessed with BAM and GWP in this study.

MATERIALS AND METHODS

Herbicides alachlor, butachlor, metolachlor and propachlor with purities of 98.5, 93.0, 97.5 and 99.0%, respectively, were purchased from Labor Dr. Ehrenstorfer-Schafers, Augsburg, Germany. Acetonitrile solutions of 0.8, 0.8, 0.4 and 1.0 mg/mL for alachlor, butachlor, metolachlor and propachlor, respectively, were

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prepared as stock solutions. Soil samples were collected from the surface (0 to 25 cm depth) of field soil at Shimon of the Tauyuan prefecture, Puli of the Nantou prefecture and Nantzu of the Kaohsiung prefecture, the subtropics, located in northern, central and southern Taiwan, respectively. Soil samples were air-dried, crushed, and sieved through a 2-mm mesh screen. The physicochemical properties of the soil samples are detailed in Table 1.

Table 1. Physicochemical properties of the soils in this study

Soil Locations	Particle analysis				pH (Soil: H_2O= 1:1)	Organic matter (%)	Soil moisture (%)
	Soil texture	Clay (%)	Silt (%)	Sand (%)			
Shimon, Tauyuan	Clay loam (CL)	31	29	40	3.3	1.33	22.4
Puli, Nantou.	Loam (L)	24	41	35	6.3	1.12	31.1
Nantzu, Kaohsiung	Sandy loam (SL)	11	30	59	4.0	0.54	11.9

Each 10 g air-dried sample of Tauyuan CL, Nantou L or Kaohsiung SL was weighed and packed in a 50-mL plastic centrifuge tubes. For each herbicide, a total of 729 tubes (3x3x3x9x3, for use in 3 herbicide concentrations, 3 moisture contents, 3 temperatures, 9 sampling times and triplicate, respectively) in each soil sample were prepared. The acetonitrile solution (0.5 mL) of each herbicide was added to the soil samples to make form concentrations of 40, 40, 20 or 50 μg per g soil for alachlor, butachlor, metolachlor or propachlor, respectively. After thorough mixing, the lids of the tubes were removed and the solvent was allowed to evaporate for 2 days. The soil samples were divided into three groups to be treated with three different soil moisture contents, i.e. 30, 60 and 90% of field capacity. The centrifuge tubes of each group were covered with lids but not so screwed too tightly in order to maintain the aerobic conditions. They were divided into three subgroups for incubating under 10, 25 or 40°C in the incubator. Evaporated water was amended during the incubation period through adding distilled water to the original weight. Soil samples were taken at 0, 7, 14, 21, 49, 75, 100, 125 and 145 days in triplicate from each subgroup. The residual herbicide in the soil sample was extracted with 30 mL of acetonitrile. Extracts were centrifuged, filtrated and then analyzed by HPLC (describe below). Degradation of herbicides in sterilized soil was performed with a soil moisture content at 90% of field capacity of soil contents and autoclaved twice in 0.10 Mpa (15 lb/in^2) at 121°C for 1 hr.

For the study of adsorption isotherms, herbicide of 2, 4, 6, 8 or 10 μg/mL (in 0.01 *M* $CaCl_2$, 20 mL) were separately added to 50-mL plastic centrifuge tubes containing 2 g of soil. The soil-water suspensions were continuously agitated with a shaker at 100 rpm for 24 hr in a water bath under 25 or 37°C. Following agitation and then standing for 20 min, the supernatant was filtered with 0.45 μm of Millipore and analyzed by HPLC.

Surface-applied alachlor, butachlor, metolachlor or propachlor was leached through acrylic columns (48 × 6.5 cm i.d.) at room temperature. Columns were uniformly packed with air-dried Tauyuan CL, Nantou L or Kaohsiung SL, separately, to height of 40 cm, and saturated with 5 m*M* $CaSO_4$ solution from the bottom up to 72 hr to remove air and to prevent soil particle dispersion and then drained for 24 hr. Columns were then topped up with 30 g of soil containing herbicides (40 mg herbicides dissolve in 1 mL acetonitrile then added to soil, the solvent was allowed to evaporate). Five columns were prepared for each soil, four for each herbicide and one for blank. The herbicide was leached daily through the soil columns with 5 m*M* $CaSO_4$ solution for 20 (butachlor), 10 (alachlor and metolachlor) and 5 (propachlor) days (100 mL/day). Leachate fractions were collected separately each day to determine herbicide contents. After leaching, soil columns were sliced into 8 sections (each 5 cm), from which the remaining herbicide was extracted with acetonitrile prior to HPLC analysis.

For HPLC analysis, an L-6200 intelligent pump, an L-6000 pump, an L-4200 UV-Vis detector and a D-2500 chromato-integrator (Hitachi Co., Japan) were employed. The mobile phase (acetonitrile:H_2O = 80:20, by volume) was pumped through a reversed-phase column [E. Merck, LiChrospher 100 RP-18 endcapped (5 μm), 250×3.9 mm i.d.] with an isocratic flow rate of 1.0 mL/min. The wavelength of the UV detector was set at 205 nm, and chromatography was performed at room temperature. The injection volume was 20 μL for all samples. The retention times under this condition were 4.15, 7.64, 4.27 and 3.14 min for alachlor, butachlor, metolachlor and propachlor, respectively.

RESULTS AND DISCUSSIONS

Adsorption isotherms for herbicides in three soil samples at various soil temperatures (25°C and 37°C) were observed (data not shown). It could be seen from the coefficient of determination that linear and Freundlich equations were more appropriate than the Langmuir equation to describe the adsorption of herbicides to soils. In order to fit the results into the computer model for simulating the movement of the herbicides in the soil column, the linear isotherm equation was used to describe the absorption in this study. The linear adsorption coefficient (K_d) of herbicides in different soils and temperatures are shown in Table 2. The adsorption coefficient was increased as the soil temperature increased. The results in Table 2 showed that the linear adsorption coefficient of alachlor, metolachlor and propachlor in three soils at 37 °C was approximately two times higher than that of 25 °C, and approximately ten times of that found in butachlor, although the adsorption reaction is an exothermic reaction. Sato et al. (1987) also reported that increase in soil temperature leads to increase in the soil adsorption of butachlor and alachlor. According to Moreale and Van Bladel (1979), because the water layer attached to the surface of the soil particles is released at a higher temperature, more adsorption sites become empty to provide greater herbicide adsorption. In addition, adsorption of acetanilide herbicides onto the soils was related to the soil organic matter content, Kaohsiung SL contained the lower organic matter (0.54%, Table 1) and showed the lowest absorption coefficients. The order of adsorption coefficient in the soils were butachlor >>alachlor≒metolachlor > propachlor.

Table 2. Linear adsorption coefficient (K_d) of herbicides in different soils and temperatures

Herbicide	Temp. (°C)	K_d (L/Kg)		
		Tauyuan CL	Nantou L	Kaohsiung SL
Alachlor	25	2.275	2.267	1.983
	37	5.269	4.800	4.664
Butachlor	25	64.09	60.56	59.17
	37	736.4	417.8	728.4
Metolachlor	25	3.182	2.904	2.841
	37	6.127	4.641	4.969
Propachlor	25	0.3971	0.6234	0.2040
	37	0.7730	0.9474	0.4269

Table 3. Half-life ($t_{1/2}$) and dissipation coefficient (K) of herbicides in soils under different conditions

Soil moisture (% FC)*	Incubation temperature. (°C)	Tauyuan CL		Nantou L		Kaohsiung SL	
		$t_{1/2}$ (days)	K (day^{-1})	$t_{1/2}$ (days)	K (day^{-1})	$t_{1/2}$ (days)	K (day^{-1})
Alachlor							
90	10	187	0.0037	92	0.0075	187	0.0037
30	25	210	0.0032	45	0.0154	182	0.0038
60	25	121	0.0057	44	0.0155	92	0.0075
90	25	61	0.0113	29	0.0234	68	0.0101
90	40	17	0.0406	8.6	0.0805	13	0.0508
Butachlor							
90	10	187	0.0037	102	0.0068	178	0.0039
30	25	210	0.0033	57	0.0121	257	0.0027
60	25	106	0.0065	58	0.0120	77	0.0090
90	25	15	0.0460	9.5	0.0733	13	0.0529
90	40	13	0.0533	6.9	0.1005	12	0.0585
Metolachlor							
90	10	301	0.0023	124	0.0056	216	0.0032
30	25	433	0.0016	105	0.0066	257	0.0027
60	25	126	0.0055	57	0.0121	151	0.0046
90	25	70	0.0099	51	0.0136	94	0.0074
90	40	43	0.0160	23	0.0304	35	0.0196
Propachlor							
90	10	157	0.0044	79	0.0088	178	0.0039
30	25	133	0.0052	24	0.0282	115	0.0060
60	25	80	0.0086	26	0.0269	71	0.0097
90	25	54	0.0128	21	0.0300	41	0.0144
90	40	20	0.0340	9.4	0.0734	17	0.0398

* %FC: Soil moisture contents at percentage of field capacity.

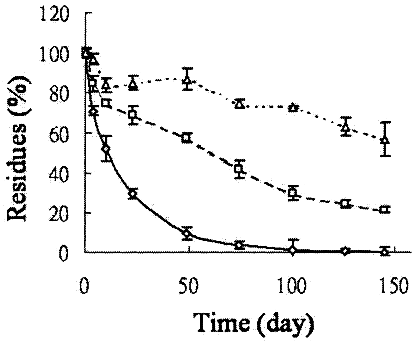

Figure 1. Residues of alachlor in Tauyuan clay loam incubated in 40°C (—◇—) 、25°C (— □ —) or 10°C (- -△- -) under 90 % field capacity of moisture contents

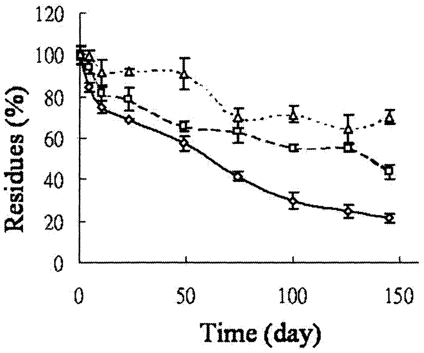

Figure 2. Residues of alachlor in Tauyuan clay loam incubated with 90 % (—◇—)、60 % (—□—) or 30 % (- -△- -) field capacity of moisture contents at 25°C.

Residues of the herbicide in the soils at different temperatures and different soil moisture contents were measured at predetermined intervals (detailed data not shown, only the data for alachlor residues in Tauyuan CL are shown in Figs. 1 and 2).

Herbicides dissipation in the soils along with first-order kinetic, the dissipation coefficient (*K*) and half-life ($t_{1/2}$) of four herbicides in soils under different conditions can be calculated (Wang et al. 1994) and are shown in Table 3. From the results, it can be seen that the rate of dissipation depends on the both temperature and soil moisture content. Temperature seems to be an important factor affecting dissipation. Fig. 1 indicates that in Tauyuan CL, after incubation at 90% field capacity of soil moisture content at 40°C for 150 days, almost no alachlor residue was observed but about 60% of alachlor remained at 10°C. This situation can also be observed from the results of other acetanilide herbicides and soil samples in this study. For the dissipation rate of alachlor in different soil moisture contents of Tauyuan CL at 25°C, the lower the alachlor residues were the greater the soil moisture contents (Fig. 2). In addition, for herbicides incubated in sterilized Tauyuan CL, Nantou L or Kaohsiung SL with 90% field capacity of soil moisture contents at 25°C for 100 days, no significant difference in the residues were found among the three soil samples. The main pathway for dissipation of acetanilide herbicide has been reported to be degradation by microbes (Beestman and Deming, 1974).

The main parameter values of soils, environments and herbicides used in BAM and GWP models are shown in Table 4. In a simulation of the BAM model with a leaching rate of 2.7 cm/day (from experimental value) for 20 days, there were no significant differences in the mobility of alachlor and metolachlor

Table 4. Parameter values for three soils, environments and herbicides used in BAM and GWP model

Parameters (signal; unit)	Tauyuan CL	Nantou L	Kaohsiung SL	References
Porosity (f)	0.514	0.468	0.408	Exp. data*
Water content (θ ; v/v)	0.224	0.311	0.119	Table 1
Organic carbon fraction (f_{oc}; g/g)	0.0133	0.0112	0.0054	Table 1
Bulk density (B_d; g/cm^3)	1.288	1.410	1.568	Exp. data
Air diffusion coefficient (D^{air}; cm^2/day)		4.32×10^3		Jury et al. 1983
Liquid diffusion coefficient (D^{liquid}; cm^2/day)		4.32×10^{-1}		Jury et al. 1983
Boundary layer thickness (d; cm)		0.475		Simulate
Incorporation thickness (L; cm)		3		Simulate
Leaching rate (J_w; cm/day)		2.7		Exp. value
Henrys constant (K_h)				**
Alachlor		9.456×10^{-7}		
Butachlor		1.512×10^{-6}		
Metolachlor		9.856×10^{-7}		
Propachlor		1.548×10^{-6}		
Organic C partition coeff. (K_{oc}; cm^3/g)				***
Alachlor	171.1	202.4	367.2	
Butachlor	4819	5406	10957	
Metolachlor	239.2	259.3	526.1	
Propachlor	29.8	55.6	37.8	
Half life ($t_{1/2}$; day)****				Table 3
Alachlor	121	44.8	92.4	
Butachlor	106	58	77	
Metolachlor	126	57	151	
Propachlor	80	26	71	
Water solubility (S; g/L)				**
Alachlor		242×10^{-3}		
Butachlor		20×10^{-3}		
Metolachlor		488×10^{-3}		
Propachlor		580×10^{-3}		
Groundwater depth (H; m)		3		Simulate
Root zone depth (L; cm)		50		Simulate
Annual drainage (J_w; cm/yr)		300		Simulate
Dissipation coefficient (K; day^{-1}) ****				Table 3
Alachlor	0.0057	0.0155	0.0075	
Butachlor	0.0065	0.0120	0.0090	
Metolachlor	0.0055	0.0121	0.0046	
Propachlor	0.0086	0.0269	0.0097	

*f=1-(bulk density/particle density). **K_h= (vapor density/solubility)x(1/RT). The values for vapor density and solubility obtained from The Pesticide Manual, 11th ed. British Crop Protection Council, UK (1997). ***K_{oc}=K_d (Table 2)/% organic matter (Table 1). ****At 60% FC of moisture contents and 25°C (in Table 3).

Table 5. Evaluation of travel time and residual mass percentage of herbicides to groundwater layer at 3 m depth by GWP model under the local drainage of 300 cm/yr

Herbicides	Soil types	Travel time (yr)	Residual mass (%)
Alachlor	Tauyuan clay loam	3.16	2.69
	Nantou loam	3.51	0.2
	Kaohsiung sandy loam	3.23	3.66
Butachlor	Tauyuan clay loam	82.8	0
	Nantou loam	85.7	0
	Kaohsiung sandy loam	95.9	0
Metolachlor	Tauyuanclay loam	4.32	1.31
	Nantou loam	4.41	0.23
	Kaohsiung sandy loam	4.57	3.24
Propachlor	Tauyuan clay loam	0.73	38.6
	Nantou loam	1.19	2.69
	Kaohsiung sandy loam	0.44	52.7

among the three different soils. The simulated values were shown to move depths of 15-20 and 12-17 cm in soils (data not shown) for alachlor and metolachlor, respectively. However, propachlor showed a mobility of more than 40 cm in depth and butachlor showed almost no mobility in the three soils. From experimental data, the distribution of maximum residue of alachlor, butachlor, metolachlor and propachlor in three soils occurred at depths of 25-30, 0-3, 20-25 and 30-35 cm, respectively, after leaching for 10, 20, 10 or 5 days, also respectively. As to the movement of herbicides in the soil profile, the experimental data seemed a little greater than the simulated removal in the shorter term. Generally, the BAM model was found to be more than adequate for predicting the behavior of chemicals movement in the longer term. Following incubation for 20 days in soils, the behavior of herbicides simulated using BAM was recorded. It was found that more than 70% of alachlor and metolachlor remained in Tauyuan CL and Kaohsiung SL, and about 20% was degraded. Greater rates of degradation and lower amounts of chemical remaining in the soils were found in Nantou L than in Tauyuan CL and Kaohsiung SL. However, approximately 65 to 75% of butachlor was degraded and only 25 to 35% was remaining in the soils. However, no herbicide dissipation was revealed through volatilization. Evaluation by GWP model, the travel time and the percentage of residues for herbicides to a depth of 3 m into the groundwater layer in the three soils under local drainage of 300 cm/yr were simulated and given in Table 5. In Kaohsiung SL, propachlor leaching to the groundwater layer would only equal 0.44 yr, and the residual mass of herbicide at that time was found to be 52.6%, indicating that propachlor may contaminate the groundwater in Kaohsiung SL under local meteorological conditions. Under conditions of low mobility and rapid degradation, there seems no possibility that butachlor could contaminate the groundwater of the three soils.

Acknowledgments. The research was supported in part with a grant from the National Science Council of the Republic of China (NSC 89-2317-B-002-010).

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