Abiotic Degradation of the Herbicide Rimsulfuron on Minerals and Soil

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Abstract

The photochemical behaviour of the sulfonylurea herbicide rimsulfuron, *N*-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfon amide, on silica and clay minerals, used as soil surrogates, was investigated and compared to a natural soil sample. The antagonistic behaviour of adsorption process and chemical degradation with respect to photodegradation was assessed and the formation of photoproducts was also determined. Results showed that all chemical and photochemical processes responsible for the disappearance of the herbicide follow a second order kinetic. The photochemical degradation of rimsulfuron was strongly affected by retention phenomena: with increasing of the adsorption capability of supports the photoreactivity of the herbicide decreased. The extraction rate of the herbicide covered the following values: soil 59.5%, illite 48.5%, aerosil 22.2%, montmorillonite 21.0%, showing that silica and clay minerals can retain and protect rimsulfuron from photodegradation much more than soil. Though, adsorption of the herbicide was always accomplished to a chemical reactivity of solid substrates. *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyridineamine and *N*-(4,6-dimethoxy-2-pyrimidinyl)-*N*-[(3-(ethylsulfonyl)-2-pyridinyl)]urea were found both as photochemical and chemical metabolites.

Key words: rimsulfuron, soil adsorption, silica, clay minerals, chemical degradation, photodegradation

46.1
Introduction

Photochemical reactions contribute to abiotic degradation of pesticides in the environment (Scheunert 1992). The study of photodegradation processes is on different levels of development. The progress is highest for studies in the atmosphere, lower for surface water studies and lowest for investigations on soil compartment (Scheunert 1993). The main reason for the unsatisfactory status of development in the soil compartment is the inherent difficulty involved in working on non-homogeneous surfaces (Mingelgrin and Prost 1989). Therefore, it is recommended to simplify the investigation by using models which behaviour can be transferred to the natural environment (Klöpffer 1992). In the soil and colloidal fractions of soil, only surfaces exposed to solar irradiation can contribute to photodegradation (Albanis et al. 2002; Klöpffer 1992; Konstantinou et al. 2000). Considering the limitations and having in mind that adsorption is the most important reaction in soil, different surrogates can be used to simulate soil and soil component influences on pesticide fate (Jones 1991).

Generally, photolysis in soil will occur within a shallow surface zone, the depth of which depends on soil characteristics and photochemical properties of the target reactant. Direct absorption of light and photolysis of organic contaminants may be

influenced by soil surface adsorption that is related to the content of colloidal materials. Indirect process could also be occurring depending on the presence of sensitising substances and singlet oxygen formation. Vertical depth for direct photolysis is generally restricted to 0.2–0.3 mm, indirect photolysis also below a layer of 0.7 mm (Herbert and Miller 1990). Humic substances in soil often act as sensitizers producing reactive intermediates such as singlet oxygen, hydroxyl radicals, superoxide anions, hydrogen peroxides and peroxy radicals. Such reactive species can potentially diffuse to a depth of 1 mm depending on soil moisture, porosity, and thermal gradient in sunlight exposed soil surface. Moreover, electronic structures, absorption spectra, and excited state lifetimes of soil adsorbed compounds are generally different from their solution properties, making it very difficult to predict what effects may result from soil-contaminant interactions (Albanis et al. 2002).

With respect to pesticide application on soil, a new class of agrochemicals named sulfonylureas has been developed in the last decade and offered on the market. The acceptance of sulfonylureas is mainly based on their low application rate (10–80 g ha^{-1}) and favourable environmental and toxicological properties (Beyer et al. 1988). Rimsulfuron is a selective sulfonylurea herbicide (compound 1 in Fig. 46.1) for the post-emergence control of many crops. It was commercialised in Europe in 1992 by Du Pont de Nemours & Co. The pure active ingredient (a.i.) is a white odourless solid; its solubility is <10 mg l^{-1} in distilled water and 7 300 mg l^{-1} in buffer solution at pH 7 (25 °C); pK_a = 4.1; K_{OW} = 0.034 at pH 7; vapour pressure = 1.1 × 10^{-8} Torr at 25 °C. This product has little or no toxicological effects on mammals with oral LD$_{50}$ > 5 000 mg kg^{-1} in rats and with dermal LD$_{50}$ > 2 000 mg kg^{-1} in rabbits (Schneider et al. 1993). Using ^{14}C-labelled rimsulfuron Schneider et al. (1993) showed that degradation in aqueous solutions and soil environment does not depend on irradiation under natural sunlight, though it undergoes hydrolysis reactions. Besides, the same authors observed some effects of the natural light at pH 5. Neither rimsulfuron nor its metabolites were detected at soil depths lower than 8 cm in experimental fields under different crop management, in which manure treatments prolonged the herbicide half-life in the 0–8 cm surface soil
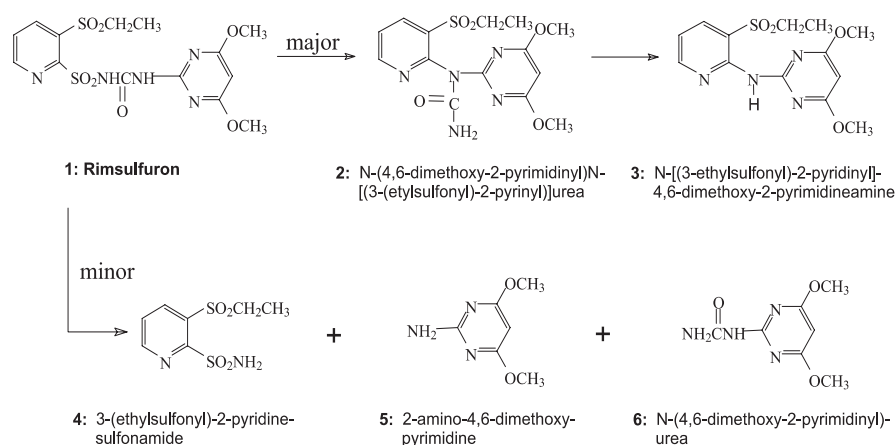

1: Rimsulfuron

2: N-(4,6-dimethoxy-2-pyrimidinyl)N-[(3-(etylsulfonyl)-2-pyrinyl)]urea

3: N-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine

4: 3-(ethylsulfonyl)-2-pyridine-sulfonamide

5: 2-amino-4,6-dimethoxy-pyrimidine

6: N-(4,6-dimethoxy-2-pyrimidinyl)-urea

Fig. 46.1. Chemical structure and degradation pathways of rimsulfuron

layer from a minimum of 14 d (control) to a maximum of 46 d (Rouchaud et al. 1997). Scrano et al. (1999) showed that, under simulated sunlight in water, the half-life of photolysis reaction ranged from 1 to 9 d at pH 5 and 9, respectively. The hydrolysis rate was as high as the photolysis rate, and decreased on increasing pH values of the solution. The main metabolite identified in neutral and alkaline conditions as well as in acetonitrile was #3, *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyridine-amine, while #2, *N*-(4,6-dimethoxy-2-pyrimidinyl)-*N*-[(3-(ethylsulfonyl)-2-pyridi-nyl)]urea, and minor metabolites prevailed in acidic conditions (Fig. 46.1). Pantani et al. (1996) stated that rimsulfuron can be adsorbed on Al-hectorite (a smectite clay mineral), and decomposes on clay surfaces into two main metabolites.

The aim of the presented investigation was to study and compare the photochemi-cal degradation of rimsulfuron adsorbed on a siliceous material and two clay miner-als, used as soil surrogates, and a natural soil. The antagonistic behaviour of adsorp-tion and other chemical processes with respect to photodegradation and the forma-tion of photoproducts have been also considered.

46.2
Experimental

46.2.1
Materials

Solvent (pesticide grade), reagents (analytical grade) and filters (disposable sterilised packet) were purchased from Fluka and Sigma-Aldrich (Milan, Italy), aerosil 200 from Degussa (Dusseldorf, Germany), illite and montmorillonite from Ward's N.S.E. (Monterey, CA-USA). Ultrapure water was obtained with a Milli-Q system (Millipore, Bedford, MA-USA). Soil (Typic Rhodoxeralf) was sampled from *Sellata* area in Basilicata region, Southern Italy.

To avoid hydrolysis of rimsulfuron (Schneider et al. 1993), a stock solution (100 mg l^{-1}) of pure standard a.i. (98% – Dr. Ehrenstorfer GmbH, Augsburg, Germany) was prepared using anhydrous acetonitrile as solvent. This solution was maintained in the darkness at +4 °C and used to prepare working solutions (10 mg l^{-1}). Com-pounds #2 and #3 (Fig. 46.1) were prepared according to literature methods (Marucchini and Luigetti 1997; Rouchaud et al. 1997). All glass apparatus were heat sterilised by autoclaving for 60 min at 121 °C before use. Aseptic handling materials and laboratory facilities were used throughout the study to maintain sterility.

46.2.2
Adsorbed Phase Preparation

Physical and chemical properties of selected substrates are shown in Table 46.1. The soil was sieved (1 mm) and sterilised before use in order to avoid microbiological degradation (Cambon et al. 1998). Three replicates of each substrate were weighed and spiked drop by drop (with gentle stirring) with 0.2897 mmol kg^{-1} of rimsulfuron in acetonitrile (0.0232 mM). The paste thus prepared was spread on a glass plate in order to obtain 1 mm thick substrate layer. The plates were air dried in the darkness

Table 46.1. Composition of solid substrates. *SS* = specific surface; *CEC* = cationic exchange capacity; pH(H_2O) = 6.50; pH(KCl 1N) = 5.63

Adsorbent	Unit	Aerosil	Illite	Montmorillonite	Soil
SiO_2	%	99.55	54.71	54.30	45.82
TiO_2	%	0.00	0.91	0.71	0.81
Al_2O_3	%	0.36	18.90	18.66	19.69
Fe_2O_3	%	0.01	8.06	6.97	8.29
CaO	%	0.03	0.60	1.06	1.37
MgO	%	0.00	1.89	1.87	1.95
P_2O_5	%	0.00	0.21	0.02	0.08
K_2O	%	0.01	4.31	2.11	1.97
Na_2O	%	0.03	0.39	1.06	0.18
H_2O	%	0.45	10.01	13.22	19.44
SS	$m^2\,g^{-1}$	220	80	300	–
Size	μm	0.12	≤1	≤0.4	≤1 000
Org-C	%	–	–	–	4.78
Total-N	%	–	–	–	0.77
Sand	%	–	–	–	19.6
Silt	%	–	–	–	39.4
Clay	%	–	–	–	41.0
pH$_{(H_2O)}$	1:10	–	7.20	10.02	7.45
	1:20	5.07	7.32	10.14	7.52
pH$_{(KCl\,1N)}$	1:10	–	6.32	7.79	6.38
	1:20	4.45	6.40	8.01	6.49
ΔpH	1:20	+0.62	+0.92	+2.13	+1.03
CEC	$cmol_+\,kg^{-1}$	51.5	18.8	56.9	12.4

at room temperature for one day. Adsorption supports were divided into two sub-sample groups. One group of sub-samples was used for irradiation experiments, and the other (control sub-samples) was kept in the dark at the same temperature.

46.2.3
Irradiation Experiments

Photochemical reactions were performed using a solar simulator (Suntest CPS+, Heraeus Industrietechnik GmbH, Hanau, Germany) equipped with a xenon lamp (1.1 kW), protected with a quartz plate (total passing wavelength: 280 nm < λ < 800 nm). The irradiation chamber was maintained at 20 °C by both circulating water from a thermostatic bath and through 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 (Volman and Seed 1964; Murov et al. 1993). The disappearance of oxalate was 7.2×10^{-4} mol s^{-1}.

46.2.4
Extraction and Analysis

At the same prefixed times 1×1-cm width strips of the solid layers were scraped off from glass plates both irradiated and kept in the dark and rimsulfuron was extracted and detected. Extraction was carried out adding acetonitrile to solid materials at a ratio of 50/1 (v/w) and shaking for 30 min. After centrifugation at 5 000 rpm for 15 min the liquid phase was decanted. A second extraction was performed with another aliquot of acetonitrile (50/1, v/w), and the two liquid phases were combined and concentrated by fluxing nitrogen in a rotary evaporator; the final sample volume was adjusted to 5 ml with acetonitrile. The disappearance of rimsulfuron at various experimental times was determined by liquid chromatography after filtration over a 0.2 μm membrane. Analyses were performed on a HP 1090 (Hewlett Packard) liquid chromatograph equipped with a diode array detector (fixed at 230 nm), and a Dionex Omnipac PCX-500 5 μm packed column (18 cm long, 3.2 mm i.d.) + pre-column. The mobile phase used for all experiences was a acetonitrile-water mixture (1+1 by volume), containing a H_3PO_4 buffer (pH 3), at a flow rate of 1 ml min^{-1}. The retention time of rimsulfuron was 8.4 min. The calibration plot was performed in the concentration range 0.015–30 mg l^{-1} giving a linear correlation coefficient $r > 0.99$. At a signal-to-noise ratio of three, the limit of quantitation in the acetonitrile standard solutions was 0.011 mg l^{-1}. Metabolites #2 and #3 (Fig. 46.1) were also determined and confirmed by ion spray LC/MS/MS technique on a Perkin Elmer API 300 (coupled with a Waters 600 pump) using literature criteria (Li et al. 1996; Scrano et al. 1999).

46.3
Results and Discussion

46.3.1
Adsorption of Rimsulfuron on Soil and Soil Surrogates

To quantify and evaluate the influence of adsorption process, all supports were treated in triplicate with 0.2897 mmol kg^{-1} of rimsulfuron; but with the first extraction ($t = 0$) a large part of spiked herbicide was not recovered (C_0 values in Table 46.2). In order to improve the extraction efficiency, numerous solvents were furthermore applied: ethyl acetate; acetone; 1/1 (v/v) mixture of acetone/water; 2/1 (v/v) mixture of acetonitrile/water. But no significant increases of the herbicide recoveries were obtained. Such a disappearance of the herbicide can be slightly due to volatilisation and/or hydrolysis of rimsulfuron during the preparation of adsorption substrate layers on glass plates and 1-day air drying. In fact, vapour pressure of rimsulfuron is not very high (1.1 10^{-8} Torr at 25 °C), as compared to mostly used herbicides (Beyer et al. 1988), and hydrolysis is limited in our experimental conditions, being important in acidic aqueous solutions (Scrano et al. 1999). Though, the formation of bond residues reasonably plays a most important role in the limiting the extractability of rimsulfuron from our sorbent materials, as was previously ascertained for other sulfonylurea herbicides in soil (Albanis et al. 2002). The extraction rate covered the following values: soil 59.5%, illite 48.5%, aerosil 22.2%, montmorillonite 21.0%. The extraction efficiency for the herbicide was higher from soil sample as compared to the

clay minerals and the siliceous material. The adsorption behaviour, and consequently the amount of the non-extractable herbicide are influenced by chemical and physico-chemical properties of the solid. With respect to aerosil and montmorillonite, they can be correlated to the high values of cationic exchange capacity (CEC) and specific surfaces (SS) shown in Table 46.1. Illite and the soil sample also retained the herbicide but at minor level. Illite is a clay mineral of the "smectites" family; it is a swelling material and can adsorb interlayer inorganic and organic molecules by means of cation or H$^+$ bridges as well as montmorillonite. The selected soil is a forestry soil rich in organic matter, which capability to retain organic chemicals is well known. Aerosil is a synthetic amorphous flame silica material used for its high retention properties.

Observing the behaviour of the herbicide kept in the dark, we note that it is characterised by a lasting reactivity (Figs. 46.2–46.5), since its extractability was going diminishing in the time. The interaction between rimsulfuron and sorbing materials does not occur very immediately, but shows varying durations depending on the chemical properties of the adsorbents. Kinetic parameters of this time dependent process were calculated using zero, first and second (Langmuir-Hinshelwood) order equations. The best fit was checked by statistical analysis using the determination coefficient (r^2) values. Apparently, all measured depletion rates of the extracted herbicide in the darkness were better described by a second order equation (Table 46.2). The rationale behind such a finding may be found considering that the amount of the xenobiotic disappeared at each time "t" is affected by its concentration in soil and also by the number of molecules which have reached the most effective steric arrangement on sorption sites (Mingelgrin and Prost 1989; Jones 1991); in turn this number depends again by the herbicide concentration in soil.

Table 46.2. Kinetic parameters of time dependent rimsulfuron depletion on adsorbed phase: *n*: reaction order; r^2: determination coefficient; C_0: extractable quantity at initial time ($t = 0$); Q_{max}: maximum amount of the adsorbed herbicide; τ: half-life; *k*: kinetic constant. Reported values are the mean of three replicate experiments

Support	Reaction or environment	*n*	r^2	C_0 (mmol kg^{-1})	Q_{max} (mmol kg^{-1})	τ (h)	*k* (mmol^{-1} kg^{-1} h^{-1})
Aerosil	Light	2	0.9987	0.0642	0.0439	3.95	5.765
	Darkness	2	0.9995	0.0642	0.0225	1.55	28.75
	Photolysis	2	0.9981	0.0642	0.0239	12.0	3.496
Illite	Light	2	0.9952	0.1404	0.0543	1.87	9.850
	Darkness	2	0.9917	0.1404	0.0097	4.30	23.90
	Photolysis	2	0.9999	0.1404	0.0447	1.55	14.40
Montmorillonite	Light	2	0.9983	0.0607	0.0433	1.66	13.94
	Darkness	2	0.9968	0.0607	0.0342	2.66	10.99
	Photolysis	2	0.9999	0.0607	0.0091	0.94	116.3
Soil	Light	2	0.9938	0.1725	0.1067	2.94	3.182
	Darkness	2	0.9986	0.1725	0.0590	5.35	3.174
	Photolysis	2	0.9998	0.1725	0.0492	1.52	13.40

46.3.2
Photochemical Degradation versus Adsorption

Kinetic parameters (Table 46.2) of rimsulfuron disappearance under irradiation conditions (Figs. 46.2–46.5) were calculated as mentioned above for samples kept in the dark. From r^2 values we stated that all measured reaction rates of adsorbed herbicide can be better described also in this case by a second order degradation equation:

$$-\mathrm{d}C_t/\mathrm{d}t = kC_t^2 \qquad\qquad (46.1)$$

where C_t is the amount (mmol) of the herbicide extracted at time t per kilogram of adsorbing phase, and k is the rate (or kinetic) constant.

The extent of Eq. 46.1 can be written as:

$$\mathrm{d}Q_t/\mathrm{d}t = k(Q_{max} - Q_t)^2 \qquad\qquad (46.2)$$

were Q_t is the quantity of disappeared (retained and/or degraded) herbicide per kilogram of adsorbent substrate, and Q_{max} is the maximum amount of the herbicide that disappears at the end of the process, i.e. if the reaction would be carried to completion. Integrating Eq. 46.2 and solving for Q_t it yields:

$$Q_t = Q_{max}t/(t + \tau) \qquad\qquad (46.3)$$

where $\tau =$ half-life $= 1/Q_{max}k$.

Fig. 46.2.
Rimsulfuron extracted from aerosil: (■) in the dark; (●) under light irradiation; (△) contribution to herbicide disappearance due to photolysis
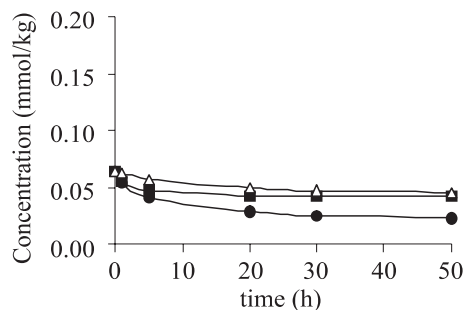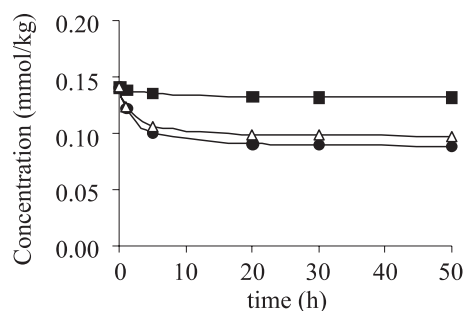

Fig. 46.3.
Rimsulfuron extracted from illite: (■) in the dark; (●) under light irradiation; (△) contribution to herbicide disappearance due to photolysis

Owing to the coexistence of adsorption (and other chemical reactions) and photolysis during the irradiation experiments, the contribution of the photolysis reaction to the disappearance of the herbicide was obtained adding the quantity $(C_0 - C_t)_{dark}$, which disappeared at each experimental time "t" in the darkness (adsorption), to the remaining $(C_t)_{light}$ concentration detected in the irradiated sub-sample at the same time (total reaction i.e. photolysis and adsorption); C_0 is the initial concentration (mmol kg^{-1}) of the herbicide extracted at beginning of the experiment ($t = 0$). This procedure is not fully rigorous since cannot take into account the synergistic effect between photolysis and adsorption during irradiation experiments. In fact, the herbicide adsorption continuously reduces the effective concentration of organic molecules, which can be photodegraded (see above); though, degraded rimsulfuron cannot be rapidly replaced by retained molecules. However, both processes occurring in the dark (adsorption) and under light irradiation (photolysis and adsorption) are of the same kinetic order and start from the same initial concentration (C_0). In these conditions calculations can meet theoretically a good approximation.

In all performed experiments the evolution of photodegradation processes, calculated as above, can be described by a second order kinetic. In this case the quantity Q_t in the Eq. 46.2 assumes the significance of "amount of photodegraded herbicide per kilogram of solid substrate at time t", and Q_{max} is the maximum degradable quantity. The photodegradation of rimsulfuron is strongly affected by retention phenomena. Generally, with increasing of the adsorption capability of supports the photo-

Fig. 46.4.
Rimsulfuron extracted from montmorillonite: (■) in the dark; (●) under light irradiation; (△) contribution to herbicide disappearance due to photolysis
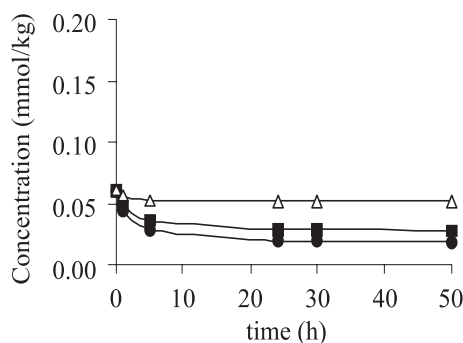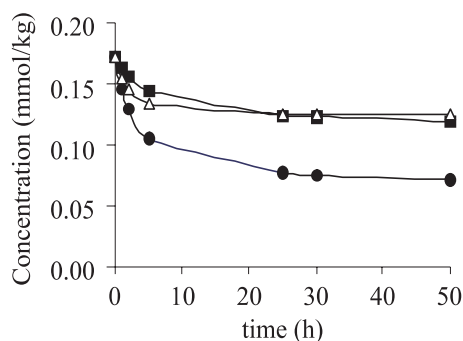

Fig. 46.5.
Rimsulfuron extracted from soil: (■) in the dark; (●) under light irradiation; (△) contribution to herbicide disappearance due to photolysis

reactivity of the herbicide decreases. Contribution of photodegradation to the disappearance of rimsulfuron adsorbed on aerosil seems to have the same importance as compared to the adsorption reaction (Fig. 46.2). The value of Q_{max}-*photolysis* is very close to Q_{max}-*adsorption* (darkness) in Table 46.2. But the photolytic reaction is slower than the adsorption ($\tau = 12.0$ and 1.55 h, respectively). The photoreaction is very evident in the case of illite (Fig. 46.3), on which rimsulfuron shows a value of Q_{max}-*photolysis* much more higher than Q_{max}-*adsorption*. Also the photolysis half-life is more important with respect to adsorption half-life ($\tau = 1.55$ and 4.30 h, respectively). The contribution of photolysis is almost negligible in the case of montmorillonite, on which adsorption is mostly responsible of the disappearance of rimsulfuron (Fig. 46.4). Soil shows a Q_{max}-*photolysis* value close to Q_{max}-*adsorption* as well as aerosil (Table 46.2). The contribution of photodegradation is almost equal to adsorption (Fig. 46.5), but the first reaction in soil is more important from a kinetic point of view ($\tau = 1.52$ and 5.35 h, respectively). Moreover, soil represents the unique case in which the sum of the maximum amount of rimsulfuron extracted, C_0-*light*, and the maximum amount of herbicide disappeared, Q_{max}-*light*, is very close to the value of spiked rimsulfuron (0.2792 and 0.2897 mmol kg^{-1}, respectively). For the other substrates this sum ranged from 0.1040 to 0.1501 mmol kg^{-1}.

The differences between the spiked quantity and the values of the sum C_0-*light* + Q_{max}-*light* are due to the fact that Eq. 46.2 cannot consider the fraction of herbicide disappeared by volatilisation, hydrolysis and adsorption occurring between the preparation of spiked samples and the first extraction. In the case of soil, Eq. 46.2 can work better than other supports because of the presence of organic colloids. In fact, soil organic matter can adsorb the herbicide with a mechanism of solubilization/repartition, after that it becomes a sort of reservoir that supplies herbicide reactions (desorption, hydrolysis, photolysis) with "served" molecules.

46.3.3
Degradation Products

Metabolites #2 and #3 (Fig. 46.1) were extracted from adsorbing substrates and subsequently identified. They were also found as main hydrolysis products in soil by Shalaby et al. (1992) and Schneiders et al. (1993), and on Al-hectorite by Pantani et al. (1998). Table 46.3 shows the metabolite concentrations obtained at half-life time by LC/MS/MS technique. Compound #2, previously identified in acidic conditions (Scrano et al. 1999), was extracted from treated aerosil. This compound can derive from hydrolysis as well as photolysis reaction of rimsulfuron because it was also found in the sub-sample kept in the dark. The presence of such a product on aerosil is justified with the acidic value of measured pH for this substrate (Table 46.1). Compound #3, previously identified in neutral and alkaline conditions (Scrano et al. 1999), was found on the other treated substrates, which measured pH were neutral or sub-alkaline (Table 46.1). Also compound #3 can derive from both hydrolytic and photolytic reactions. Finally, from calculated mass balance we ascertained that a large molar fraction of metabolites formed during experiment time was not extracted because adsorption affected also the retention of these substances.

Table 46.3. Concentrations of rimsulfuron metabolites extracted at time of half-life from adsorbing supports and identified by LC/MS/MS technique (*hy:* hydrolysis; *ph:* photolysis)

Support	Environment	Reaction	Concentration (mmol kg^{-1}) / metabolite	
			#2	#3
Aerosil	Light	hy + ph	0.0114	–
	Darkness	hy	0.0056	–
Illite	Light	hy + ph	–	0.0629
	Darkness	hy	–	0.0012
Montmorillonite	Light	hy + ph	–	0.0165
	Darkness	hy	–	0.0140
Soil	Light	hy + ph	–	0.0489
	Darkness	hy	–	0.0293

46.4
Conclusion

On the basis of our findings and literature data, we realised that photolysis can be a way of degradation of rimsulfuron and similar pesticides as important as hydrolysis. This result is more important in the case of post-emergence herbicides because they are usually sprayed on soil surfaces and plant leaves. A variable fraction of herbicide could be retained by adsorbing surfaces, which can protect chemicals with respect to further degradation reactions because of their steric rearrangement into the adsorption sites. This process does not occur very immediately, but can have varying durations depending on the chemical properties of the xenobiotic substances and adsorbents. Moreover, adsorption process can be accomplished by other chemical reactions, which contribute in different extent to the degradation of the pesticide on solid surfaces. The antagonistic behaviour of adsorption, photolysis and other chemical degradation pathways is proven by the presence of metabolites both in dark conditions and under light irradiation. Obviously, the amount of each metabolite and the quantity and rate of degraded herbicide depend by the chemical and physico-chemical properties of adsorbing materials. The soil experimented in this investigation shows the most equilibrate situation with respect to soil surrogates.

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