Comparison of the Persistence of Atrazine and Metolachlor under Field and Laboratory Conditions

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A study was carried out in a loamy soil to evaluate the degradation of atrazine and metolachlor under laboratory-controlled and field-variable conditions as a function of temperature and soil moisture content. In laboratory trials, metolachlor showed fast degradation, with half-lives from 100 to 5.7 days in a temperature range from 5 to 35 °C at 100% of field capacity, whereas in the same conditions the degradation rate of atrazine was relatively slow, with half-lives from 407 to 23 days. Modeling of laboratory degradation data to predict field persistence was carried out. Field persistence of atrazine and metolachlor was measured in the same soil during the corn growing seasons in 1993, 1994, and 1996. In the three years the mean half-dissipation times for atrazine and metolachlor were 36 and 21 days, respectively. Calculations from model equations gave acceptable prediction of field dissipation of both herbicides. Limitations and perspectives of employed modelization procedure are discussed.

Keywords: *Atrazine; metolachlor; soil degradation; field persistence; persistence modelization*

INTRODUCTION

In recent years there has been an increasing interest in the study of the relationship between herbicide degradation under laboratory and field conditions to predict the variability in environmental behavior by mathematical models and to perform risk assessment in different situations. In Europe, pesticide regulation has developed into a controlled system with the aim of ensuring the safety of agrochemicals for the operator, consumer, and environment (Vischetti et al., 1998). Laboratory information is an essential component for the development and validation of computer simulation models. Several predictive models, including PELMO, PESTLA, LEACHP, VARLEACH, and PERSIST, contain similar subroutines to describe pesticide degradation as a function of soil temperature and soil moisture content (Jurado-Exposito and Walker, 1998). Assuming pesticide degradation in agreement with first-order kinetics, these models predict field soil degradation under continuously variable environmental conditions from degradation rates measured in the same soil under laboratory constant conditions (Jurado-Exposito and Walker, 1998).

Field and laboratory degradation of atrazine and metolachlor has been the focus of a number of studies (Walker and Zimdahl, 1981; Buttle, 1990; Rocha and Walker, 1995; Miller at al., 1997; Pussemier et al., 1997). In soil, dissipation of atrazine is due to both biochemical and chemical processes. Chemical transformation mainly occurs under acid conditions and is catalyzed by soil organic matter (Armstrong et al., 1967, 1968). Metolachlor soil degradation was postulated as an exclusive biochemical process (Lebaron et al., 1987). Field persistence of both chemicals is dependent on many factors, such as weather conditions, soil pH, moisture level, and organic matter content (Bowman, 1988; Pussemier et al., 1997). Although extensive literature is available on the soil degradation and environmental fate of atrazine and metolachlor, relatively few papers report all of the key parameters to model their field persistence (Walker and Zimdahl, 1981; Smith and Walker, 1989; Rocha and Walker, 1995). In particular, a laboratory data set including information on soil degradation in a wide range of temperature and soil moisture conditions, representative of cold and warm seasons, is the basic requirement for successful parametrization and prediction of field dissipation in the environment.

The objectives of this study were (i) to evaluate the degradation kinetics of atrazine and metolachlor in a useful range of temperature and soil moisture conditions in the laboratory, (ii) to find the best parametrization procedure of laboratory data to obtain model equations for the prediction of herbicide dissipation, and (iii) to validate model equations using the observed persistence of atrazine and metolachlor under field conditions typical of northern Italy (Po valley).

MATERIALS AND METHODS

Chemicals and Soil. For both laboratory and field studies, the water dispersible granule commercial formulations of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine; 90% of active ingredient (ai)] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide; 80% of ai] were kindly supplied by Novartis AG (Basel, Switzerland). Analytical grade metolachlor (96.1%) and atrazine (99.1%) were furnished by Dr. Ehrenstorfer (Augsburg, Germany) and employed as analytical standards. Solvents for high-performance liquid chromatography (HPLC) separation and soil extraction were of pesticide grade and supplied by Sigma Chemical Co. (St. Louis, MO).

Degradation of atrazine and metolachlor under laboratory and field conditions was investigated in the soil of the research station of Ozzano (Bologna, Italy). The soil is loamy with 420 g kg^{-1} sand, 240 g kg^{-1} clay, 340 g kg^{-1} silt, organic matter

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content of 17 g kg^{-1}, pH (1:2.5 soil/water) of 7.7, cation exchange capacity of 35.9 meq 100 g^{-1}, and water content of 24% at an applied pressure of 33 kPa.

Laboratory Studies. Degradation of atrazine and metolachlor was evaluated as a function of soil moisture and temperature. The soil was collected from the top 10 cm of plots uncropped for 5 years at the research station of Ozzano (Bologna, Italy). Before use, the soil was air-dried and passed through a 2-mm sieve. Twenty-five gram (oven dry weight basis) samples of soil were weighted into 648 sterile screw-top culture tubes (3 i.d. × 10 cm) and treated with appropriate herbicide water solutions to provide final concentrations of 1.1 and 2.2 mg of ai kg^{-1} of atrazine and metolachlor, respectively. These concentrations correspond to 1000 g of ai ha^{-1} of atrazine and 2000 g of ai ha^{-1} of metolachlor incorporated to a depth of 10 cm, with a soil bulk density (w/v) of 1.1. Soil moisture of the samples was adjusted to 40, 70, and 100% of field capacity (FC) by adding sterile ultrapure water. The 324 sample tubes containing soil at the FC were kept in the dark and incubated under aerobic conditions in a climatic chamber at temperatures of 5, 10, 15, 20, 25, and 35 °C. Similarly, the 162 sample tubes containing soil at 70% of FC and the 162 sample tubes containing soil at 40% of FC were incubated at temperatures of 15, 25, and 35 °C. The moisture of soil samples was checked daily by weighing and was adjusted as required. For each temperature and moisture level, triplicate soil samples of atrazine were removed at 0, 7, 14, 21, 35, 42, 56, 70, and 90 days after treatment, whereas those of metolachlor were removed at 0, 1, 3, 7, 14, 21, 35, 42, and 56 days after treatment. Soil samples were stored at −20 °C until extraction and residue analysis. The whole experiment was a randomized-block design (benches being blocks) with three replicates.

Field Studies. The field research was conducted in 1993, 1994, and 1996 at Ozzano Research Station, Bologna, Italy. This experiment was part of a larger study that began in 1989 to examine the effect of tillage systems on runoff losses of nutrients and herbicides. The experimental site was 200 m asl and 0.7 ha^{-1} large and had a northern exposure, and the mean slope, after laser surface-modeling, was 15%. The eight experimental plots were rectangular and measured 7 × 50 m, with the longest side perpendicular to contour lines. The plots were hydrologically isolated and separated by 5 × 50 m buffer plots. The experimental station was equipped for the automatic monitoring of runoff and leaching in the eight plots (Rossi Pisa et al., 1994). Corn was planted in each plot on April 26, 1993, April 27, 1994, and April 30, 1996. Each year, four replicate plots were treated with atrazine and metolachlor soon after corn sowing at the rates of 1000 and 2000 g of ai ha^{-1}, respectively. Standard crop management practices were employed. Soil sampling in the four treated plots was conducted before herbicide application and at six (1993 and 1994) and five (1996) time intervals over the subsequent 160 days after herbicide application (from May 1 to September 28). On each sampling date, 10 soil cores (5 cm diameter to a depth of 50 cm) were randomly taken at each of the four treated plots with a stainless steel coring tube. Soil cores were divided into five segments: 0−10, 10−20, 20−30, 30−40, and 40−50 cm. Segments of like depth were bulked, ground, and thoroughly mixed in a soil mixer and passed through a 2-mm sieve. Soil samples were stored at −20 °C until extraction and residue analysis. Additional five soil cores (5 cm diameter to a depth of 50 cm) were taken in a similar way at weekly intervals after herbicide application and oven-dried (24 h; 105 °C) to determine the moisture content in the 0−50 cm soil profile of each plot. During field experiments, the soil temperature of each plot was recorded on daily basis at three depths (5, 15, and 45 cm) using three-way probe soil thermographs. Air temperatures (maximum and minimum) and rainfall were daily recorded by the meteorological station located in the experimental area. The meteorological conditions during the field experiments and soil temperature and moisture levels are reported in Table 1. Soil temperature and moisture levels were employed in conjunction with the laboratory-observed breakdown data to calculate the rate of herbicide loss in the field.

Table 1. Weather Conditions, Soil Temperature, and Moisture Levels (0−20 cm Soil Profile) during the Experimental Periods[a]

temp range	1993	1994	1996
av air temp (°C)	20.3	21.1	19.9
total rainfall (mm)	289	475	365
no. of days with rainfall (days)	40	42	38
av temp of 0−20 cm soil profile (°C)	21.8	22.7	20.9
av moisture of 0−20 cm soil profile (% of FC[b])	65.4	63.6	63.4

[a] Soil temperature and moisture are the mean values of four experimental plots. [b] FC, field capacity.

Extraction and Soil Residue. Extraction of soil samples was performed by adding 10 and 20 mL of acetonitrile to glass test tubes (5 cm i.d. × 10 cm) containing 25 g of laboratory soil samples and 50 g of field soil samples, respectively (soil/extraction solvent ratio equivalent to 2.5). The capped test tubes were shaken for 2 h at room temperature in a horizontal shaker and sonicated for 15 min in a sonicator bath. The slurry was centrifuged for 10 min at 9500*g*. The slurry was filtered at 0.2 μm and directly analyzed by reversed phase (RP) HPLC. Preliminary studies showed that the mean recoveries in soil samples spiked in the 0.1−2 mg of ai kg^{-1} of soil range were 93 ± 5% (n = 10) for atrazine and 92 ± 4% for metolachlor (n = 10).

Residue analysis was carried out by RP-HPLC. The HPLC system was a Beckman (Palo Alto, CA) System Gold 126 with two pumps and a Spark Holland (Emmen, The Netherlands) Basic Marathon autosampler. A Beckman model 168 diode array detector was used. The C_{18} column was a Beckman Ultrasphere (25 cm × 4.6 mm i.d., 5-μm particle size). Analyses were done in gradient mode at the flow rate of 1 mL min^{-1}. The gradient separation was performed by maintaining initial conditions at water/acetonitrile (70:30) for 1 min and then increasing the acetonitrile content linearly for 10 min to reach a final water/acetonitrile ratio of (40:60). The injection volume was 50 μL. Detection was performed at 222 and 210 nm. Retention times were 5.4 ± 0.1 min for metolachlor and 7.5 ± 0.1 min for atrazine. Determination limits in soil samples were 0.040 mg of ai kg^{-1} for both atrazine and metolachlor. Retention time and diode array scan of analytical grade atrazine and metolachlor were employed for the identification of the active ingredient in soil extracts. Previous experiments confirmed that control field samples collected before herbicide application contained no compounds interfering with the detection of atrazine and metolachlor. Peak area was used for residue determination. Herbicide remaining was expressed as a percentage of concentration before incubation (laboratory studies) or after the first sampling (field studies). Half-lives and half-dissipation times were determined by linear regression of the natural logarithm of percentage of herbicide remaining against time and the slope of each line compared with analysis of variance.

RESULTS AND DISCUSSION

Laboratory Studies. The results of the laboratory degradation studies are summarized in Table 2. Degradation of atrazine and metolachlor as a function of soil moisture and temperature followed first-order kinetics. The determination coefficients of the natural logarithm of herbicide residue against time ranged from 0.98 to 0.99 and were highly significant ($P < 0.01$), thus indicating that the assumption of first-order kinetics was acceptable. This observation is in agreement with the literature (Walker and Zimdahl, 1981; Smith and Walker, 1989; Vischetti et al., 1998). As reported in previous studies (Walker and Brown, 1985; Rocha and Walker, 1995), degradation of both chemicals was accelerated by the increase of soil moisture and temperature (Table 2). Over the entire range of temperature and soil moisture content, metolachlor showed half-lives

Table 2. Half-Lives (± Standard Deviation), Degradation Constants (k), and Determination Coefficients (r^2) of Atrazine and Metolachlor under Laboratory Conditions[a]

		atrazine			metolachlor		
temp (°C)	moisture[b] (%)	$t_{1/2}$	k	r^{2c}	$t_{1/2}$	k	r^{2c}
35	100	20.2 ± 1.1	0.034	0.999	5.7 ± 1.1	0.120	0.998
35	70	25.2 ± 1.6	0.027	0.994	7.3 ± 0.5	0.094	0.997
35	40	27.1 ± 2.4	0.025	0.994	11.3 ± 1.2	0.061	0.995
25	100	31.2 ± 2.7	0.022	0.998	8.6 ± 0.8	0.080	0.998
25	70	39.6 ± 4.1	0.017	0.992	10.2 ± 0.8	0.067	0.997
25	40	45.5 ± 5.8	0.015	0.991	15.2 ± 3.2	0.045	0.994
20	100	39.5 ± 4.4	0.017	0.997	12.2 ± 2.5	0.058	0.985
15	100	50.5 ± 4.9	0.014	0.995	18.0 ± 2.1	0.038	0.978
15	70	70.8 ± 7.1	0.009	0.989	21.4 ± 1.5	0.032	0.987
15	40	88.2 ± 7.4	0.008	0.988	27.4 ± 3.2	0.025	0.981
10	100	173.2 ± 21.5*	0.004	0.990	47.5 ± 5.6	0.014	0.989
5	100	366.9 ± 40.7*	0.002	0.995	100.7 ± 12.3*	0.006	0.981

[a] Each value is the average of three replicates; k values in days^{-1}; $t_{1/2}$ values in days; $t_{1/2}$ values followed by an asterisk were extrapolated by the regression curve. [b] Expressed as percent of field capacity. [c] $P < 0.01$.

lower than those of atrazine. Observed half-lives are consistent with those reported under laboratory conditions with the same herbicides by Walker and Zimdahl (1981), Walker and Brown (1985), Smith and Walker (1989) and Rocha and Walker (1995).

The influence of temperature on the soil degradation of atrazine and metolachlor was characterized by the logarithmic form of the Arrhenius equation

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A \qquad (1)$$

where k is the degradation constant, E_a is the activation energy expressed in J mol^{-1}, R is the universal gas constant equal to 8.31 (kJ mol^{-1}), T is the absolute temperature, and A is the pre-exponential factor (or collision factor). When k, expressed as natural logarithm, is plotted against $1/T$, it is possible to obtain lines having slopes, when multiplied by R, that give the relative value of the activation energy. At field capacity, a nonlinear relationship between the logarithm of the degradation rate and the inverse of the absolute temperature was observed for both herbicides (Figure 1). As postulated by Ingraham (1958), a linear Arrhenius diagram is typical for chemical reactions over a narrow temperature range, whereas a curved one is expected for biological reaction with a temperature optimum. This is consistent with the stability of atrazine to chemical hydrolysis under subalkaline conditions (i.e., pH of the investigated soil equal to 7.7) and the dominant role of microbial decomposition for metolachlor soil degradation (Armstrong et al., 1968; Buttle, 1990). Even if nonlinear Arrhenius diagrams for sulfonylureas and flumetsulam were reported (Lehmann et al., 1992; Cambon et al., 1998; Dinelli et al., 1998), no previous reports of this pattern were found for atrazine and metolachlor. Although the Arrhenius diagrams were curved, two linear regression lines ($r^2 > 0.98$; $P < 0.01$) were fitted to experimental points in the 5−15 and 15−35 °C ranges to allow calculation of activation energies for degradation processes (Figure 1; Table 3). In the 15−35 °C range the resulting activation energies are in good agreement with values reported for the same herbicides (Walker and Zimdahl, 1981; Smith and Walker, 1989; Rocha and Walker, 1995). In the 5−15 °C range activation energies of both herbicides were ∼3−4 times higher than those calculated for the 15−35 °C range. Consequently, between 5 and 15 °C the degradation rate of both active ingredients was most influenced by temperature variations. Finally, in the 15−35 °C range an increase for atrazine and a decrease for metolachlor of the activation energy as a function of decreasing soil moisture content was observed (Figure 1, Table 3).

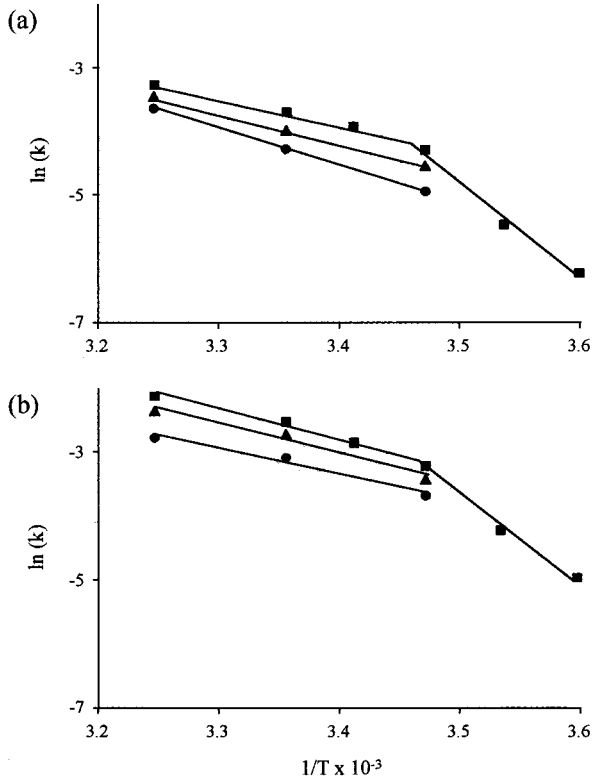

Figure 1. Arrhenius diagrams of atrazine (a) and metolachlor (b) as a function of soil moisture. The line slopes indicate activation energies (see text). Soil moisture content: (■) 100% of FC; (▲) 70% of FC; (●) 40% of FC. X-axis, inverse ratio of absolute temperature (T, Kelvin) employed for soil incubation; Y-axis, natural logarithm of degradation constant (k) observed at a given temperature.

To parametrize soil degradation of active ingredients for field persistence prediction, it was necessary to derive from laboratory results a quantitative relationship between the degradation rate as a function of soil temperature and the degradation rate as a function of soil moisture content. The approach first described by Walker and Barnes (1981), consisting of the characterization of temperature responses by the Arrhenius equation and moisture responses by an empirical equation, gave not quite acceptable results, as the correlation

Table 3. Arrhenius Equations, Determination Coefficients (r^2), and Activation Energies of Atrazine and Metolachlor as a Function of Temperature Range and Soil Moisture

		atrazine			metolachlor		
temp range (°C)	moisture[a] (%)	Arrhenius equation[b]	r^{2c}	activation energy[d]	Arrhenius equation[b]	r^{2c}	activation energy[d]
35−15	100	$\ln k = -4.06\ (1000/T) + 9.82$	0.999	33.1	$\ln k = -4.97\ (1000/T) + 14.81$	0.992	40.4
35−15	70	$\ln k = -4.59\ (1000/T) + 11.33$	0.997	37.3	$\ln k = -4.75\ (1000/T) + 13.1$	0.964	38.1
35−15	40	$\ln k = -5.23\ (1000/T) + 13.34$	0.997	42.5	$\ln k = -3.96\ (1000/T) + 10.12$	0.975	32.2
15−5	100	$\ln k = -15.85\ (1000/T) + 48.28$	0.980	128.9	$\ln k = -13.71\ (1000/T) + 44.32$	0.993	111.9

[a] Expressed as percent of field capacity. [b] k = degradation constant; T = absolute temperature (Kelvin). [c] $P < 0.01$. [d] kJ mol^{-1}.

Table 4. Regression Equations, Determination Coefficients (r^2), and Extrapolated Equations of the Dependence of Slope ($-E_a/R$) and Pre-exponential Factor (ln A) of Atrazine and Metolachlor Arrhenius Equations, Calculated in the 35−15 and 15−5 °C Ranges as a Function of Soil Moisture

	temp range (°C)	atrazine	r^{2a}	metolachlor	r^2
regression eq[b]	35−15	$-E_a/R = 1.27\ \ln(M\%) - 9.93$	0.993	$-E_a/R = -1.13\ \ln(M\%) + 0.15$	0.963
		$\ln A = -3.83\ \ln(M\%) + 27.48$	0.997	$\ln A = 4.42\ \ln(M\%) - 6.02$	0.975
extrapolated eq[c]	15−5	$-E_a/R = 1.27\ \ln(M\%) - 21.69$		$-E_a/R = -1.13\ \ln(M\%) - 8.52$	
		$\ln A = -3.83\ \ln(M\%) + 68.28$		$\ln A = 4.42\ \ln(M\%) + 23.98$	

[a] $P < 0.01$. [b] M% = soil moisture expressed as percent of field capacity. [c] See text for the extrapolation procedure.

Table 5. Model Equations for the Prediction of the Degradation Rate of Atrazine and Metolachlor in the Loamy Soil as a Function of Soil Moisture and Temperature

herbicide	temp range (°C)	eqs[a]
atrazine	35−15	$\ln k = [1.27\ \ln(M\%) - 9.93](1000/T) + [-3.83\ \ln(M\%) + 27.48]$
	15−5	$\ln k = [1.27\ \ln(M\%) - 21.69](1000/T) + [-3.83\ \ln(M\%) + 68.28]$
metolachlor	35−15	$\ln k = [-1.13\ \ln(M\%) + 0.15](1000/T) + [4.42\ \ln(M\%) - 6.02]$
	15−5	$\ln k = [-1.13\ \ln(M\%) - 8.52](1000/T) + [4.42\ \ln(M\%) + 23.98]$

[a] k = degradation constant; M% = soil moisture expressed as percent of field capacity; T = absolute temperature (Kelvin).

between laboratory observed and mathematically estimated half-lives for atrazine and metolachlor was <0.80 ($P > 0.01$) (data not shown). The low fitting could be due to the fact that a linear Arrhenius diagram and no change of activation energy as a function of soil moisture are the basic requirements of the parametrization proposed by Walker and Barnes (1981). Consequently, an alternative parametrization was employed. In the 15−35 °C range a logarithmic dependence ($r^2 > 0.96$, $P < 0.01$) of the slope ($-E_a/R$) and pre-exponential factor (ln A) of atrazine and metolachlor Arrehenius equations as a function of soil moisture content was observed (Table 4). Due to the slow degradation rate, the moisture-dependent degradation of active ingredients was not experimentally determined for temperature <15 °C. As a consequence, in the 5−15 °C range extrapolated equations were obtained by shifting the logarithmic regression lines obtained in the 15−35 °C range, without changing the respective slopes, throughout the $-E_a/R$ and ln A values determined for both chemicals at field capacity (Table 4). The $-E_a/R$ and ln A terms of atrazine and metolachlor Ahrrenius equations were substituted with the respective regression, and the extrapolated equations are shown in Table 4). For each active ingredient, the resulting model equations were two, because each herbicide was characterized by two Ahrrenius equations (5−15 and 15−35 °C ranges) (Table 5). To statistically verify these equations, regression analysis yielded coefficients of correlation highly significant ($r > 0.99$; $P < 0.01$) between observed and estimated half-lives determined by model equations. The slopes of the regression lines were 1.03 for atrazine and 1.01 for metolachlor, demonstrating that observed and estimated half-lives were correlated near the theoretical optimum value (Figure 2).

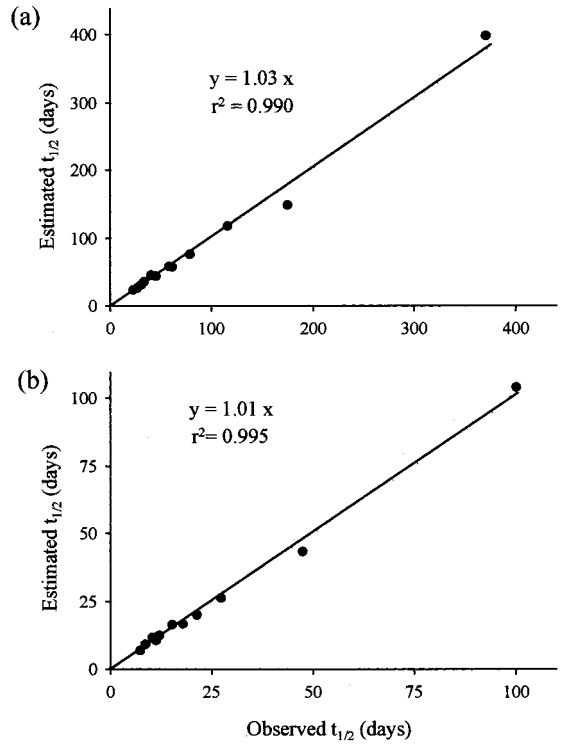

Figure 2. Comparison between laboratory observed and mathematically estimated half-lives of atrazine (a) and metolachlor (b). Regression equations and determination coefficients (r^2) are reported.

Model equations were represented by three-dimensional graphs, which were realized by calculating half-life as a function of temperature in the temperature range of 5−35 °C and in the soil moisture range from

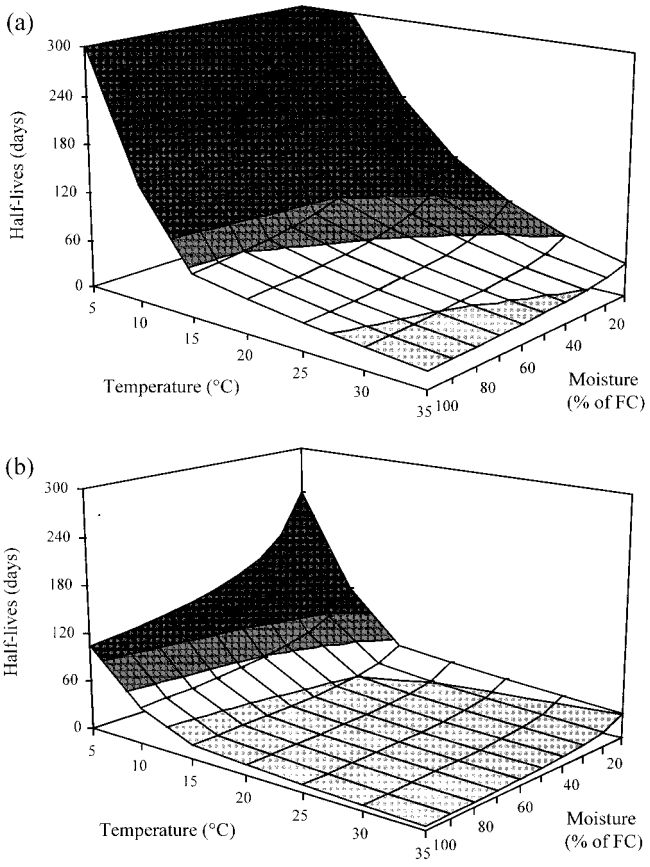

Figure 3. Atrazine (a) and metolachlor (b) degradation in the loamy soil estimated by model equations (see Table 6): half-life (days; light gray area, <30; unmarked area, 30−60; gray area, 60−90; solid black area, >90) as a function of temperature and soil moisture content.

10 to 100% of FC (Figure 3). For temperature <10 °C, independently from the soil moisture content, the half-life of atrazine was >90 days (solid black area, Figure 3a). For this herbicide, the half-life was <30 days only for temperature and soil moisture content higher than 28 °C and 40% of FC, respectively (light gray area, Figure 3a). The three-dimensional graph of metolachlor exhibited a shape similar to that of atrazine, even if the solid black area, indicating extremely low degradation, is limited to temperature <10 °C (Figure 3b). Moreover, the light gray area, which indicates half-life <30 days, represented ∼65% of the total surface of the three-dimensional graph, thus confirming a faster degradation of metolachlor with respect to atrazine (Figure 3b). The half-lives of atrazine and metolachlor calculated with model equations were in agreement with the half-lives reported by different authors for a wide range of temperatures and soil moisture contents (Bouchard et al., 1982; Lebaron et al., 1987; Levanon, 1993; Kolpin and Kalkhoff, 1993; Miller et al., 1997).

Field Studies. In all experiments no leaching of metolachlor was observed below 30 cm. In 1993 leaching of atrazine was confined in the 0−30 cm soil profile and in the 0−40 cm soil profile in 1994 and 1996. In addition, >90% of the total amounts of atrazine and metolachlor detected during field experiments was found in the 0−20 cm soil profile. Loss of both herbicides under field conditions followed an exponential decline in agreement with a first-order kinetic of dissipation ($r^2 > 0.97$; $P < 0.01$) (Table 6). In all experiments, the rate of dissipation of metolachlor (mean $DT_{50} = 21$ days) was

Table 6. Observed and Predicted Half-Dissipation Times (DT_{50}) of Atrazine and Metolachlor in the Loamy Soil[a]

	atrazine			metolachlor		
year	obs DT_{50}	r^{2b}	pred DT_{50}	obs DT_{50}	r^{2b}	pred DT_{50}
1993	23.5	0.978	47.7	17.7	0.985	16.9
1994	39.7	0.982	43.1	28.8	0.989	15.9
1996	45.8	0.988	44.3	17.2	0.978	17.3
mean ± SD	36.3 ± 11.5		45.1 ± 2.4	21.2 ± 6.5		16.7 ± 0.7

[a] Determination coefficients (r^2) of observed DT_{50} are reported. [b] $P < 0.01$.

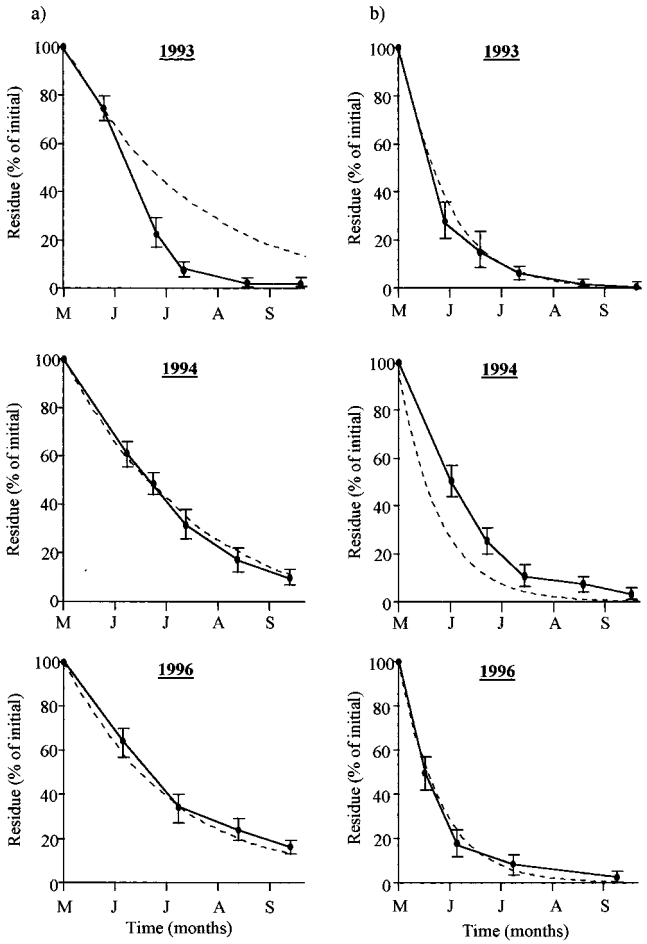

Figure 4. Observed and predicted field persistence of atrazine (a) and metolachlor (b) in loamy soil: solid line, observed residue; dotted line, predicted residue. Standard deviations of observed residues are reported.

more rapid than that of atrazine (mean $DT_{50} = 36$ days), confirming the results obtained under laboratory conditions (Figure 4; Table 6). Field persistence of both herbicides fits the mean DT_{50} values (45 and 20 days for atrazine and metolachlor, respectively) reported under normal climatic conditions by *The Pesticide Manual* (1998). For both herbicides, there were significant variations between predicted and observed carryover concentrations in at least one of the three years studied. In particular, in 1993 observed atrazine persistence was less than predicted, and it was approximately half of that observed in 1994 and 1996. In 1994, predicted metolachlor persistence was less than was observed. Furthermore, observed metolachlor persistence was approximately double with respect to that observed in 1993 and 1996 (Table 6). Considering that in the three years similar weather and soil conditions were recorded (Table 1), the significance of the observed

variability is difficult to assess. Many biological, chemical, and physical factors control field distribution of microorganisms and their degradative response to herbicide treatments (Smith, 1990). Persistence variability of both herbicides probably reflects the natural field variability of microbial biomass. Residues of atrazine and metolachlor 140 days after application (average of all years) were 10.7 ± 7.7 and 3.5 ± 1.8% of the initial dose, respectively. These soil residues remaining after trial periods are in agreement with those reported for atrazine and metolachlor in loam soils under similar temperature and moisture regimes (Walker and Zimdahl, 1981; Rocha and Walker, 1995; Gaynor et al., 1998).

Results from persistence prediction are also shown in Figure 4. Rate constants (k) were calculated from daily basis soil temperature and weekly basis soil moisture content by model equations reported in Table 5. Because the largest amount of active ingredients (~90% of the amount detected) was experimentally detected in the field from 0 to 20 cm, the mean temperature and moisture of the 0−20 cm soil profile were employed for persistence prediction. Using measured herbicide concentration at time 0, weekly values of k were inserted into model equations to calculate residue remaining at the beginning of the next week. Successive iterations led to predicted dissipation curves (Figure 4). A computer program (in Visual Basic) was complied to perform these calculations. In 1994 and 1996 a satisfactory agreement between observed and predicted dissipation of atrazine occurred, whereas in 1993 the model overpredicted atrazine soil residues (Figure 4a). In 1993 and 1996 the model prediction was in agreement with observed dissipation of metolachlor, whereas in 1994 the model underestimated metolachlor residues (Figure 4b). It has been suggested that if a model could predict residues within 30% of those observed, this would be sufficiently accurate for the practical purpose of carry-over forecasting (Walker and Bond, 1978; Rocha and Walker, 1995). When the final residues were considered, the predictions were within this error limit in all experiments (Figure 4). Comparison of all observed soil residues of both herbicides with those predicted by model equations shows that 24 of the 28 (85%) measured residues were within 20% of the predicted values. Finally, even if in single years some discrepancy between observed and predicted dissipation was observed, model equations were validated by the prediction of field persistence of both atrazine and metolachlor, as evidenced by the acceptable matching between the mean DT_{50} observed values and the mean DT_{50} values predicted values in the three years (Table 6).

Because parametrization of field persistence was based only on laboratory degradation of both chemicals as a function of two parameters (temperature and soil moisture), several factors contributing to field dissipation were not take into account in the model equations. As a consequence, it is not surprising that such simple and empirical model equations were not appropriate for the accurate prediction of soil residue in some years. However, obtained results indicate that prediction accuracy markedly increases in the case of long-term study (i.e., average persistence values of the three-year experiment). Although the persistence prediction based on the sole parametrization of herbicide degradation under laboratory conditions presents evident limitations, this modeling approach exhibits some attractive features for persistence prediction, such as the easy utilization, the finite required field inputs (i.e., soil temperature and moisture) for proper running, and the acceptable prediction of herbicide degradation in field. Overall, the forecasting precision mainly depends on the accuracy of laboratory data set employed for the parametrization. In particular, the results of the present research indicate that the use of herbicide degradation rates as a function of temperature and soil moisture content under controlled conditions, representative of those detected in a specific environment, allows extrapolation of field persistence under variable conditions. Conversely, it is puzzling to determine the soundness of laboratory data in the description of field variability of some soil components, such as microbial biomass, involved in herbicide dissipation. Usually, laboratory degradation trials are carried out using a restricted amount of soil, which does not fit the within-field variability of some biological and physicochemical soil properties. In conclusion, only the widespread adoption of standardized procedures for soil degradation studies under controlled and field conditions (i.e., number of temperature and moisture levels investigated, soil amount, soil treatment, detection method, sampling) will increase the capability of pesticide persistence modelization and environmental risk assessment.

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