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Sabino A. Bufo^a; Laura Scrano^a; Corinne Emmelin^b; Ahmed Bouhaouss^c

^a Dipartimento di Scienze dei Sistemi Colturali, Forestali e dell'Ambiente, Università di Basilicata, 85100 Potenza, Italy ^b Université Claude Bernard, 69622 Villeurbanne Cedex, France ^c Department of Chemistry, Université Mohammed V-Agdal, Morocco

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Effect of soil organic matter destruction on sorption and photolysis rate of rimsulphuron

SABINO A. BUFO*†, LAURA SCRANO†, CORINNE EMMELIN‡
and AHMED BOUHAOUSS§

†Dipartimento di Scienze dei Sistemi Colturali, Forestali e dell'Ambiente,
Università di Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

‡Lace, Université Claude Bernard, Boulevard du 11 novembre 1918,
69622 Villeurbanne Cedex, France

§Department of Chemistry, Université Mohammed V-Agdal,
52 Avn Ibn Batouta Rabat, Morocco

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In order to elucidate the behaviour of sulphonylurea herbicides in soil and the influence of soil organic matter (OM), the sorption and photolysis reactions of rimsulphuron have been studied in a soil suspension and on the sorbed phase. An Italian soil sampled from Sellata Mountain was utilized for sorption and light irradiation experiments. Natural soil samples and samples oxidized with H₂O₂ (to destroy OM) were treated with the herbicide and exposed to light irradiation or kept in the dark, as control sorption samples. The irradiation was carried out using a solar simulator (Suntest). Kinetic parameters of reactions were calculated. Herbicide sorption was ascertained to be the more important reaction in the soil, but the retention of rimsulphuron was significantly diminished after H₂O₂ treatment of soil and the consequent reduction of the natural organic matter content. Photoreaction kinetics of the herbicide were influenced by the sorbent capability of soil samples used in the experiments and the natural organic content.

Keywords: Soil; Organic matter; Sorption; Photolysis; Rimsulphuron; Kinetics

1. Introduction

Rimsulphuron is a selective sulphonylurea herbicide (figure 1) for the post-emergence control of many crops. The acceptance of this herbicide is mainly based on its low application rate (80–100 g ha⁻¹) and favourable environmental and toxicological properties. Commercialized in Europe in 1992 by Du Pont de Nemours & Co., this product shows few or no toxicological effects on mammals with oral LD₅₀ > 5000 mg kg⁻¹ in rats and with dermal LD₅₀ > 2000 mg kg⁻¹ in rabbits [1].

Using ¹⁴C-labelled rimsulphuron, Schneiders *et al.* [1] asserted that degradation in aqueous solutions and soil environment does not depend on irradiation under natural

*Corresponding author. Fax: +39–971–206226. Email: bufo@unibas.it

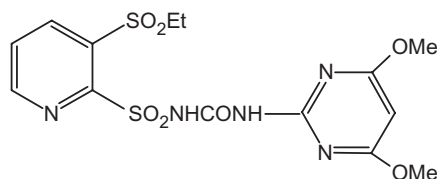


Figure 1. Chemical structure of rimsulphuron.

sunlight, though it undergoes hydrolysis reactions. Besides, the same authors observed several effects of natural light at pH 5. Neither rimsulphuron nor its metabolites were detected at soil depths lower than 8 cm in experimental fields under different crop management regimes, in which manure treatments prolonged the herbicide half-life in the 0–8 cm surface soil layer from a minimum of 14 days (control) to a maximum of 46 days [2]. Scrano *et al.* [3] showed that, under simulated sunlight in water, the half-life of photolysis reaction ranged from 1 to 9 days at pH 5 and 9, respectively. The hydrolysis rate was as high as the photolysis rate, and decreased on diminishing the pH values of the solution. Sorption and photolysis reactions of rimsulphuron on silica and clay minerals were also investigated and compared with a natural soil sample [4]. The photochemical degradation of the herbicide was strongly affected by retention phenomena, showing that silica and clay minerals can retain and protect rimsulphuron from photodegradation much more than soil.

The aim of this research was to study the reactivity of rimsulphuron retained on soil surface and investigate the influence of soil organic matter content on the sorption and photodegradation rate of this herbicide in two different experimental conditions: soil suspension and sorbed phase.

2. Experimental

2.1 Chemicals

Rimsulphuron (purity 97%; MW 431.45), *N*-[[4,6-dimethoxy-2-pyrimidinyl]amino]carbonyl]-3-(ethylsulphonyl)-2-pyridinesulphonamide (CAS RN 122931-48-0), was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The pure active ingredient (AI) is a white odourless solid; its solubility is $<10 \text{ mg L}^{-1}$ in distilled water and 7300 mg L^{-1} in buffer solution at pH 7 (25°C); $\text{p}K_{\text{a}}=4.1$; $K_{\text{ow}}=0.034$ at pH 7; vapour pressure = 1.1×10^{-8} Torr at 25°C [1].

Anhydrous acetonitrile (pesticide grade), H_2O_2 , and uranyl oxalate (analytical grade) were purchased from Sigma-Aldrich (St. Louis, MO); filters (disposable sterilized packet) were acquired from Fluka Chemie (Buchs, Switzerland). Ultrapure water was obtained by means of a Millipore (Billerica, MA) Milli-Q system.

2.2 Preparation of solutions and soil samples

All glass apparatus were heat-sterilized by autoclaving for 60 min at 121°C before use. Aseptic handling materials and laboratory facilities were used throughout the study to maintain sterility. A stock solution (100 mg L^{-1}) of the pure standard AI in anhydrous acetonitrile was prepared and kept in the dark at 4°C. Calibration and working

Table 1. Chemical composition (%) of the selected soil (Soil-S).

SiO ₂	45.82
TiO ₂	0.81
Al ₂ O ₃	19.69
Fe ₂ O ₃	8.29
CaO	1.37
MgO	1.95
P ₂ O ₅	0.08
K ₂ O	1.97
Na ₂ O	0.18
Humidity	19.44

Table 2. Characteristics and mechanical analysis of the selected soil (Soil-S).

CEC ^a (cmol ₊ kg ⁻¹)	12.4
Organic C (%)	4.78
Total N (%)	0.77
Sand (%)	19.6
Silt (%)	39.4
Clay (%)	41.0
pH (H ₂ O) ^b (1:10 (w:v))	7.45
pH (H ₂ O) ^b (1:20 (w:v))	7.52
pH (KCl 1 N) ^c (1:10 (w:v))	6.38
pH (KCl 1 N) ^c (1:20 (w:v))	6.49

^aCEC: cation exchange capacity. ^bpH of pure H₂O = 6.50.

^cpH of KCl 1 N = 5.63.

solutions of AI were prepared when used by dilution from stock solution. The choice of acetonitrile as a suitable solvent for our experiments follows the need for a better comprehension of the photochemical and spectroscopic behaviour of the organic compound [5], avoiding as much as possible the undesirable hydrolysis reaction [1, 3].

A soil sampled from Sellata Mountain in the south of Italy, and characterized by a high content of organic matter (OM), was selected as the sorption medium. Table 1 shows the chemical composition of sampled soil, and the characteristics and mechanical analysis are referred to in table 2. Soil was sieved (1 mm) and sterilized before use in order to avoid microbiological degradation: according to Cambon *et al.* [6], soil with the addition of sodium azide (0.05%) was incubated for 24 h (FTC 90E Refrigerated Incubator, Velp Scientifica, Milan). The investigation was carried out on the sterilized soil sample without further treatment (Soil-S) and a sample treated with a hot (60°C) solution (30%) of H₂O₂ (Soil-O) to destroy the soil organic fraction.

2.3 Preparation of sorbed phase and extraction

A working solution (10 mg L⁻¹, 0.0232 mM) of the AI was added drop by drop to soil samples (Soil-S or Soil-O) with gentle stirring up to a concentration of 0.2897 mmol kg⁻¹. The soil paste thus obtained was spread on two glass TLC plates (20 × 20 cm) in order to obtain a soil layer of 1 mm thickness. The plates were air-dried and equilibrated in the darkness at room temperature for one day. The first plate was used for the irradiation experiment, and the second was used as a control

sample in dark conditions. All samples were protected with quartz cover plates to prevent herbicide volatilization. Each experiment was performed in triplicate.

The reaction kinetics were followed by scraping off soil strips of about 18 cm² from the TLC plates (excluding border strips) at various experimental times, as described in Konstantinou *et al.* [7]. The collected material (ca 2 g of soil) was put into a test tube, weighed, and added with anhydrous acetonitrile. The mixture was stirred (Vortex) for 1 min and sonicated for 10 min. The solution was separated, and the procedure was repeated twice. The resulting solution was centrifuged (15 min; 3000 g) and concentrated by fluxing nitrogen; the final volume of the solution was adjusted to 5 mL. Samples were filtered over 0.2 µm cellulose acetate membranes and kept in the dark at 4°C. The disappearance of rimsulphuron was determined by liquid chromatography. Other plates were prepared and kept in the dark in order to perform recovery tests.

2.4 Preparation and sampling of soil suspension

To obtain a favourable sorption ratio, two different quantities of soil samples (Soil-S or Soil-O) were suspended in 50 mL of AI solution (10 mg L⁻¹, 0.0232 mM) acidified with H₃PO₄:

- (1) 1 g of soil [herbicide/soil = 1.16 mmol kg⁻¹, corresponding to about 1/100 CEC of Soil-S (124 mmol₊ kg⁻¹) and 1/60 CEC of Soil-O (71 mmol₊ kg⁻¹)];
- (2) 0.25 g of soil [herbicide/soil = 4.64 mmol kg⁻¹, corresponding to about 1/25 CEC of Soil-S and 1/15 CEC of Soil-O].

During the irradiation experiments (in triplicate), the solution was sampled at different times, filtered on cellulose acetate 0.2 µm filters (Millipore), and analysed by liquid chromatography.

2.5 Irradiation experiments

UV spectra of rimsulphuron AI in anhydrous acetonitrile were recorded on a Cary 2300 spectrophotometer (Varian, Harbor City, CA).

Photochemical reactions were performed by using a solar simulator (Suntest CPS+, Heraeus Industrietechnik GmbH, Hanau, Germany), equipped with a xenon arc lamp (1.1 kW) that was protected with a quartz plate (total passing wavelength: 280 nm < λ < 800 nm). During xenon irradiation, samples were maintained at 20°C using both circulating water from a thermostatic bath and a conditioned airflow. Before the beginning of the experimental work, the light emission effectiveness of the irradiation system was tested by using the uranyl oxalate method [5, 8]. The disappearance of oxalate was 7.2 × 10⁻⁴ mol s⁻¹. The mean integrated irradiance was 632 W m⁻² (280–800 nm), and the radiant exposure for the whole irradiation time of 60 h was 137 MJ m⁻² (280–800 nm).

2.6 Analytical procedure

Analyses were performed on a Hewlett Packard 1090 liquid chromatograph equipped with a diode array detector (fixed at 230 nm), and a C18-5 µm packed column (Dionex Omnipac), 25 cm long, 3.2 mm i.d., plus guard column. The mobile phase

used for all experiences was 50% acetonitrile and 50% water (acidified to pH 3 with H_3PO_4 ; flow rate 1 mL min^{-1}). The retention time of rimsulphuron AI was 8.4 min ($k' = 3.1$). The calibration plot was performed in the concentration range $0.015\text{--}30 \text{ mg L}^{-1}$ giving a linear correlation coefficient $r > 0.99968$. The detection limit of the analytical method for the determination of AI was 0.011 mg L^{-1} .

3. Results and discussion

3.1 Photochemical properties

The UV spectrum of rimsulphuron presented three absorption maxima at $\lambda_{\text{max}_1} = 216 \text{ nm}$ ($\epsilon_1 = 1.05 \times 10^4 \text{ mmol}^{-1} \text{ cm}^2$), $\lambda_{\text{max}_2} = 240 \text{ nm}$ ($\epsilon_2 = 0.87 \times 10^4 \text{ mmol}^{-1} \text{ cm}^2$), and $\lambda_{\text{max}_3} = 298 \text{ nm}$ ($\epsilon_3 = 0.79 \times 10^4 \text{ mmol}^{-1} \text{ cm}^2$). The values and intensities of absorption maxima exhibit an adequate interaction of light with the herbicide molecule and an acceptable reacting potential for the rimsulphuron photolysis. From the interaction of xenon arc emissions and the whole absorption of the herbicide in the ultraviolet range $280\text{--}360 \text{ nm}$ (not shown), one can calculate an effective irradiance of 24.8 W m^{-2} and an efficient light dose of 89.3 kJ m^{-2} per hour of irradiation.

3.2 Kinetics

For each experiment, kinetic parameters were calculated by means of integrated equations describing zero-, first-, and second-order reactions using mean values of triplicate data. According to Snedecor and Cochran [9], the best fit was checked by the least-squares method of estimation (data not shown). Apparently, all measured reaction rates of the retained herbicide in the soil suspension and on sorbed phase, either in the darkness or under irradiation conditions, were best fitted by a Langmuir–Hinshelwood type equation (table 3), which describes a second-order reaction [10–12] as:

$$D_t = \frac{D_{\text{max}}t}{t + t_{0.5}}, \quad (1)$$

where D_t = AI disappearing at time t per kilogram of soil; $D_t = C_0 - C_t$; C_0 = AI extracted at $t = 0$ per kilogram of soil; C_t = AI extracted at time ' t ' per kilogram of soil; D_{max} = maximum amount of AI that could disappear at the end of the process, i.e. if the reaction would be carried to completion (asymptote); $t_{0.5}$ = half-life; k = kinetic constant = $1/(D_{\text{max}}t_{0.5})$; ' D_{max} ' and ' $t_{0.5}$ ' can be calculated, developing the function obtained through the linearization of equation (1) as:

$$\frac{t}{D_t} = \frac{t}{D_{\text{max}}} + \frac{t_{0.5}}{D_{\text{max}}}. \quad (2)$$

Table 3. Kinetic parameters of rimsulphuron under irradiation, in the darkness, and estimated photodegradation in sorbed and suspension samples: determination coefficient (r^2), half-life ($t_{0.5}$), maximum disappearing quantity as percent of initial AI content ($D_{\max}\%$); kinetic constant (k).^a

		r^2	$D_{\max}\%$	$t_{0.5}$	k
Sorbed phase of Soil-S	Reaction under irradiation	0.999	78.6	0.29	0.0432
	Reaction in the dark	0.999	72.1	0.17	0.0819
	Photodegradation estimated	0.994	6.6	2.85	0.0528
Sorbed phase of Soil-O	Reaction under irradiation	0.997	86.1	2.90	0.0040
	Reaction in the dark	0.998	66.9	2.56	0.0058
	Photodegradation estimated	0.994	19.1	3.32	0.0157
Suspension 1 g of Soil-S	Reaction under irradiation	0.998	71.9	1.34	0.0104
	Reaction in the dark	0.999	60.9	1.15	0.0143
	Photodegradation estimated	0.996	11.1	2.92	0.0307
Suspension 1 g of Soil-O	Reaction under irradiation	0.999	48.3	12.76	0.0016
	Reaction in the dark	0.997	19.4	9.48	0.0054
	Photodegradation estimated	0.999	30.0	17.70	0.0019
Suspension 0.25 g of Soil-S	Reaction under irradiation	0.996	61.3	5.49	0.0030
	Reaction in the dark	0.996	27.4	12.29	0.0030
	Photodegradation estimated	0.994	36.5	4.70	0.0058
Suspension 0.25 g of Soil-O	Reaction under irradiation	0.997	93.1	4.95	0.0022
	Reaction in the dark	0.990	16.6	9.93	0.0061
	Photodegradation estimated	0.997	77.1	4.36	0.0030

^aValues were obtained on the basis of three replicate experiments.

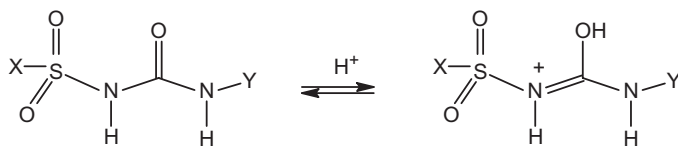


Figure 2. Ionization of ureic moiety in the sulphonylurea herbicides [13, 14].

3.3 Dark reaction on sorbed phase

All soil samples were treated with about 0.3 mmol kg^{-1} of rimsulphuron. From the first extraction at $t=0$ (24 h from the preparation of TLC plates), we ascertained that a significant quantity of the herbicide was not recovered. In the dark conditions, the retained fraction was more important in the natural soil than in the soil treated with H_2O_2 for the destruction of OM (recoveries were: 59.5% from Soil-S; 83.2% from Soil-O).

The evidenced low recovery rate of rimsulphuron can be due to the physico-chemical properties of both the soil and the AI. The formation of 'bond residues', and the ionization processes of the ureic moiety in the herbicide molecule [13, 14] (figure 2), favoured by a neutral or acidic environment, can be stressed as phenomena rising from ionic sorption on this soil, which is characterized by an elevated percentage of fine fractions (silt and clay), a high exchange capability, and an important OM content [15].

On the other hand, insignificant augments of the herbicide recoveries were obtained (data not shown) using stronger extractants and solvent mixtures as ethyl acetate, acetone, acetone/water (1:1 v:v), and acetonitrile/water (1:1 v:v); meanwhile,

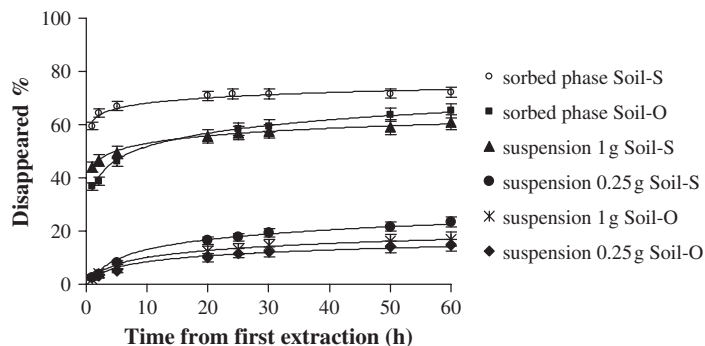


Figure 3. Disappearance rate of rimsulphuron in the dark due to sorption reaction (percentage of added herbicide).

the use of an aqueous solution at pH 9 helped to improve the extraction efficiency but led to a hydrolysed product.

Figure 3 shows the disappearance rate of rimsulphuron measured in the dark, which can be attributed to the sorption process onto soil particles and components [10, 12]. We note that all represented samples are characterized by a continuous reactivity during the experimental time, from the first extraction ($t=0$) up to 60 h, giving depletion curves which can all be described by second-order kinetics (table 3). The rationale behind such a finding may be found considering that the number of herbicide molecules reaching an effective steric arrangement into the sorption sites of soil was continuously increasing, and consequently, the AI retention was going reinforcing in the time.

Table 3 lists the kinetic parameters calculated for the retention process in the dark. The ' D_{\max} ' values in equation (1), expressed as a percentage of the added rimsulphuron, indicate a maximum herbicide disappearance of 72.1% from Soil-S, and 66.9% from Soil-O. This finding demonstrates that the AI is sorbed more into the natural soil than into the soil deprived of OM. The half-lives ($t_{0.5}$) of 0.17 and 2.56 h, for Soil-S and Soil-O respectively, confirm the rule played by the soil OM in the retention phenomenon of rimsulphuron into the soil: the destruction of OM seems to bring about a reduction in the number of sorption sites in the soil.

3.4 Dark reaction in the soil suspension

In the suspensions kept in the dark, the same retention behaviour as for the sorbed phase (on TLC plates) was observed. In particular, in the suspensions containing 1 g of soil, the differences between the half-lives of Soil-S and Soil-O are more evident than in the sorbed TLC samples. In contrast, in the suspensions containing 0.25 g of soil, these differences are not marked, due to an excess of herbicide in the solution with respect to the amount of suspended soil and, consequently, of sorption sites.

3.5 Photochemical degradation

During the xenon-Suntest irradiation, the sorption and photodegradation reactions coexist. Therefore, the disappearance rate measured in the lighting conditions (not shown) is due to the sum of sorption and photodegradation phenomena. For estimating the exclusive contribution of the light on the herbicide disappearance, the quantity C_t

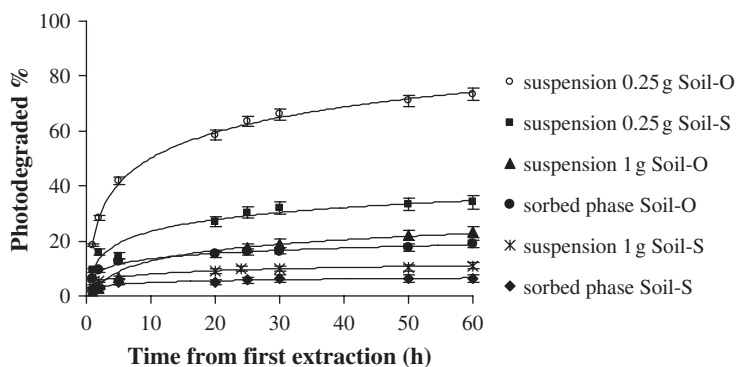


Figure 4. Disappearance rate of rimsulphuron due to the exclusive contribution of photodegradation (percentage of added herbicide).

extracted during the irradiation time of the herbicide was added to the quantity ($C_0 - C_t$) disappeared during the reaction in the dark [4, 10, 12]. Table 3 lists the kinetic parameters of the second-order photodegradation reactions. Figure 4 illustrates the curves relative to the exclusive contribution of the light on herbicide disappearance. The maximum amount of rimsulphuron that can be photodegraded (D_{\max}) depends on the experimental method and the soil sample used in the tests. This quantity ranged from 6.6% for the herbicide sorbed on Soil-S to 77.1% for the AI in the suspension of 0.25 g of Soil-O.

The results obtained show that the photodegradation is strongly influenced by the sorption phenomena linked to the OM content of the soil. The maximum photodegradation rate that could be reached at the end of the reaction was higher in the soil where the OM was destroyed than in the natural soil. In contrast, the kinetic constant was higher in the presence of OM, thus signifying that the natural organic fraction of the soil can catalyse the reaction, perhaps through a mechanism of photo-sensitization [7].

4. Conclusion

The experimental data confirm that sorption is a very important reaction for rimsulphuron in the soil. The retention is greatly favoured by the presence of natural organic matter and the chemical characteristic of the xenobiotic molecule. The photodegradation is also an important reaction on the soil surface but is strongly influenced by the retention phenomena and, in particular, by the natural organic content of soil. The natural OM not only contributes to the herbicide retention in soil but also can have a catalytic effect on the photolysis reaction of rimsulphuron.

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