

## Soil Transformation of Prosulfuron

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The transformation of prosulfuron [1-(4-methoxy-6-methyltriazine-2-yl)-3-[2-(3,3,3-trifluoropropyl)phenylsulfonyl]urea] in three soils at different pH values (sterilized and unsterilized) was studied, and it was shown that the rate of transformation was high in acidic soil. From the results obtained in sterile soils, it is shown that the mechanism of dissipation was mainly chemical in acidic soils. A new metabolite, 2-(3,3,3-trifluoropropyl)phenylsulfonic acid, was identified.

**KEYWORDS:** Sulfonyleurea herbicide; soil transformation; metabolites; chemical hydrolysis

### INTRODUCTION

The sulfonyleurea herbicide prosulfuron [1-(4-methoxy-6-methyltriazine-2-yl)-3-[2-(3,3,3-trifluoropropyl)phenylsulfonyl]urea] (**Figure 1**) is used for weed control in corn, sorghum, and cereal crops. This compound has a  $pK_a$  of 3.8, a solubility in water of 4000 ppm at pH 7, and half-lives of 1 day at pH 2 and 225 days at pH 6.5 in aqueous solution (7). The major metabolite isolated from soil is trifluoropropyl phenylsulfonamide (1), but under the experimental conditions used by Hultgren et al. (1), a large amount of metabolites is unextractable after a short time of degradation. The degradation mechanism of prosulfuron (biological or chemical) in soil is not known. The only reported results concern the biotransformation of prosulfuron in a pure culture of microorganisms or in a soil suspension (2). The more commonly isolated metabolites are hydroxylated compounds that are different from the metabolites identified in soils (1).

The purpose of this work was to investigate the transformation mechanism of prosulfuron in three soils at different pH values.

### MATERIALS AND METHODS

Three soils were sampled from the top 15 cm of the profile in several locations in Pyrénées-Orientales (France). All soils were passed through a 2 mm diameter mesh sieve and stored in plastic bags at 5 °C until use. The physical characteristics of the soils are shown in **Table 1**.

**Chemicals.** Prosulfuron was obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany.

The following products were synthesized at our laboratory.

**2-(3,3,3-Trifluoropropyl)phenylsulfonamide (2).** Prosulfuron (0.2 g) was dissolved in 18 mL of a buffer solution (acetic acid/sodium acetate, pH 3.8), and the mixture was stirred for 27 h at 70 °C. After extraction and flash chromatography, 60 mg of compound **2** was isolated: <sup>1</sup>H NMR (MeOD)  $\delta$  2.57 (2H, m), 3.22 (2H, m), 4.90 (2H, s), 7.41 (1H, ddd,  $J = 7.7, 7.3,$  and 1.5 Hz), 7.45 (1H, dd,  $J = 7.7$  and 1.1 Hz), 7.5 (1H, ddd,  $J = 7.7, 7.3,$  and 1.5 Hz), 7.99 (1H, dd,  $J = 7.7$  and 1.5 Hz).

**2-(3,3,3-Trifluoropropyl)phenylsulfonic acid (3).** Prosulfuron (10 mg) was dissolved in a mixture (15 mL) of methanol/2.4 M HCl (66:34,

**Table 1.** Soil Characteristics

	soil texture	sand (%)	silt (%)	clay (%)	OC (%)	CEC (mequiv/kg)	water pH
Bolquere	silty clay sand	41.3	39.7	19	2.95	98	6.4 4.9 <sup>a</sup>
St. Jacques I	silty sand	56.7	38.5	4.8	0.9	95	7.9 7.2 <sup>a</sup>
St. Jacques II	silty sand	56.7	38.5	4.8	0.9	95	6.1 5.9 <sup>a</sup>

<sup>a</sup> After sterilization.

v/v) and stirred at 25 °C for 1 h. After cooling, the pH of the solution was adjusted to 5.3 and the solution was purified by elution on a Sep-Pak C<sub>18</sub> cartridge. Subsequent elution with water (12 mL), chloroform (10 mL), ethyl acetate (9 mL), and methanol (3 mL) gave compound **3** (2 mg): <sup>1</sup>H NMR (MeOD)  $\delta$  2.56 (2H, m), 3.3 (2H, m), 7.27 (1H, ddd,  $J = 7.7, 7.3,$  and 1.1 Hz), 7.31 (1H, dd,  $J = 7.3$  and 1.1 Hz), 7.39 (1H, ddd,  $J = 7.7, 7.3,$  and 1.1 Hz), 7.94 (1H, dd,  $J = 7.7$  and 1.1 Hz).

**Methyl 2-(3,3,3-Trifluoropropyl)phenylsulfonate (4).** Compound **3** was dissolved in methanol (1 mL), and diazomethane was added at 0 °C until the solution was colored. Evaporation of the solvent gave compound **4**: <sup>1</sup>H NMR (MeOD)  $\delta$  2.54 (2H, m), 3.31 (2H, m), 7.29 (1H, dd,  $J = 7.7$  and 7.3 Hz), 7.3 (1H, d,  $J = 7.3$  Hz), 7.43 (1H, dd,  $J = 7.7$  and 7.3 Hz), 7.98 (1H, d,  $J = 7.7$  Hz); M ( $m/z$ ) 267 (21), 237 (2.3), 172 (34).

#### Prosulfuron Degradation in Microbially Active and Sterile Soils.

Soils were sterilized by autoclaving three times at 121 °C for 20 min, at 24 h intervals, in flasks containing soil samples (20 g dry wt basis). Flasks containing sterile or nonsterile soils were treated with a filtered (0.2  $\mu$ m) solution of prosulfuron in a pH 7 phosphate buffer to obtain a final concentration of 10 mg kg<sup>-1</sup> of dry soil. Sterile water was added to give a moisture content of 20% (w/v of dry weight of soil). The soil was mixed using a stainless steel spatula, and the flasks were sealed and kept in an incubator at 30 °C  $\pm$  1 °C. For sterile soils, the experiments were carried out under sterile conditions. A flask of soil was used to test soil pH. Two replicates were prepared for each experiment.

**Soil Extraction.** At predetermined times, two flasks of soil (20 g wt basis) were extracted by shaking for 1 h with a mixture of water/methanol/acetic acid (90:10:1, 25 mL). After centrifugation, the supernatant was analyzed directly by HPLC. The extraction efficiency was determined by spiking soils with compounds **1–3**, extraction after 2 h, and HPLC analysis under the reported conditions. In these conditions, the extraction ratio was >93% for prosulfuron **1**, >90%

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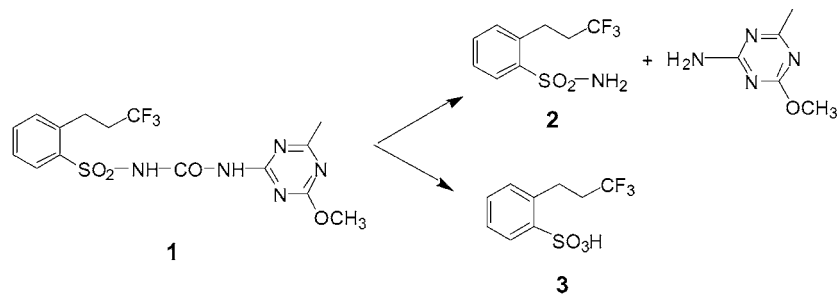


Figure 1. Pathway of prosulfuron transformation.

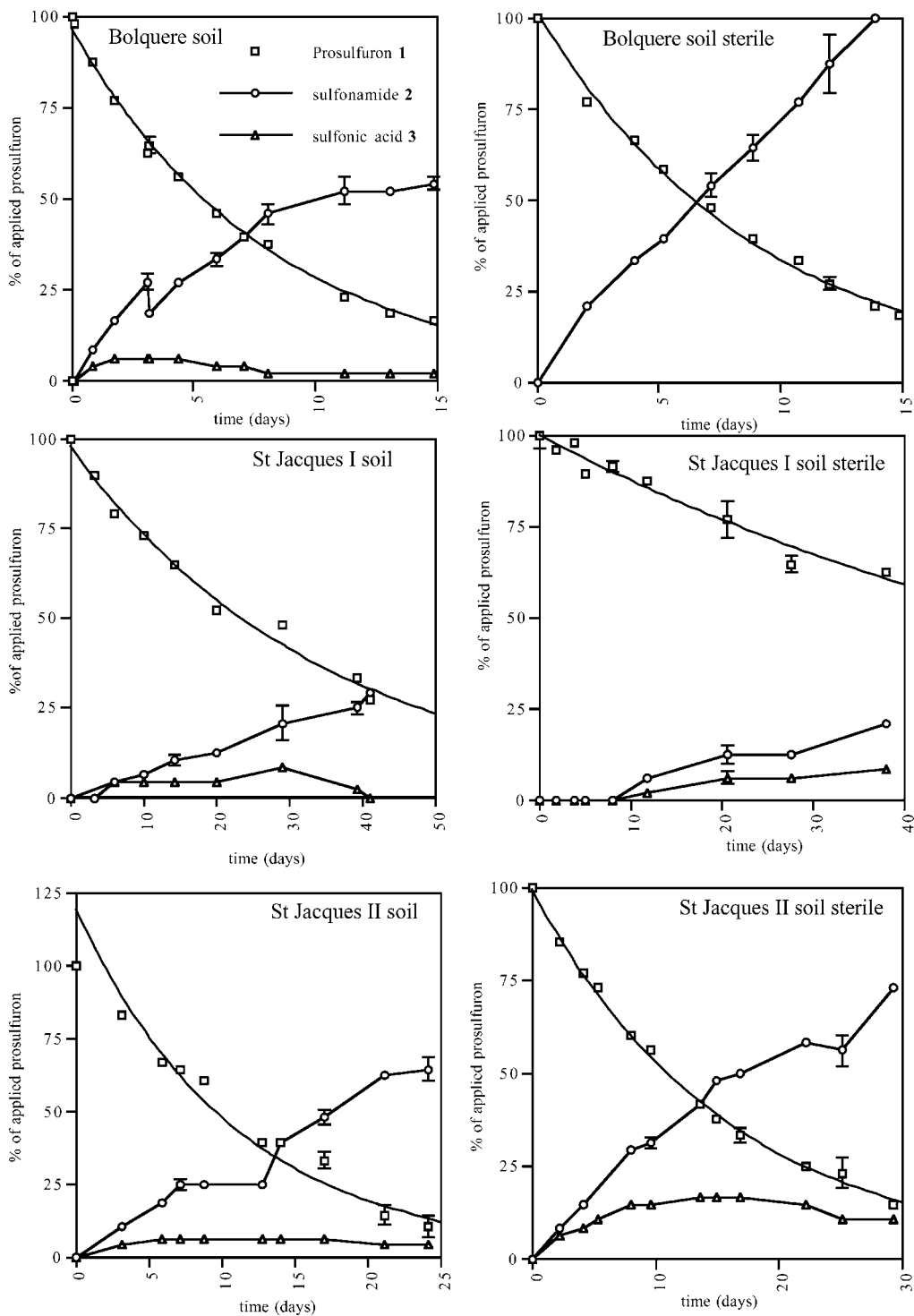


Figure 2. Concentration of prosulfuron and metabolites in soils. The prosulfuron degradation curve is represented by an exponential function. The error bars are represented for all points but in some cases are too low to appear on the graph.

**Table 2.** Half-Lives of Prosulfuron Transformation in Soils

soil		$k$ (days <sup>-1</sup> )	$R^2$	$t_{0.5}$ (days)	DT <sub>50</sub> <sup>a</sup> (days)
Bolquere	unsterilized	0.123	0.996	5.60	5.4
	sterilized	0.111	0.994	6.25	6.74
Saint Jacques I	unsterilized	0.029	0.978	24.05	24.5
	sterilized	0.013	0.959	52.50	ND
Saint Jacques II	unsterilized	0.059	0.948	11.67	10.81
	sterilized	0.059	0.994	11.67	11.29

<sup>a</sup> DT<sub>50</sub> values were estimated by interpolating the values between successive residue measurements (4).

for sulfonamide **2**, and between 50 and 75% for sulfonic acid **3**, depending on the soil.

**Chromatography.** HPLC conditions were as follows: 4.6 mm × 25 cm ODS 3 Inertsil column; mobile phase, water/acetonitrile/trifluoroacetic acid, 50:50:0.1, v/v/v; flow rate, 1 mL/min; UV detector, SpectroMonitor II LDC,  $\lambda = 220$  nm. The retention times of prosulfuron **1**, phenylsulfonamide **2**, and sulfonic acid **3** were 15.3, 8.4, and 5.6 min, respectively. The quantitation limits are 0.1, 0.1, and 0.05 mgL<sup>-1</sup> for **1**, **2** and **3**, respectively.

## RESULTS AND DISCUSSION

**Transformation Rates.** The rate of transformation of prosulfuron in the studied soils followed first-order kinetics, and a half-life ( $t_{0.5}$ ) was calculated (Table 2).

In contrast to the results of Hultgren et al. (1), the half-life ( $t_{0.5}$ ) calculated from first-order kinetics was very close to the DT<sub>50</sub> estimated graphically (Figure 2). The transformation was more rapid in acidic soils than in neutral soils. Numerous reports on the transformation of sulfonylurea herbicides agree with this result (3).

In Bolquere and Saint Jacques II soils, the degradation rates of prosulfuron in unsterilized and sterilized soil samples were similar. However, in Saint Jacques I, prosulfuron degraded 2 times more rapidly in unsterilized than in sterilized soil samples. This pH-related difference in the effect of sterilization on the transformation of sulfonylureas has already been observed for chlorsulfuron (4, 5). In Saint Jacques II soil, at pH 6.1 and 5.9, the major process of degradation may be chemical. On the other hand, in Saint Jacques I soil, at pH 7.9, microbial activity accounts for the greater degradation in nonsterile soil.

The soil pH was modified by sterilization, becoming 4.9, 5.9, and 7.2 for Bolquere, Saint Jacques II, and Saint Jacques I soils, respectively. The rate of hydrolysis of prosulfuron in sterile soils can be compared to the rate of hydrolysis in solution at the same pH. At pH 5, the reported hydrolysis rates were different: Bray et al. (6) reported a value of  $t_{0.5}$  of ~10 days; Dinelli et al. (7) reported a  $t_{0.5}$  of 19 days. The latter authors reported a relationship between hydrolysis rate, pH, and temperature:  $\log k = (-86080/R)(1/T - 1/298) + (-1.42\text{pH} + 4.01)$ . Using this relation, the calculated reaction rates at 30 °C and pH 4.9, 5.9, and 7.2 were 7.5, 31, and 195 days, respectively. At each pH value, the transformation rate was lower in solution than in soil, except for the most acidic pH value. The same comparison in the case of other sulfonylureas [chlorsulfuron (5, 8), metsulfuron-methyl (9, 10), chlorimuron-ethyl (11, 12), and triflusulfuron-methyl (13)] gave a similar result, with a higher rate of transformation in sterilized soils than in solution, under the same conditions. Hence, the solid soil constituents play a catalytic role in the degradation.

**Degradation Products and Pathway.** Two products of transformation were quantified in the soils by HPLC: sulfonamide **2** and sulfonic acid **3** (Figure 2). Sulfonic acid was

synthesized from prosulfuron and identified by NMR and by derivatization in its methyl ester. In sterile soils, prosulfuron was quantitatively transformed to two metabolites **2** and **3**. In nonsterile soils, when 50% of the prosulfuron had been transformed, 90% of the metabolites were recovered. This recovery ratio decreased to around 75% when 90% of the prosulfuron had been transformed. At that point, sulfonamide **2** and sulfonic acid **3** may have undergone subsequent transformation to unidentified metabolites. The difference between our results and those reported by Hultgren et al. (1) may be related to the extraction method; the "bound residue fraction" they reported may be polar metabolites that were not extracted by their solvent mixtures. Two different metabolites were observed by Hultgren et al. (1): desmethyl prosulfuron and an unidentified compound, "product C". The retention time of product C is compatible with the retention time of sulfonic acid identified in this work; product C and sulfonic acid may well be the same metabolite.

From the data reported we propose the pathway shown in Figure 1, including two parallel paths.

In conclusion, chemical hydrolysis of prosulfuron is the dominant degradation pathway in soil, corresponding to the breaking of the sulfonylurea bridge to produce the sulfonamide metabolite **2**. A minor, secondary pathway leads to sulfonic acid **3**.

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