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Original article

Degradation and mobility of metolachlor and terbuthylazine in a sandy clay loam soil

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Abstract – The degradation of metolachlor and terbuthylazine, two maize herbicides, was studied in laboratory in a sandy clay loam soil under different temperature and soil moisture conditions and in drainage field lysimeters. Identification of the main degradation products of the two herbicides was attempted both in laboratory and field lysimeter soil samples. The results show that the degradation of the two herbicides in laboratory followed a first order kinetics influenced by temperature and soil moisture. Metolachlor disappeared in soil more rapidly than terbuthylazine. Metolachlor moved more rapidly than terbuthylazine through the soil profile in field lysimeters and noticeable quantities were found in drainage water. In the laboratory degradation studies, the main degradation products of both herbicides were found in soil samples as early as the first week of incubation, while in the field lysimeter studies only the degradation product of terbuthylazine was found in soil samples. (© Inra/Elsevier, Paris.)

metolachlor / terbuthylazine / degradation / transformation products / field lysimeters

Résumé – Adsorption, dégradation et mobilité du métolachlore et du terbuthylazine au laboratoire et dans des lysimètres de terrain. La dégradation du métolachlore et du terbuthylazine, deux herbicides du maïs, a été étudiée au laboratoire dans un sol de limon argilo-sableux dans différentes conditions de température et d'humidité du sol et dans des lysimètres de terrain. L'identification des principaux produits de dégradation des deux herbicides a été entreprise sur des échantillons de sol à la fois au laboratoire et dans des lysimètres de terrain. Les résultats montrent qu'au laboratoire la dégradation des deux herbicides a suivi une cinétique de premier ordre influencée par la température et l'humidité du sol. Le métolachlore a disparu du sol plus rapidement que le terbuthylazine et a migré plus rapidement que celui-ci à travers le profil pédologique dans les lysimètres de terrain et des quantités notables ont été retrouvées dans les eaux de drainage. Au laboratoire, les principaux produits de dégradation des deux herbicides ont été retrouvés dans les échantillons de sol dès la première semaine d'incubation, tandis que dans les lysimètres de terrain, seul le produit de dégradation du terbuthylazine a été retrouvé dans les échantillons de sol. (© Inra/Elsevier, Paris.)

herbicide / métolachlore / terbuthylazine / dégradation / produit de transformation / lysimètre de terrain

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1. INTRODUCTION

In the industrialized nations of Europe and in North America, pesticide regulation has developed into a controlled system with the aim of ensuring the safety of new chemicals for the operator, consumer and environment [1]. Proper regulation can be envisaged only if many studies concerning environmental fate and behaviour of pesticides are carried out in all countries and in varying conditions.

Over the last 30–40 years persistent pesticides have been developed, many of which are in use today. The two chemicals under study, metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide) and terbuthylazine (2-chloro-4-ethylamino-6-terbuthylamino-s-triazine), are used together as herbicides in maize crops. The environmental fate of metolachlor and terbuthylazine has been the focus of a number of studies in the past and more recently has been given major attention [2, 4, 6]. These studies point to the persistence of metolachlor and terbuthylazine as being dependent on pH, soil moisture and organic matter content. As regards the degradation pathway of metolachlor, numerous degradation products have been identified through microbial, chemical and photolytic reactions [4]. Chloro-triazine herbicides, including terbuthylazine, in soil can undergo both partial and total microbial N-dealkylation and chemical hydrolysis of C-Cl bound.

The purpose of the present investigation was to study the degradation of metolachlor and terbuthylazine in a sandy clay loam soil both in laboratory and field lysimeters with the aim of checking and identifying any possible transformation products and hypothesizing the mechanism through which they are formed.

2. EXPERIMENTAL

2.1. Soil and herbicides

The soil for adsorption and degradation studies under laboratory conditions was the same as the soil used for the lysimeter experiment and its characteristics are reported in *table I.*

Table I. Main properties of soil used.

Sand (%)	49
Silt (%)	23
Clay (%)	28
Field capacity (v/v)	24.5
Wilting point (v/v)	10.5
pH (H_2O)	8.0
Organic matter (%)	1.9
CEC (meq/100g)	16.5

Analyses were carried out according to Cavazza [3] (hydrologic properties) and Page [8] and Klute [5] (physico-chemical properties).

Analytical-grade metolachlor (96.1 %) and terbuthylazine (99.9 %), produced by Dr. Ehrenstorfer, D-8900 Augsburg, were used as analytical standards.

2.2. Degradation studies

Chemically inert PVC containers for each herbicide were filled with 1 kg of air-dried sieved (2 mm) soil to which 1.6 mg $kg^{-1}$of metolachlor or 0.8 mg kg^{-1} of terbuthylazine were added. Soil samples were incubated in the dark at different temperature and soil moisture conditions [20 °C and 75 % field capacity (fc); 20 °C and 33 % fc; 10 °C and 75 % fc]. Experiment was performed in triplicate.

2.3. Field lysimeter experiment

The assay was carried out near Udine (north-east Italy, 46° 03' N) in four 4 × 7 m plots cultivated with a corn crop with a drainage lysimeter (1.6 m^2 in area, 1.5 m deep) buried at the center of each plot. The main properties of soil are reported in *table I.* The lysimeters were filled with 1 m of sieved soil over a graveled bed. A bulk of topsoil was sieved with a 25 mm mesh and tamped layer after layer by saturations on a graveled draining layer in each iron tank; the soil mass was laid on a drainage layer of gravel of increasing diameter (2 to 25–mm) towards the bottom. The soil profile in the lysimeters was reconstructed with the aim to simulate the nature of the outer soils. At the moment of the experiment the soil was aged for about 10 years, thus a new soil structure was likely to be established. Pre-emergence herbicide treatment was applied on 7 May using a commercially formulated product (Primagran TZ, Ciba-Geigy) at the recommended rate of 6.6 kg ha^{-1} in 870 l ha^{-1} of water, thus distributing 1 kg ha^{-1} a.i. of terbuthylazine and 2 kg ha^{-1} a.i. of metolachlor. Drip irrigation was supplied in order to maintain the soil water content near the field capacity so that every rain event could induce drainage. The leachates at the bottom of the lysimeters were collected whenever rainfall or irrigation induced drainage of water along the soil profile (3, 11, 19, 40 days after treatment). After measuring the drainage volume, three 200 mL samples of water were stored at –10 °C before the analytical determinations.

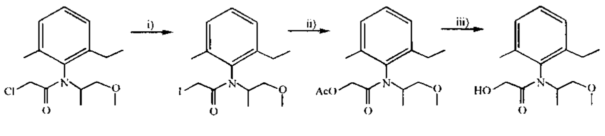
2.4. Sampling and analyses

For the field studies, three soil cores were taken from each lysimeter at 10 cm increments to a depth of 50 cm at different times after treatment (0, 7, 15, 22, 29, 36, 44, 55 and 80 days). The holes were refilled with the same soil type immediately after collection so as to avoid any changes in leaching patterns. For the laboratory degradation studies 50 g samples were taken from each container at different times after treatment. Metolachlor and terbuthylazine residues were extracted with methanol and the extracts diluted in water, partitioned in chloroform, evaporated to dryness and rinsed with methanol (1 mL).

These samples were analyzed by gas-chromatography according to the procedure described by Leita et al. [6].

2.5. Identification of degradation products

The degradation product of metolachlor, 2-hydroxy-N-(2-ethyl-6-methylphenyl)-N-(hydroxyprop-2-yl) acetamide, was prepared as follows:



i) KI in acetone at reflux for 5 h; ii) tetrahethylammonium acetate in CH_3CN (one day at r.t.); iii) NaOH in 1:2 water:ethanol (one day at r.t.).

The identity of chromatographic peaks was verified by GC/MS using a Hewlett-Packard model MS 5970 spectrometer with electronic impact (70 eV) [7] and by ^{1}H-NMR ($CDCl_3$) (as a mixture of diastereomers) δ 1.13-1.18 (2d,3H,J=6.8Hz), 1.25 (t,3H,J=7.5Hz), 2.2-2.4 (2s,3H), 2.44-2.65 (m,2H), 3.24-3.3 (2s,3H), 3.44-3.5 (m,3H), 3.64-3.78 (2dd,1H,J=4.4, 9.4Hz), 4.3 (m,1H), 7.2 (m,3ArH).

The degradation product of terbuthylazine, N-dealkylate metabolite (2-chloro-4-ethylamino-6-amino-s-triazine), was identified by GC/MS using a Perkin-Elmer Sigma 10 gas chromatograph with an ion source of the mass spectrometer as detector. The identification of GC peaks was obtained by comparison with the spectra library. Mass spectra in the electron impact positive ions mode were obtained with a Finnigan 1020 mass spectrometer equipped with a conventional ion source operating at 70 eV, a quadripole filter and detector of ions.

3. RESULTS AND DISCUSSION

In *table II* are reported the degradation rate (k) and the half-life ($t_{1/2}$) values for the two herbicides at different incubation conditions. In all cases degradation followed first order kinetics. In particular, terbuthylazine showed a slower degradation rate than metolachlor under all the conditions tested, which is in agreement with results reported by Zimdahl [10], and Vischetti and Businelli [9]. The influence of temperature and soil moisture on degradation was evident. The effect of temperature seemed to be more pronounced than that of soil moisture for both herbicides used. The change in soil moisture from 75 % of field capacity (fc) to 33 % fc produced increases in half-life values of 105.5 and 182.0 % for metolachlor and terbuthylazine, respectively, while the change in temperature from 20 to 10 °C amounted to increases of 133.3 and 410.7 %.

Table III shows the distribution of the two herbicides through the profile of the lysimeters. Both the herbicides accumulated in the 0–10 cm soil

Table II. Parameters of laboratory degradation kinetics for metolachlor and terbuthylazine under different incubation conditions.

Pesticide	Incubation conditions	k (d^{-1})	r	half-life (d)
Metolachlor	20 °C–75 % fc	0.035	0.999**	19.8
	20 °C–33 % fc	0.017	0.968**	40.7
	10 °C–75 % fc	0.015	0.957**	46.2
Terbuthylazine	20 °C–75 % fc	0.024	0.960**	28.9
	20 °C–33 % fc	0.008	0.929**	81.5
	10 °C–75 % fc	0.006	0.965**	147.6

fc = field capacity; ** = significant at $P \leq 0.01$.

Table III. Concentration of metolachlor and terbuthylazine (mg m^{-2}) in the profile of the lysimeters (mean of four data ± standard deviation).

Days	Pesticide	Depth, cm 0–10	10–20	20–30	30–40	40–50
0	m	200				
	t	100				
7	m	175.3 ± 12.1				
	t	92.55 ± 10.0				
15	m	74.8 ± 14.3	30.8 ± 7.1	8.2 ± 0.3		
	t	51.15 ± 10.1	23.6 ± 8.2	2.6 ± 3.2		
22	m	51.6 ± 9.7	19.2 ± 6.1	8.3 ± 1.5	6.1 ± 1.1	1.1 ± 0.7
	t	27.3 ± 8.4	19.2 ± 3.4	8.2 ± 6.3		1.3 ± 0.5
29	m	24.7 ± 3.5	11.5 ± 2.4	7.1 ± 0.8	1.6 ± 0.5	
	t	20.0 ± 2.1	18.6 ± 6.3	7.3 ± 1.1		
36	m	9.4 ± 2.5	4.4 ± 1.1	6.7 ± 1.2	3.1 ± 0.2	
	t	6.2 ± 1.1	17.2 ± 1.5	10.4 ± 2.2	3.3 ± 1.7	
44	m	3.6 ± 0.9	1.3 ± 0.3	2.4 ± 1.7		
	t	4.1 ± 1.2	6.0 ± 3.8	3.3 ± 1.0		

m = metolachlor; t = terbuthylazine
Data at 55 and 80 days after treatment were equal to zero and thus omitted.

layer after the first week, after which they moved deeper into the soil. On average metolachlor showed a more pronounced mobility than terbuthylazine. Moreover, the determinations carried out on leachates showed noticeable amounts of metolaclor (max. 25 μg L^{-1}), whereas terbuthylazine was never found *(table IV)*. Forty days after treatment no residues of the two herbicides were found in drainage water and 7.3 % of metolachlor and 13.4 % of terbuthylazine remained in the lysimeter profile. Two other leaching events occurred at 55 and 80 days after treatment, but no traces of pesticides were found in leachates nor in the lysimeter soil cores. The DT50 (time to 50 % field loss) values in lysimeters were 9.5 days for metolachlor and 16.8 days for terbuthylazine. However, the faster dissipation of metolachlor coincided with 0.5 % of the compound leaching below 50 cm depth. On the other hand, terbuthylazine had a slower dissipation and never moved below 50 cm depth. The high concentration of metolachlor in leachates from lysimeters would have been caused by the particular experimental hydrologic conditions applied to create a worst case. Maintaining soil moisture near the field capacity with irrigations is not normal practice, but it was needed to obtain drainage from lysimeters after rain events in an area with dry soil conditions during late spring or summer.

GC/MS analyses of soil samples from laboratory trials revealed the presence of additional peaks at retention times slightly lower than those of terbuthylazine and metolachlor. The metabolites of both herbicides were found in the laboratory soils degradation samples as early as the first week of incubation, while only the N-dealkylate metabolite of terbuthylazine was found in field lysimeter samples, 1 week after herbicide application in the 0–10 cm layer and subsequently in the 10–20 cm layer.

The mass spectrum of the unknown compound occurring in soil samples related to metolachlor was identified as 2-hydroxy-N-(2-ethyl-6-methylphenyl)-N-(hydroxyprop-2-yl) acetamide, characterized by comparison with the spectrum of the standard synthesized in laboratory. The mass spectrum of the unknown compound related to terbuthylazine was very similar to that of parent compound, with almost the same fragmentation pattern. The mass spectrum of terbuthylazine gave a signal at m/e 229, corresponding to the molecular ion; the signal at m/e 214 was due to the loss of the methyl group from the terbuthyl chain and the radical ion at m/e 173 to the loss of 2-methylpropene. The molecular ion of the unknown compound was found at a signal m/e 201. The signal at m/e 186 represents dealkylated molecular ion and the signal at m/e 145 is due to a McLafferty rearrangement with loss of propylene. The hypothesis of degradation pathways reported in *figure 1* suggests that the transformation product of metolachlor could derive from a nucleophyl substitution of C-Cl bond, and that of terbuthylazine from a N-dealkylation reaction probably catalyzed by a monoxigenase.

Table IV. Lysimeter percolate during the experimental period.

Dat	pw	Metolachlor			Terbuthylazine		
	mm	μg L^{-1}	g ha^{-1}	% of applied	μg L^{-1}	g ha^{-1}	% of applied
3	10.0	15	1.50	0.075	n.d.	–	–
11	48.5	10	4.85	0.242	n.d.	–	–
19	15.0	25	3.70	0.187	n.d.	–	–
40	15.0	n.d.	–	–	n.d.	–	–

Dat = days after treatment; pw = percolated water; n.d. = not detected
Data at 55 and 80 days after treatment were equal to zero and thus omitted.

4. CONCLUSIONS

The present research has pointed out that, in the conditions tested, metolachlor was rapidly dissipated in soil and noticeable amounts were found in leachates, while terbuthylazine, although more persistent than metolachlor, never moved below 50 cm deep.

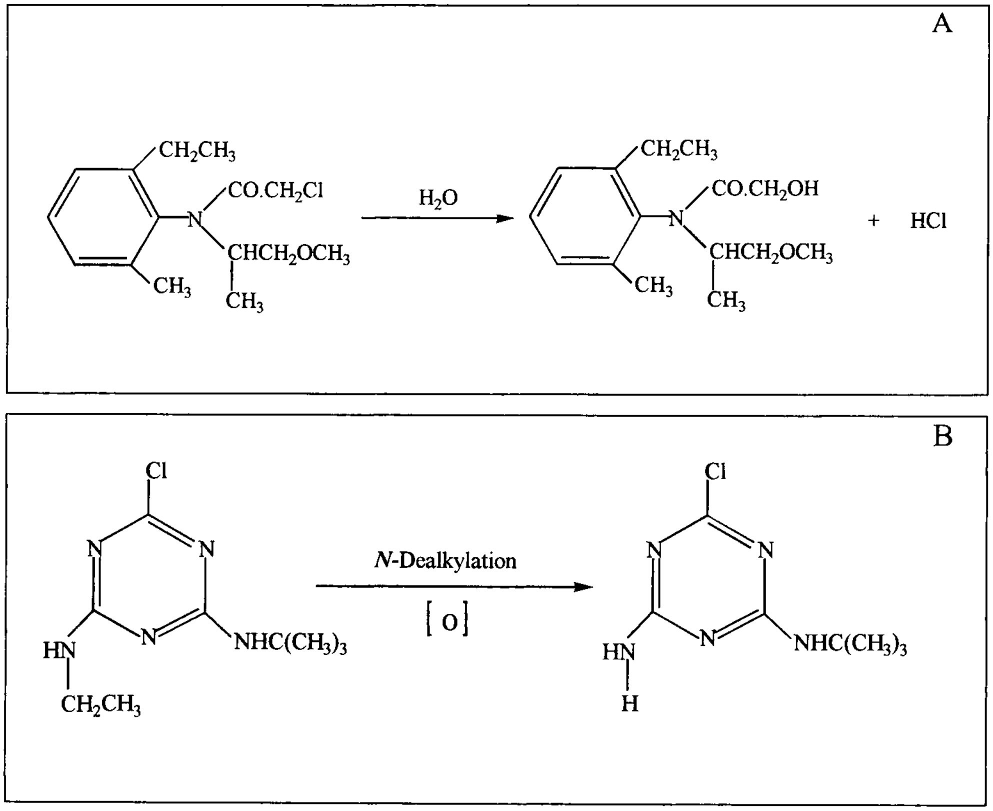


Figure 1. Degradation pathways of metolachlor (A) and terbuthylazine (B) assessed in the soil studied.

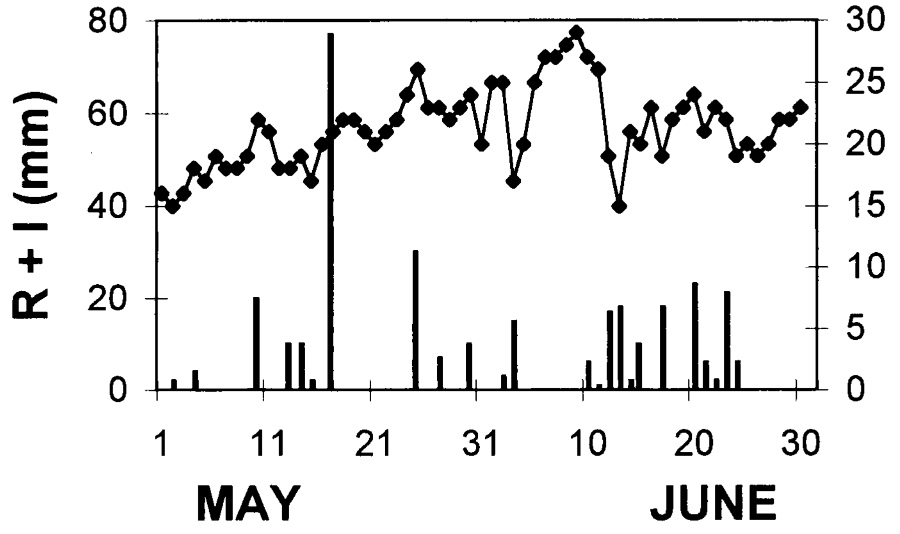


Figure 2. Time course of daily mean air temperature, rainfall (R) and irrigation (I) during the field experiment.

The main transformation products of the two herbicides were successfully found and identified in the laboratory samples, while in the field lysimeter samples only the terbuthylazine metabolite was detected. However, while pesticide metabolite detection in field soil and water samples is laborious and time-consuming, in a thorough study of the environmental fate of pesticides these compounds should never be overlooked.

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