Triflusulfuron-methyl Dissipation in Water and Soil

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This paper reports laboratory studies of the behavior and fate of triflusulfuron-methyl in aqueous buffer and soils. Aqueous hydrolysis was pH-dependent and fast in acidic buffer solutions. In basic buffers, the hydrolysis rate variation was low between pH 7 and pH 10. The degradation pathway in the range of pH 4−10 was via cleavage of the sulfonylurea bridge to form two transformation products: 2-amino-4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine (**2**) and 6-methyl-2-methylcarboxylate benzene sulfonamide (**3**). Comparison of transformation rates in sterile and nonsterile soils indicates that chemical and microbial processes are important in soil degradation. The former is more important in acidic soils, and the latter is more important in basic soils. A biphasic model fits well with dissipation of triflusulfuron-methyl in soil. The triazine formed during the first step of transformation was degraded more rapidly in basic soils than in acidic soils.

Keywords: *Triflusulfuron-methyl; sulfonylurea herbicides; hydrolysis; degradation; soil; water*

INTRODUCTION

Triflusulfuron-methyl [methyl-2-(4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2-ylcarbamoysulfamoyl)-*m*-toluate] is a selective, post-emergence sulfonylurea herbicide used for weed control (broadleaf and grasses) in sugar beet cultivation (Peeples et al., 1991).

Hydrolysis rates of sulfonylurea herbicides showed variations with pH. This pH dependence exhibits two different relationships depending on chemical structure: for some sulfonylureas, the rapid reaction rates at acidic pH decrease until pH 7 and then remain relatively constant until pH 10; for other sulfonylureas, the rate variations were analogue until pH 7, but between pH 7 and pH 10, the transformation rate increases. In the first case, the hydrolysis mechanism is via the breakdown of the sulfonylurea bridge and in some cases the hydrolysis of the methoxy group of the triazine ring. This has been reported by Sabadie (1991) (chlorsulfuron), Vega et al. (1992) (metsulfuron-methyl), and both Cambon et al. (1992) and Anderson and Dulka (1985) (sulfometuron-methyl). In the second case, the degradation pathway in acidic solutions was via the breakdown of the sulfonylurea bridge, but in alkaline solution, another pathway was observed. For example, hydrolysis of the ester function of thifensulfuron-methyl has been reported by Cambon et al. (1992), and Sabadie (1996) reported similarly for bensulfuron-methyl. Accordingly, the mechanism of hydrolysis of sulfonylureas is related to the chemical structure of these compounds.

Similarly, differences in transformation rates in soil may be observed. Variations in the degradation mechanism may be responsible for these differences. Comparison of transformation rates between sterilized and nonsterilized soils has shown the magnitude of the chemical and microbial transformations occurring in soils. For some sulfonylureas, microbial transformation was the major mode ($k_{nonsterile}/k_{sterile} > 5$) for metsulfuron-methyl (Pons and Barriuso, 1998), triasulfuron (Sarmah et al.,1999), thifensulfuron-methyl (Cambon et al., 1992), chlorimuron ethyl (Brown, 1990), and chlorsulfuron (Sarmah et al.,1999; Brown, 1990). For other sulfonylureas, the two modes, chemical and microbial transformation, have an equivalent magnitude ($k_{nonsterile}/k_{sterile} = 2$) for rimsulfuron and triasulfuron (Dinelli et al., 1998). However, the soil pH has a great effect on this ratio. For example, the herbicide metsulfuron-methyl has a half-life in sterile soil twice that in nonsterile soil at pH 6.2 and a half-life 8 times greater in sterile soil than in nonsterile soil at pH 8.1 (Pons and Barriuso, 1998).

The only reported study on triflusulfuron-methyl indicates that microbial degradation is important at alkaline pH but plays a minor role at neutral to acidic pH (Peeples et al., 1991). The objective of this study was to determine the role of chemical and biological degradation of this compound in different soils and to relate the chemical transformation in soil to the chemical hydrolysis in solution.

MATERIALS AND METHODS

Chemicals. Triflusulfuron-methyl [methyl-2-(4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2-ylcarbamoysulfamoyl)-*m*-toluate] (**1**) was a gift from Dupont de Nemours, France. All solvents were HPLC grade (Carlo Erba reagents).

2-Amino-4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine (2). Sodium (0.5 g) was slowly added to 15 mL of 2,2,2-trifluoroethanol. When the last trace of sodium disappeared, 2-amino-4-(dimethylamino)-6-chloro-1,3,5-triazine (3.5 g), prepared according to Pearlman and Banks (1948), was added with continued stirring. Refluxing was continued until the white crystal was consumed. The mixture was then filtered, and the filtrate was poured into ice and water (500 g). The product was filtered, washed with water, and recrystallized from cyclohexane; 20% yield. NMR (DMSO-d_6) 3.04 (6H, s); 4.8 (2H, dd); 6.9 (2H, s). MS(EI) = *m*/*z* (%) 237 (100), 222 (54), 208 (30), 194 (10), 168 (10), 111 (32), 69 (18), 83 (36), 69 (57).

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Table 1. Soil Characteristics

	sand %	silt %	clay %	organic carbon %	pH
Perpignan	42.9	34.4	22.7	0.66	8.0
Villeneuve	50.4	29.8	19.8	0.75	8.5
Bolquere	41.3	39.7	19.0	2.95	6.05
Saint Jacques	56.7	38.5	4.8	0.90	5.8

6-Methyl-2-methylcarboxylate Benzene Sulfonamide (3). Triflusulfuron-methyl (0.5 g) was dissolved in a mixture of methanol (80 mL) and concentrated HCl (0.5 mL). The mixture was stirred 3 days at ambient temperature, after which time the precipitate that formed was collected by filtration (0.1 g). Pf = 205−206 °C, IR (Nujol) cm^{-1} 3272, 3175, 1731, 1698. NMR ($CDCl_3$): 2.18 (3H, s); 3.8 (3H, s); 5.85 (2H, s); 6.61 (1H, dd); 7.2 (1H, d); 7.8 (1H, d).

Buffer Solutions. Eight aqueous buffer solutions were used. Buffers at pH 4 and pH 5 consisted respectively of 30.7 or 24.3 mL of 0.1 M citric acid solution and 19.3 or 25.7 mL of 0.2 M Na_2HPO_4 to a total of 100 mL. Buffers at pH 6, 6.5, 7, and 8 consisted respectively of 88.9, 70, 41.3, and 3.7 mL of KH_2PO_4 (1/15 M) and of 11.1, 58.7, and 96.3 mL of Na_2HPO_4 (1/15 M). Buffer at pH 9 consisted of 50 mL of a mixture of both KCl (0.1 M) and boric acid (0.1 M) and 20.8 mL of a 0.1 M NaOH solution diluted to a total of 100 mL. Buffer at pH 10 consisted of 50 mL of a mixture of both KCl (0.1 M) and boric acid (0.1 M) and 43.7 mL of a 0.1 M NaOH solution diluted to a total of 100 mL with water. Buffer at pH 13 was a 0.1 M NaOH solution.

Hydrolysis Rate Determination. The hydrolysis rates were determinated by monitoring the rate of disappearance of triflusulfuron-methyl (**1**) in the buffers. Buffers solutions were sterilized by filtration (Sartorius Minisart NML, 0.22 μm). Aseptic techniques were used during the study to maintain sterility.

A stock solution containing 2 g L^{-1} triflusulfuron-methyl in acetonitrile was prepared. Aliquots of 75 or 250 μL of this solution were added aseptically to 50 mL of sterilized buffers at pH 4 or pH 5 and to sterilized buffers at pH 6−13, respectively. All these solutions were maintained at 30 °C in the dark. At appropriate times, the aliquots were aseptically removed from each flask and analyzed by HPLC. Each experiment was duplicated.

Soil Properties. Soil samples were collected from a depth of 0−20 cm at Perpignan, Villeneuve, Bolquere, and Saint Jacques, four sites in south France. All samples were air-dried, sieved (2 mm), and stored in plastic bags at 5 °C. Water content was determined by drying soil aliquots for 24 h at 105 °C. Soils properties are listed in Table 1.

Triflusulfuron-methyl Degradation in Microbially Active and Sterile Soils. Soils were sterilized by autoclaving at 121 °C for 20 min three times at 24-h intervals. Flasks containing soil equivalent to 20 g of the oven-dried weight of soil were treated with a filtered (0.2 μm) aqueous buffer solution (pH 8) (Na_2HPO_4, KH_2PO_4 1/15 M) of triflusulfuron-methyl (214 mg L^{-1}) to obtain a final concentration of 1, 3.5, 4.4, 9.6, and 19.8 mg kg^{-1} dry soil. Water was added to give a moisture content of 25% (w/w of dry weight of soil). Flasks containing the soil−herbicide mixture were sealed with Parafilm and kept in an incubator at 30 ± 1 °C. Duplicate samples were periodically removed and frozen (−20 °C) until extraction and analysis as described below.

Triazine Degradation in Soils. An aqueous buffer solution (pH 8) (Na_2HPO_4, KH_2PO_4 1/15 M) of triazine (**2**) (130 mg L^{-1}) was added to samples of 20 g equivalent dry soil (Bolquere and Perpignan soils) in a 125-mL flask to obtain a final concentration of 5.2 mg kg^{-1} dry soil. Water was added to give a moisture content of 25% (w/w of dry weight of soil). The soil was thoroughly mixed, and the flasks were sealed with Parafilm and kept in an incubator at 30 ± 1 °C. Duplicate samples were periodically removed and frozen (−20 °C) until extraction and analysis as described below.

Soil Extraction. Soil samples (20 g) were extracted by shaking for 1 h with 25 mL of methanol/water/acetic acid (45:5:0.5, v/v/v). After decanting and centrifuging for 5 min, the supernatant was directly analyzed by HPLC.

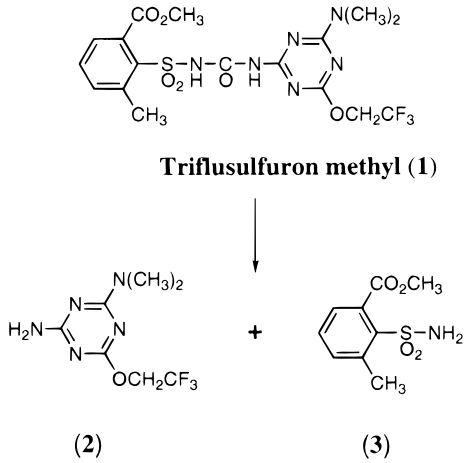

Figure 1. Pathway of triflusulfuron-methyl (**1**) transformation. Transformation products: 2-amino-4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine (**2**) and 6-methyl-2-methylcarboxylate benzene sulfonamide (**3**).

Table 2. Half-Lives (h) of Triflusulfuron-methyl at Differents pH Values at 30 °C

pH	$t_{1/2}$ (h)	pH	$t_{1/2}$ (h)	pH	$t_{1/2}$ (h)
4	21.5	6.5	470	9	835
5	65	7	614	10	848
6	332	8	717	13	18.5

Analytical Methods. Concentrations of triflusulfuron-methyl and its metabolite products were determined by HPLC. HPLC analysis were performed on a system with a Beckman pump and a Shimadzu SPD 2A UV detector (235 nm wavelength). The operating parameters were as follows: column, Kromasil C8 Hypersil KR 235−5 μm; mobile phase, acetonitrile/water/acetic acid (70:30:0.1)(v/v/v), delivered at a flow rate of 1 mL min^{-1}. All compounds studied were quantified using external standards.

RESULTS AND DISCUSSION

Hydrolysis Degradation Pathway. In aqueous buffer solutions, hydrolysis results in the cleavage of the sulfonylurea bridge to give the corresponding sulfonamide (**3**) and heterocyclic amine (**2**) identified by their chromatography properties (Figure 1). For example, in a buffer solution at pH 5, 20.2 μmol L^{-1} of triflusulfuron-methyl gave after 48 h incubation 12.2 μmol L^{-1} of remaining triflusulfuron-methyl, 8.3 μmol L^{-1} of **2**, and 6.4 μmol L^{-1} of **3**. The simultaneous determination of sulfonamide (**3**) and triazine (**2**) by HPLC was very difficult, such that in subsequent experiments, only the triazine concentration was evaluated.

Kinetics Experiments at Different pH Levels. Increased hydrolysis rate with decreasing pH values was observed with triflusulfuron-methyl. However, the rate of increase was low between pH 7 and pH 10 (Table 2). At all the studied pH values, the chemical hydrolysis of triflusulfuron-methyl quantitatively led to the triazine (**2**); as shown in Figure 2 for the experiment at pH 4. The determining process of chemical hydrolysis is the ionization of the sulfonylurea bridge (Brown, 1990), with the neutral form of the sulfonylurea bridge being more susceptible to hydrolysis than its anionic form. A factor of 250−1000 times has been reported (Brown, 1990); in the present study, a factor <50 was obtained between the hydrolysis rate of triflusulfuron-methyl at pH 4 and at pH 10.

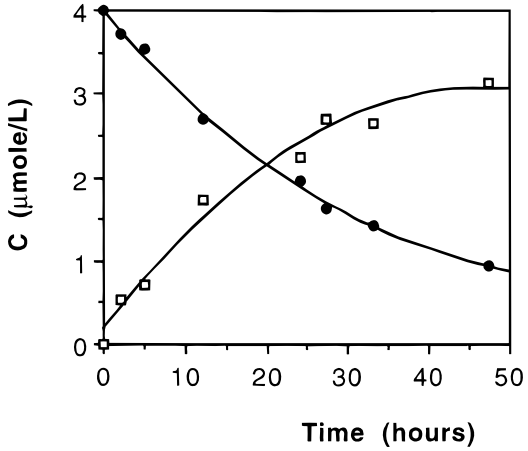

Figure 2. Hydrolysis of triflusulfuron-methyl (**1**) in aqueous buffer pH 4: (**1**) (●) and (**2**) (□).

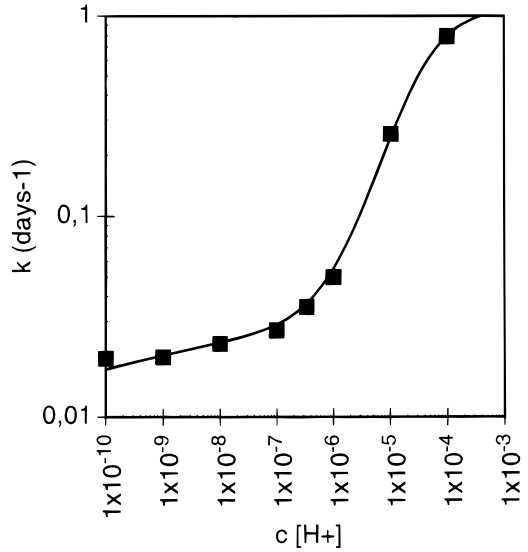

Figure 3. Triflusulfuron-methyl hydrolysis: half-life (days) as a function of pH.

The observed hydrolysis rate may be written as the sum of rates for the neutral form and the anionic form, i.e.:

$$k_{obs} = k_{neutral}C_{neutral} + k_{anionic}C_{anionic}$$

$$C_{neutral} = C[H^+]/(K_a + [H^+])$$

$$C_{anionic} = K_aC/(K_a + [H^+])$$

$$k_{obs} = k_{neutral}C[H^+]/(K_a + [H^+]) + k_{anionic}K_aC/(K_a + [H^+])$$

The hydrolysis can also be related to the pH of the solution when the relation between the rate constants and the pH of solution became

$$k_{obs} = k_{neutral}C[H^+]/(K_a + [H^+]) + k_{anionic}K_aC/(K_a + [H^+]) + b\cdot pH$$

Values obtained in this study of hydrolysis of triflusulfuron-methyl are in good agreement with this model (Figure 3) (correlation coefficient $r^2 = 0.9997$).

Table 3. Transformation Rates of Triflusulfuron-methyl in Soils[a]

soil		a	$k_1 \times 10^2$	$k_2 \times 10^2$	$t_{1/2}$ (h)
Perpignan	nonsterile	0.75	1.11	0.57	73
	sterile	0.55	0.908	0.091	172
Villeneuve	nonsterile	0.9	0.858	0.858	81
	sterile	0.85	0.311	0.311	222
Bolquere	nonsterile	0.85	1.93	0.787	40
	sterile	0.55	1.61	0.743	60
Saint Jacques	nonsterile	0.7	1.83	0.64	48
	sterile	0.75	1.33	0.086	77

[a] The values a, k_1, and k_2 were calculated by the biphasic model from the data of Figure 4. Biphasic model: $C/C_0 = a \times e^{-k_1xt} + (1 - a)e^{-k_2xt}$.

The calculated rate constants were $k_{neutral} = 1.107$ day^{-1} and $k_{anionic} = 0.041$ day^{-1}. The neutral form was hydrolyzed 27 times more quickly than the anionic form.

Different relationships between pH and log k for different sulfonylureas have been reported and represented by discontinuous linear relationships (Dinelli et al., 1997; Schneiders et al., 1993; Sabadie, 1995, 1996). However, these bilinear models give good experimental fit only over a limited pH range. At pH 13, another hydrolysis mechanism may probably occur.

Triflusulfuron-methyl Transformation in Soils. The dissipation of sulfonylurea herbicides may be represented by a first-order or a biphasic model (Li et al., 1999). The data for triflusulfuron-methyl dissipation in the four soils were fitted with a biphasic model (Table 3). The estimated DT 50 was in agreement with the measured data. The dissipation of triflusulfuron-methyl in soils involves both chemical and microbial processes. In the two acidic soils, the chemical process plays a major role, with $k_{chemical}/k_{microbial} = 1.6$ and 2 in Saint Jacques and Bolquere soils, respectively. In the two basic soils, the microbial process plays the major role, with $k_{chemical}/k_{microbial} = 0.73$ and 0.58 in Perpignan and Villeneuve soils, respectively. The dissipation was more rapid in acidic soils than in alkaline soils. However, this difference was only related to chemical processes; the microbial degradation having an equivalent rate in the four soils $k_{microbial}$ was in the range of 0.0054−0.0058 day^{-1}.

The major metabolite detected in sterile soil was 2-amino-4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine (**2**). This metabolite accumulates in sterile Perpignan, Villeneuve, and Bolquere soils and in the nonsterile Bolquere soil. In other nonsterile soils, the triazine concentration moves up a maximum, indicating a degradation of this compound (Figure 4).

Under nonsterile conditions, the rate of triflusulfuron-methyl degradation in Bolquere soil was independent of the initial concentration. For the Perpignan soil, a slight decrease in half-life was observed when a 10-fold higher concentration was applied (Table 4). Generally, the half-lives for the degradation of the sulfonylureas are not concentration dependent. This has been reported in the cases of chlorsulfuron (Walker and Brown, 1983); sulfometuron-methyl (Anderson and Dulka, 1985); metsulfuron-methyl (Vega et al., 1992); and triasulfuron, primisulfuron-methyl, and rimsulfuron (Dinelli et al., 1998). However, in the case of thifensulfuron-methyl, a relationship between degradation rates and concentrations was reported based on an enzymatic degradation of this compound in soil (Cambon et al., 1998). The slight variation obtained with triflusulfuron-methyl in the present study was different because the transformation rate increased when the concentration increased.

Table 4. Half-Lives (h) of Triflusulfuron-methyl at Different Concentrations in Two Nonsterile Soils

concn (mg kg^{-1} dry soil)	$t_{1/2}$	
	Bolquere	Perpignan
1	45.5	85
3.5		73
4.4	40	
9.6		62
19.8	38.8	

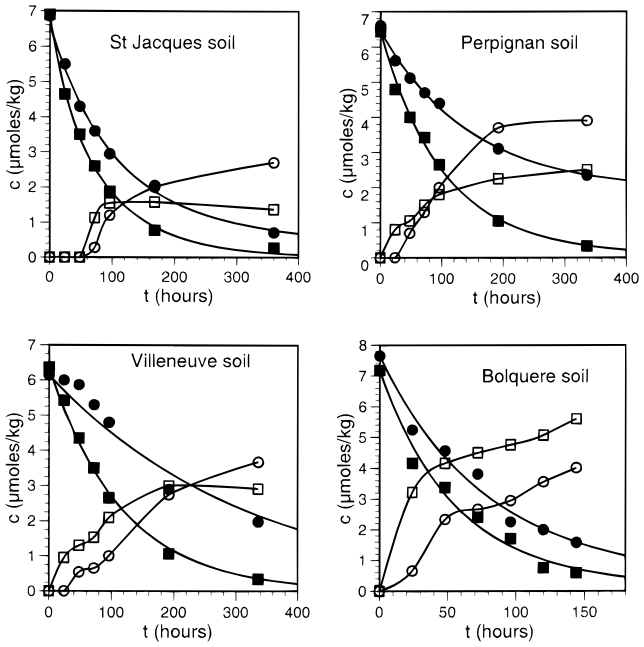

Figure 4. Triflusulfuron-methyl (**1**) transformation in soils. Products: (**1**) nonsterile soil (■), (**1**) sterile soil (●); (**2**) nonsterile soil (○), (**2**) sterile soil (□).

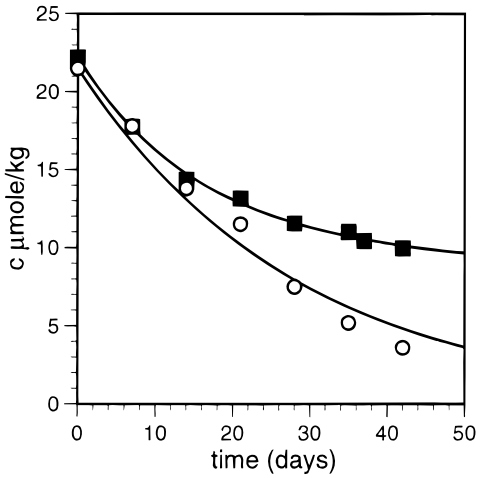

Figure 5. Triazine (**2**) degradation in soils. Bolquere (■) and Perpignan (○) soils.

Triazine Transformation in Soils. Experiments with adding triazine alone showed that the triazine degraded in the two soils with different pH values. However, the disappearance was more rapid in the basic soil than in the acidic soil, with half-lives respectively of 19.5 and 32.5 day (Figure 5). Few reports on the sulfonylurea−soil transformation have studied the dissipation of the triazine metabolite. The 2-methoxy-4-methyl-6-amino triazine resulting from chlorsulfuron transformation in soil dissipated slowly from an acidic soil with a half-life of 128 days (Strek, 1998). Li et al. (1999) obtained an accumulation of triazine in a soil (pH 5.2) after 25 days; the concentration did not change until 120 days and then decreased slowly. The triazine formed from triflusulfuron-methyl seems more easily degradable.

CONCLUSION

The rate of hydrolysis of triflusulfuron-methyl is pH-dependent, increasing with decreasing pH values. Under laboratory conditions, triflusulfuron-methyl degraded more rapidly in acidic soils than in basic soils due to the combined actions of chemical and microbial processes. The major degradation route was the cleavage of the sulfonylurea bridge and the formation of 2-amino-4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazine (**2**). This metabolite was transformed more rapidly in basic soils than in acidic soils. However, the triflusulfuron-methyl degradation rate was 4 times higher in sterilized soils than in corresponding buffer solutions at the same pH. The results indicate the importance of soil in the degradation process.

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