Hydrolytic Dissipation of Four Sulfonylurea Herbicides

Giovanni Dinelli,* Alberto Vicari, Alessandra Bonetti, and Pietro Catizone

Department of Agronomy, University of Bologna, Via Filippo Re 6/8, 40126 Bologna, Italy

The fate of prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl in aqueous solutions was investigated, using capillary electrophoresis (CE) for herbicide detection. The hydrolysis of the four sulfonylureas followed first-order kinetics and was pH dependent and accelerated at higher temperature. Rimsulfuron and thifensulfuron methyl showed fast degradation in water, with half-lives from 12 to 0.06 days in the pH range from 2 to 8.5 at 25 °C. The degradation rate of prosulfuron and primisulfuron methyl resulted relatively slow, with half-lives from 49 to 399 days in the pH range from 5 to 7.5, at 25 °C. The hydrolysis of the four sulfonylureas as a function of temperature and pH was mathematically combined. The resulting complex equations represent simple and useful models to predict the hydrolytic dissipation of these sulfonylureas. The complex equations of prosulfuron and primisulfuron methyl suggest that once these herbicides reach the groundwater, they would tend to persist, due to their slow degradation at neutral and subalkaline pHs and low temperatures. On the contrary, rimsulfuron and thifensulfuron methyl would not create problems of aquifer pollution, due to their fast hydrolysis in a wide range of pH and temperature combinations.

INTRODUCTION

Sulfonylurea herbicides are used for weed control in many crops, such as rice, wheat, soybean, sugarbeet, turnip, and corn. At present, twenty sulfonylureas are commercialized worldwide, and eight are being developed. The rapid increase of the market of this chemical class is due to their high activity at low application rates and to their low mammalian toxicity.

Chemical hydrolysis and microbial degradation represent the main degradation pathways of sulfonylureas (Fredrickson and Shea, 1986; Beyer et al., 1987). Many authors evidenced the role of hydrolysis in the environmental dissipation of these herbicides (Beyer et al., 1987; Blacklow and Pheloung, 1992). In particular, hydrolysis pathways of sulfonylureas were well characterized in literature (Schneiders et al., 1993; Dinelli et al., 1994; Sabadie, 1995; Cambon and Bastide, 1996; Berger and Wolfe, 1996). However, except for works of Sabadie (1990, 1991, 1992) and Vicari et al. (1996), few exhaustive papers about water dissipation of parent compounds in a wide range of temperatures and pHs exist in literature. It is important to note that a correct evaluation of the chemical hydrolysis not only contributes to better understanding of their environmental fate but also permits evaluation of their potential for ground and surface water contamination. The two main factors controlling sulfonylureas hydrolysis are temperature and pH (Beyer et al., 1987). In groundwater or in saturated soil (zone of capillary fringe), where in general microbial activity is strongly reduced (Bollag and Liu, 1990), the abiotic transformation processes, in particular hydrolysis, control herbicides degradation. Many laboratory and field studies showed a high leaching potential of some sulfonylureas (Rahman and James, 1989; Eklo et al., 1994; Vicari et al., 1994; Flury et al., 1995). For this reason, hydrolysis studies permit estimation of their dissipation rate in case of aquifer contamination.

The objectives of this study were (i) to evaluate the degradation kinetics in water as a function of pH and temperature of the parent compounds of four sulfonylureas, namely, prosulfuron, rimsulfuron, thifensulfuron methyl, and primisulfuron methyl, and (ii) to predict their half-lives in water using complex equations.

EXPERIMENTAL PROCEDURES

Chemicals. Prosulfuron [1-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-(2-(3,3,3-trifluoropropyl)phenylsulfonyl)urea], primisulfuron methyl [2-(4,6-bis(difluoromethoxy)pyrimidin-2-ylcarbamoylsulfamoyl)benzoic acid], rimsulfuron [1-(4,6-dimethoxypyrimidin-2-yl)-3-(3-ethylsulfonyl-2-pyridylsulfonyl)-urea], and thifensulfuron methyl [3-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)thiophen-2-carboxylic acid] were extracted from commercial formulations with freshly redistilled dichloromethane in a Soxhlet extractor for 4 h. For each active ingredient, extraction was performed by 8 g of commercial formulations, except for prosulfuron, for which 20 g was used. After dehydration with anhydrous sodium sulfate, dichloromethane was distilled off in a rotary vapor. The residual sulfonylureas were subjected to mass spectral analyses to confirm their identity and used for subsequent experiments without further purification, as reported by Galletti et al. (1995).

Reagents for capillary electrophoresis analyses were supplied by Sigma Chemical Co.

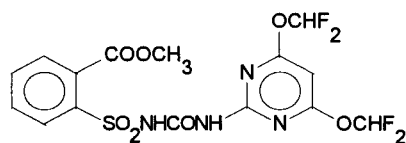All solvents, supplied by Bakerbond, were of pesticide grade.

Degradation in Aqueous Solutions. Triplicate 50 mL water samples, each containing 2 mg L^{-1} of prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl in 0.01 M acetate solution, were buffered to pH 4 with diluted hydrochloric acid. To avoid microbial degradation, buffer solutions and all glass apparatus were sterilized by autoclaving for 45 min at 105 °C and 1.5 atm before use. Samples were kept in the dark in screw-top bottles in a climatic chamber at 15, 20, 25, 30, 35, 45, and 55 °C. 2 mL aliquots from each bottle were sampled at eight appropriate time intervals, depending on herbicide and temperature, put in 2 mL vials, and stored at −20 °C until analysis.

Another set of triplicate 50 mL water samples, each containing 2 mg L^{-1} of prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl in sterile 0.01 M aqueous buffer solutions, were prepared. To test pH effects
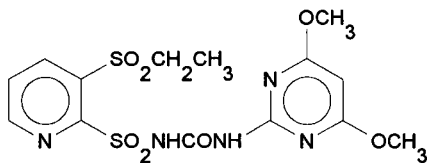
Hydrolytic Dissipation of Sulfonylureas

J. Agric. Food Chem., Vol. 45, No. 5, 1997 **1941**
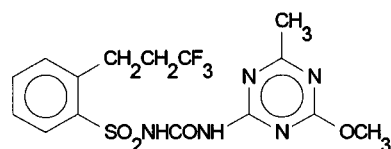
M W = 419.4
pKa = 3.80
log K_{ow} = 1.5 (25 °C, pH 5)
Solubility in water = 4000 ppm (pH 7)
Vapor pressure < 3.5 μPa
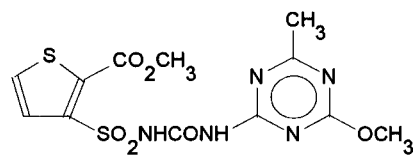
M W = 468.3
pKa = 3.3
log K_{ow} = 0.06 (25 °C, pH 5)
Solubility in water = 243 ppm (pH 7)
Vapor pressure < 5 μPa

M W = 431.4
pKa = 4.0
log K_{ow} = 0.28 (25 °C, pH 5)
Solubility in water = 7300 ppm (pH 7)
Vapor pressure = 1.5 μPa

M W = 373.4
pKa = 4.0
log K_{ow} = 0.20 (25 °C, pH 5)
Solubility in water = 6270 ppm (pH 7)
Vapor pressure = 0.017 μPa

Figure 1. Chemical structures and main physicochemical properties of the four sulfonylureas. Data from *Pesticide Manual* (Tomlin, 1994).

on hydrolysis, buffers used were sodium citrate (pH 2 and 3), acetate (pH 4 and 5), and sodium sulfate (pH 6.5, 7.5, and 8.5). Buffer solutions were brought to pH 2, 3, 4, and 5 with diluted hydrochloric acid, and to pH 6.5, 7.5, and 8.5 with diluted sodium hydroxide. Samples were kept in the dark in screw-top bottles in a 25 °C climatic chamber. 2 mL aliquots from each bottle were sampled at seven appropriate time intervals, depending on herbicide and pH of aqueous solutions, put in 2 mL vials, and stored at −20 °C until analysis.

In all trials, the pH of each sample was periodically measured and did not vary more than 0.1 pH unit for all active ingredients.

Analysis by Capillary Electrophoresis (CE). Sulfonylurea concentration in the 1715 water samples was determined by capillary electrophoresis. A complete capillary P/ACE 2000 Beckman system was employed. Separations were performed using a silica-fused capillary column 50 cm long (from injection point to detector) with an inner diameter of 75 μm, using micellar electrokinetic capillary chromatography technique as described by Dinelli et al. (1995). Aqueous samples were analyzed directly, without any preconcentration procedure and/or sample purification. The electrolyte buffer was 50 mM borate, 22.5 mM sodium dodecyl sulfate, 10% methanol (v/v), at pH 9. Separations were performed by applying a potential difference of 25 kV at 45 μA intensity and at a controlled capillary temperature of 25 ± 0.2 °C. Samples were injected under constant pressure of 3.44 mPa for 10 s at the capillary's anode end, corresponding approximately to an injection volume of 60 nL. Detection was performed at the capillary's cathode end by an UV detector set at 214 nm. Peak area was used for residue quantification (Dinelli et al., 1993a). The capability of CE for the detection and separation in water of sulfonylureas and their metabolites has been already reported (Dinelli et al., 1994, 1995). Therefore, the separations of prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl were free of any interference compounds as well as of their corresponding hydrolytic metabolites.

In all studies the dissipation of each herbicide was determined by linear regression of the natural logarithm of herbicide concentration against time.

RESULTS AND DISCUSSION

The physicochemical and structural characteristics of rimsulfuron, primisulfuron methyl, thifensulfuron methyl, and prosulfuron are reported in Figure 1. Concerning the chemical structure, primisulfuron methyl and rimsulfuron show a pyrimidinic heterocyclic group, while prosulfuron and thifensulfuron methyl show a triazinic heterocyclic group (Figure 1), primisulfuron methyl and rimsulfuron are *o*-benzene-substituted sulfonylureas, and thifensulfuron methyl and rimsulfuron are not *o*-benzene-substituted.

For each temperature and pH value hydrolysis of the four sulfonylureas followed first-order kinetics, with significant determination coefficients ($P < 0.05$) for all active ingredients (data not shown). Linear regressions were used to calculate degradation constants, k (expressed by the slope of the regression curve), and half-lives, $t_{1/2}$ (expressed by ln $0.5/k$).

As expected, sulfonylurea hydrolysis showed a marked effect of temperature on degradation rate and half-life (Table 1). The average decrease of half-life at each 5 °C increase of temperature was 1.3-, 1.6-, 2.1-, and 2.4-fold, respectively, for thifensulfuron methyl, primisulfuron methyl, prosulfuron, and rimsulfuron. Over the entire range of temperatures, prosulfuron showed higher half-lives than the other sulfonylureas. Half-lives of prosulfuron were similar to those reported by Dinelli et al. (1993b) and Sabadie (1990, 1991) with the more persistent sulfonylureas, such as triasulfuron, metsulfuron, and chlorsulfuron, in the same pH and temper-

1942 *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

Dinelli et al.

Table 1. Degradation Constants ($k \pm$ Standard Error) and Half-Lives ($t_{1/2}$) of the Four Sulfonylureas in Aqueous Solutions (pH 4) at Different Temperatures[a]

temperature (°C)	prosulfuron		primisulfuron		rimsulfuron		thifensulfuron	
	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$
15	0.08 ± 0.01	8.78	0.29 ± 0.05	2.34	0.33 ± 0.02	2.09	1.05 ± 0.12	0.66
20	0.14 ± 0.02	4.97	0.49 ± 0.01	1.41	0.62 ± 0.02	1.11	1.31 ± 0.11	0.53
25	0.26 ± 0.12	2.64	0.65 ± 0.02	1.06	2.48 ± 0.02	0.27	1.61 ± 0.14	0.43
30	0.46 ± 0.08	1.48	1.05 ± 0.01	0.65	3.29 ± 0.02	0.21	1.99 ± 0.13	0.35
35	0.88 ± 0.11	0.79	1.47 ± 0.02	0.47	6.25 ± 0.02	0.11	2.46 ± 0.28	0.28
45	2.52 ± 0.32	0.27	3.20 ± 0.21	0.22	21.81 ± 0.02	0.03	3.52 ± 0.61	0.19
55	5.85 ± 0.52	0.12	5.70 ± 1.10	0.12	31.22 ± 0.02	0.02	6.48 ± 0.21	0.11

[a] Each value is the average of three replicates. k values in days^{-1}; $t_{1/2}$ values in days.
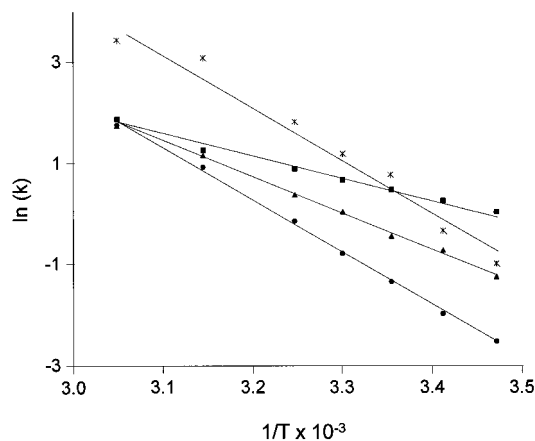

Figure 2. Arrhenius diagrams of the four sulfonylureas in aqueous solution at pH 4. The line slope indicates activation energy (see text); (●) prosulfuron; (▲) primisulfuron methyl; (∗) rimsulfuron; (■) thifensulfuron methyl.

ature range, while half-lives of primisulfuron methyl and rimsulfuron are in agreement with those determined with the same sulfonylureas by Schneiders et al. (1993) and by Vicari et al. (1996).

To better characterize temperature effect, the Arrhenius equation, expressed as natural logarithm, was employed:

$$\ln k = \ln A - E_a/RT \tag{1}$$

where k is the degradation constant, A is the preexponential factor, E_a is the activation energy expressed in J mol^{-1}, R is the universal gas constant equal to 8.31 (kJ^{-1} mol^{-1}), and T is the absolute temperature expressed in degrees Kelvin. When k, expressed as natural logarithm, is plotted against $1/T$, it is possible to obtain lines whose slopes, multiplied by R, give the relative value of the activation energy. The similar activation energies of rimsulfuron and prosulfuron (92.3 and 86.1 kJ^{-1} mol^{-1}, respectively) indicated a similar hydrolytic degradation pattern of these two sulfonylureas as a function of temperature, even if rimsulfuron presented a fastest dissipation (Figure 2; Table 2). Arrhenius diagrams of thifensulfuron methyl and primisulfuron methyl showed different patterns with respect to the other two sulfonylureas. The activation energies of primisulfuron methyl and thifensulfuron methyl, 58.0 and 34.4 kJ^{-1} mol^{-1}, respectively, were much more lower than those of the other two sulfonylureas, as showed by the lower slopes of their Arrhenius diagram (Figure 2), further supporting the different degradation patterns of these two active ingredients. At pH 4 and in a lower temperature range, from 5 to 35 °C, Vicari et al. (1996) also found an activation energy of primisulfuron methyl lower than that of rimsulfuron, respectively equal to 76.7 and 91.4 kJ mol^{-1}.

Table 2. Arrhenius Equations, Determination Coefficients (r^2), and Activation Energies ($\pm$ Standard Error) for the Four Sulfonylureas in Aqueous Solutions (pH 4)

sulfonylurea	Arrhenius equation[a]	$r^{2\ b}$	activation energy[c]
prosulfuron	$\ln k = -10.36(1/T) + 33.42$	0.988	86.08 ± 2.45
primisulfuron	$\ln k = -7.00(1/T) + 23.14$	0.998	58.02 ± 4.31
rimsulfuron	$\ln k = -11.10(1/T) + 37.72$	0.961	92.28 ± 0.14
thifensulfuron	$\ln k = -4.14(1/T) + 14.39$	0.988	34.44 ± 3.60

[a] k = degradation constant; T = absolute temperature (degrees Kelvin). [b] $P < 0.01$. [c] In kJ mol^{-1}.

Half-lives and degradation constants of the sulfonylureas as a function of water pH are reported in Table 3. Hydrolysis of prosulfuron and primisulfuron methyl in the studied pH range showed marked characteristics of acid hydrolysis. In fact, by increasing pH, degradation rate rapidly decreased with half-lives greater than 300 days at pH 7.5. In particular, in the 2−6.5 pH range, primisulfuron methyl showed half-lives slightly lower than those of prosulfuron. Half-lives of prosulfuron and primisulfuron methyl in the pH range 2−6.5 matches the half-lives of triasulfuron, chlorsulfuron, and metsulfuron observed by Dinelli et al. (1993b) and Sabadie (1990, 1991), while half-lives of primisulfuron methyl and rimsulfuron are in agreement with those determined with the same sulfonylureas by Schneiders et al. (1993) and by Vicari et al. (1996). Half-lives of thifensulfuron methyl are consistent with those reported by Cambon and Bastide (1996) at pH 4, 7, and 9, while a discrepancy was recorded in the half-life measured at pH 5.

Hydrolytic degradation rates of rimsulfuron and thifensulfuron methyl as a function of pH were between 4- and 40-fold higher than those of the other two sulfonylureas. The degradation in water of rimsulfuron and thifensulfuron methyl exhibited characteristics of acid and basic hydrolysis. In fact, at pH between 2 and 6.5 the degradation rate of both active ingredients decreased and then increased at pH values between 6.5 and 8.5.

To better characterize pH effects on hydrolysis of the four sulfonylureas, the natural logarithm of the degradation constant was plotted against the pH (Figure 3). All sulfonylureas showed a linear but discontinuous dependence at different pH levels. For primisulfuron methyl and prosulfuron, this discontinuity was near pH 4, where the slope changes. The variation occurred presumably as an effect of a different reactivity with respect to water molecules of dissociated and undissociated forms of these herbicides (Figure 1). Moreover, between pH 2 and 4 degradation rate was the highest, even if the lower slope of regression line indicates that

Hydrolytic Dissipation of Sulfonylureas

J. Agric. Food Chem., Vol. 45, No. 5, 1997 **1943**

Table 3. Degradation Constants ($k \pm$ Standard Error) and Half-Lives ($t_{1/2}$) of the Four Sulfonylureas in Aqueous Solutions (25 °C) at Different pH Values

	prosulfuron		primisulfuron		rimsulfuron		thifensulfuron	
pH	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$
2	0.71 ± 0.05	0.97	0.74 ± 0.05	0.90	8.33 ± 0.73	0.08	12.30 ± 0.09	0.06
3	0.40 ± 0.04	1.73	0.71 ± 0.05	0.97	4.04 ± 0.92	0.17	5.31 ± 0.04	0.13
4	0.26 ± 0.12	2.64	0.65 ± 0.05	1.06	2.48 ± 0.10	0.28	1.61 ± 0.14	0.42
5	$3.64 \times 10^{-2} \pm 5.45 \times 10^{-4}$	19.02	$5.61 \times 10^{-2} \pm 2.42 \times 10^{-3}$	12.34	0.29 ± 0.11	2.37	0.65 ± 0.58	1.05
6.5	$3.09 \times 10^{-3} \pm 7.58 \times 10^{-4}$	224.18*	$1.41 \times 10^{-2} \pm 9.75 \times 10^{-5}$	48.88*	$5.82 \times 10^{-2} \pm 7.93 \times 10^{-3}$	11.89	$9.81 \times 10^{-2} \pm 5.12 \times 10^{-2}$	7.07
7.5	$2.09 \times 10^{-3} \pm 1.45 \times 10^{-3}$	330.46*	$1.74 \times 10^{-3} \pm 1.15 \times 10^{-4}$	398.81*	1.13 ± 0.16	0.61	0.14 ± 0.06	4.90
8.5	nd[b]	nd	nd	nd	3.00 ± 0.41	0.23	0.21 ± 0.07	3.26

[a] Each value is the average of three replicates. Half-lives followed by an asterisk were extrapolated by the regression curve. k values in days^{-1}; $t_{1/2}$ in days. [b] Not determined.
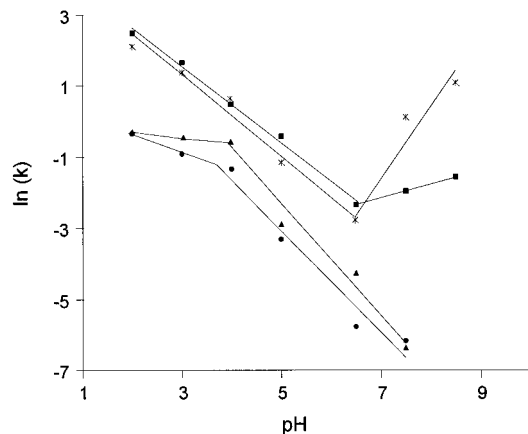

Figure 3. Relationship between natural logarithm of degradation constants of the four solfonylureas and pH of aqueous solution at 25 °C; (●) prosulfuron; (▲) primisulfuron methyl; (∗) rimsulfuron; (■) thifensulfuron methyl.

Table 4. Regression Equations and Determination Coefficients (r^2) of the Dependence of the Natural Logarithm of the Degradation Constant (k) of the Four Sulfonylureas as a Function of Water pH

sulfonylurea	pH range	regression equation	$r^{2\ a}$
prosulfuron	2–4	$\ln k = -0.49\ \text{pH} + 0.63$	0.993
	4–7.5	$\ln k = -1.42\ \text{pH} + 4.01$	0.955
primisulfuron	2–4	$\ln k = -0.06\ \text{pH} - 0.16$	0.961
	4–7.5	$\ln k = -1.57\ \text{pH} + 5.57$	0.967
rimsulfuron	2–6.5	$\ln k = -1.14\ \text{pH} + 4.78$	0.955
	6.5–8.5	$\ln k = 1.97\ \text{pH} - 15.32$	0.921
thifensulfuron	2–6.5	$\ln k = -1.07\ \text{pH} + 4.78$	0.995
	6.5–8.5	$\ln k = 0.38\ \text{pH} - 4.80$	0.999

[a] $P < 0.05$.

the increase in degradation rate was lower than that found when the pH was increased to between 4 and 7.5. For rimsulfuron and thifensulfuron methyl, the discontinuity was observed at pH 6.5. At higher pH values, as stated before, the degradation rate increased and was higher for rimsulfuron than for thifensulfuron methyl. These discontinuous linear relations were well characterized by linear regression equations of the natural logarithm of degradation rate of the four herbicides as a function of different pH intervals (Table 4). The pH dependent hydrolysis and discontinuous linear relations between pH and hydrolysis rates of primisulfuron methyl, rimsulfuron, and thifensulfuron methyl have been also reported by Schneiders et al. (1993), Vicari et al. (1996), and Cambon and Bastide (1996).

To predict the dissipation of sulfonylureas in water, Arrhenius equations were linearly combined with the regression equations of pH dependent hydrolysis. To obtain such combined equations, another form of the

Arrhenius equation was employed:

$$\ln k_2 = (-E_a/R)(1/T_2 - 1/T_1) + \ln k_1 \qquad (2)$$

where k_1 and k_2 are degradation constants at T_2 and T_1, while the other parameters were previously defined. For each active ingredient, k_1 was substituted by the equation related to the degradation rate as a function of pH, while for T_1 was set the value 298, corresponding to the temperature (25 °C) at which hydrolysis tests were performed. E_a was substituted by activation energy values reported in Table 2, but expressed in J mol^{-1}. Combined equations obtained with this procedure are reported in Table 5.

For each sulfonylurea, obtained equations by means of linear combination are two, as each active ingredient is characterized by two regression equations related to hydrolysis as a function of water pH. In order to statistically verify these equations, regression analysis yielded coefficients of correlation (R) between observed (Tables 1 and 3) and estimated half-lives determined by combined equations (Table 5) of 0.928, 0.995, 0.981, and 0.996 for prosulfuron, primisulfuron methyl, rimsulfuron and thifensulfuron methyl, respectively. These coefficients of correlation were highly significant at $P < 0.001$ for primisulfuron methyl, rimsulfuron, and thifensulfuron methyl and at $P < 0.01$ for prosulfuron, confirming the predictive reliability of the obtained equations. Therefore, even if the complex equation worked by the activation energy measured only at pH 4, they permitted an accurate evaluation of the half-lives of the four sulfonylureas over the entire range of pH studied. This suggests that the fitting procedure employed to obtain the complex equations took into account the possible change of the activation energy as a function of the pH. It is important to note that these equations intended to be open models for the prediction of sulfonylurea persistence in water. The environmental and chemical significance of the presented complex equations could be improved adding new activation energy values (e.g., activation energies calculated at different pHs) or extending the hydrolysis range of temperature and pH.

Equations shown in Table 5 are simple predictive models to give informations about hydrolytic dissipation of the studied sulfonylureas in water. In fact, given water pH and temperature values, it is possible to estimate half-lives of each sulfonylurea. Complex equations in Table 5 can be represented as tridimensional graphs. For each herbicide, such representations were realized by calculating half-life as a function of pH and temperature (Figures 4 and 5). For high pHs and low temperatures, half-lives of prosulfuron were very high (dark area, Figure 4a), up to a few thousand days. For

1944 *J. Agric. Food Chem.,* Vol. 45, No. 5, 1997

Dinelli et al.

Table 5. Combined Equations To Predict the Degradation Rate of the Four Sulfonylureas in Water as a Function of Temperature and pH

sulfonylurea	pH range	combined equation[a]
prosulfuron	2–4	$\ln k = (-86080/R)(1/T - 1/298) + (-0.49\ \text{pH} + 0.63)$
	4–7.5	$\ln k = (-86080/R)(1/T - 1/298) + (-1.42\ \text{pH} + 4.01)$
primisulfuron	2–4	$\ln k = (-58016/R)(1/T - 1/298) + (-0.06\ \text{pH} - 0.16)$
	4–7.5	$\ln k = (-58016/R)(1/T - 1/298) + (-1.57\ \text{pH} + 5.57)$
rimsulfuron	2–6.5	$\ln k = (-92285/R)(1/T - 1/298) + (-1.14\ \text{pH} + 4.77)$
	6.5–8.5	$\ln k = (-92285/R)(1/T - 1/298) + (1.97\ \text{pH} - 15.32)$
thifensulfuron	2–6.5	$\ln k = (-34442/R)(1/T - 1/298) + (-1.07\ \text{pH} + 4.77)$
	6.5–8.5	$\ln k = (-34442/R)(1/T - 1/298) + (0.38\ \text{pH} - 4.80)$

[a] k = degradation constant; R = 8.31 (kJ^{-1} mol^{-1}); T = absolute temperature (degrees Kelvin).
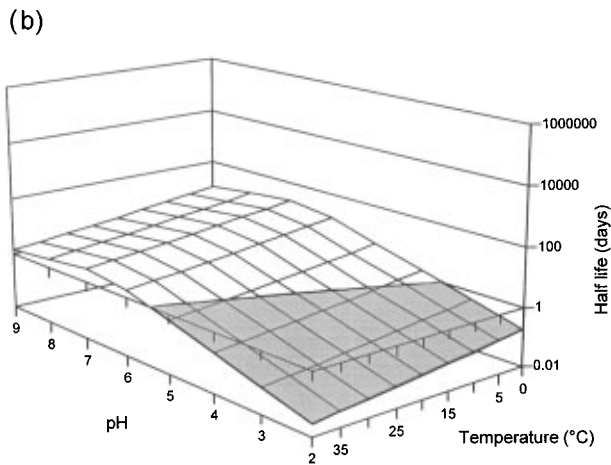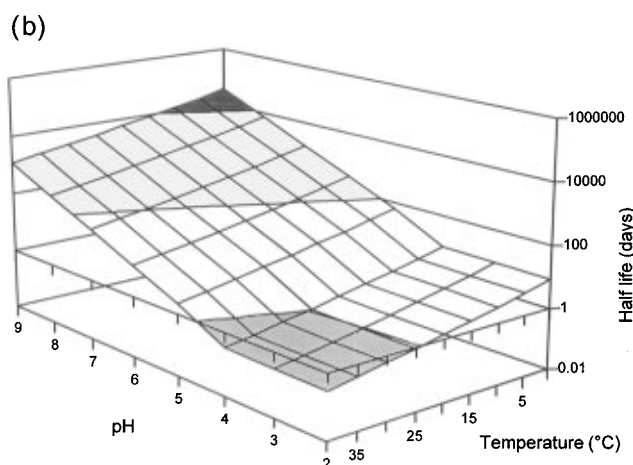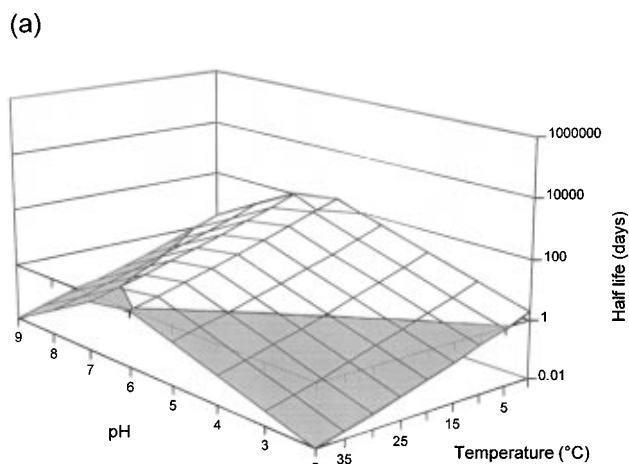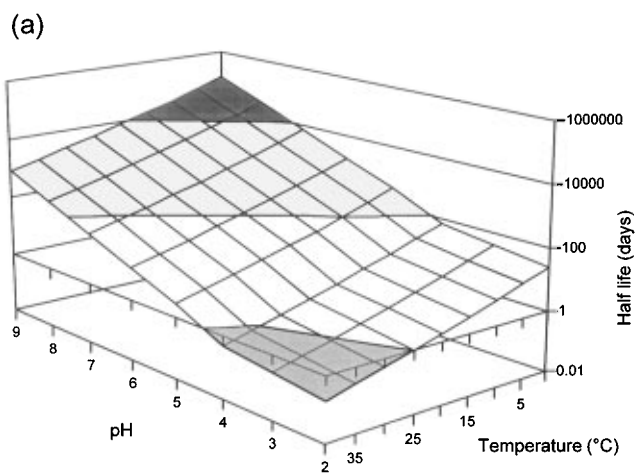
(a)

(b)

Figure 4. Prosulfuron (a) and primisulfuron methyl (b) hydrolysis: half-life (days) as a function of pH and temperature. The ordinates are logarithmic scales. Half-lives (days): solid black, 10^6–10^4; light gray, 10^4–10^2; unmarked, 10^2–1; lined, 1–10^{-2}.

(a)

(b)

Figure 5. Rimsulfuron (a) and thifensulfuron methyl (b) hydrolysis: half-life (days) as a function of pH and temperature. The ordinates are logarithmic scales. Half-lives (days): unmarked, 10^2–1 and lined, 1–10^{-2}.

this sulfonylurea, half-life was between 0.01 and 1 day (lined area, Figure 4a) only at temperatures higher than 25 °C and at acid pH values. The tridimensional graph of primisulfuron methyl exhibited a shape similar to that of prosulfuron, even if the dark area, indicating extremely slow degradation, is limited to pH values between 8.5 and 9 and to temperatures less than 10 °C (Figure 4b). Tridimensional graphs of rimsulfuron and thifensulfuron methyl showed a similar shape, with the absence of the dark area, indicating half-lives higher than 1000 days (Figure 5). The decrease of half-life at pH values higher than 6 is also evident.

CONCLUSIONS

On the basis of the degradative pattern of the four sulfonylureas, it was clear that prosulfuron is charac-

terized by a relatively low dissipation rate in water, rimsulfuron and thifensulfuron methyl are characterized by fast dissipation, whereas primisulfuron methyl shows intermediate characteristics of hydrolysis. Such different behaviors of chemical degradation were correlated to different characteristics of the chemical structures of these herbicides. In particular, rimsulfuron and thifensulfuron methyl are characterized by an arylic group with an heterocyclic ring (not *o*-benzene-substituted sulfonylureas). On the contrary, prosulfuron and primisulfuron methyl present a phenyl in arylic position (*o*-benzene-substituted sulfonylureas). It was possible to reveal different hydrolytic patterns corresponding to these structural characteristics, as evidenced by the degradation pattern of the four sulfonylureas as a function of water pH and temperature.

These results demonstrate how herbicides belonging to the same chemical class can behave in very different ways regarding degradation and dissipation in water.

From an environmental point of view, considering that groundwater generally has temperatures between 10 and 15 °C and pH values between 6.5 and 7.5 (Chang et al., 1987; Smith, 1990), tridimensional graphs showed how some sulfonylureas (i.e., prosulfuron and primisulfuron methyl) degrade relatively slowly once they reach groundwater, representing a potential problem for water contamination. At present, according to the European Community directive relating to the quality of water for human consumption adopted in 1980, the maximum admissible concentrations are 0.1 μg L^{-1} for a single pesticide and 0.5 μg L^{-1} for the sum of all pesticides (EEC, 1980). These detection limits in water, which are not based on toxicological considerations, could create problems even with herbicides with low environmental impact such as sulfonylureas, characterized by low application rates (several grams/ha) and favorable toxicological profile but with a relatively high leaching potential.

LITERATURE CITED

Berger, B. M.; Wolfe N. L. Hydrolysis and biodegradation of sulfonylurea herbicides in aqueous buffers and aerobic water–sediment systems: Assessing fate pathways using molecular descriptors. *Environ. Toxicol. Chem.* **1996**, *15*, 1500–1507.

Beyer, E. M.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. Sulfonylureas. In *Herbicides: Chemistry, degradation and mode of action*; Kearney, P. C., Kaufmann, D. D., Eds.; Dekker: New York, 1987; pp 117–189.

Blacklow, W. M.; Pheloung, P. C. Sulfonylurea herbicides applied to acidic sandy soils: Movement, persistence and activity within the growing season. *Aust. J. Agric. Res.* **1992**, *43*, 1157–1167.

Bollag, J. M.; Liu, S. Y. Biological transformation processes of pesticides. In *Pesticides in the soil environment: Processes, impacts and modeling*; Cheng, H., Ed.; SSSA Book Series 2; Soil Science Society of America: Madison, WI, 1990; pp 169–200.

Cambon, J. P., Bastide, J. Hydrolysis kinetics of thifensulfuron methyl in aqueous buffer solutions. *J. Agric. Food Chem.* **1996**, *44*, 333–337.

Chang, F. H.; Hult, M.; Noben, N. N. Quantitative studies of biodegradation of petroleum and some model hydrocarbons in ground water and sediment environments. In *Ground water quality and agricultural practices*; Fairchild, D. M., Ed.; Lewis Publishers: Chelsea, MI, 1987; pp 295–318.

Dinelli, G.; Vicari, A.; Catizone, P. Use of capillary electrophoresis for detection of chlorsulfuron and metsulfuron in tap water. *J. Agric. Food Chem.* **1993a**, *41*, 742–746.

Dinelli, G.; Vicari, A.; Bonetti, A.; Catizone, P. Triasulfuron, chlorsulfuron and metsulfuron hydrolysis and triasulfuron degradation in soil. Proceedings IX Symposium Pesticide Chemistry, Degradation and Mobility of Xenobiotics, Piacenza, Italy, October 11–13; Del Re, A., Capri, E., Evans, S. P., Natali, P., Trevisan, M., Eds.; Edizioni Biagini: Lucca, Italy, 1993b; pp 411–420.

Dinelli, G.; Bonetti A.; Catizone, P.; Galletti, G. C. Separation and detection of herbicides in water by micellar electrokinetic capillary chromatography. *J. Chromatogr.* **1994**, *656*, 275–280.

Dinelli, G.; Vicari, A.; Bonetti, A. Separation of sulfonylurea metabolites by capillary electrophoresis. *J. Chromatogr.* **1995**, *700*, 195–200.

EEC. Directive relating to the quality of water intended for human consumption (80/778/EEC). *Off. J. Eur. Community* **1980**, *23* (Aug), L229/1130.

Eklo, O. M.; Aspmo, R.; Lode, O. Runoff and leaching experiments of dichlorprop, MCPA, propinconazole, dimethoate and chlorsulfuron in outdoor lysimeters and field catchment areas. *Norw. J. Agric. Sci.* **1994**, *13*, 53–78.

Flury, M; Leuenberger, J.; Studer, B.; Fluhler, H. Transport of anions and herbicides in a loamy and a sandy field soil. *Water Resources Res.* **1995**, *31*, 823–835.

Fredrickson, D. R.; Shea, P. J. Effect of soil pH on the degradation, movement and plant uptake of chlorsulfuron. *Weed Sci.* **1986**, *34*, 328–332.

Galletti, G. C.; Bonetti, A.; Dinelli, G. High performance liquid chromatographic determination of sulfonylureas in soil and water. *J. Chromatogr.* **1995**, *692*, 27–37.

Rahman, A.; James, T. K. Comparative mobility of nine sulfonylurea herbicides in soil columns. *Proc. Asian-Pac. Weed Sci. Soc. Conf., 12th* **1989**, 213–217.

Sabadie, J. Hydrolyse chimique acide du metsulfuron méthyle. *Weed Res.* **1990**, *30*, 413–429.

Sabadie, J. Alcoolise et hydrolyse chimique acide du chlorsulfuron. *Weed Res.* **1991**, *31*, 309–316.

Sabadie, J. Réactivité de l'herbicide chlorsulfuron: Synthesè et structure de ses produits de dégradation. *Weed Res.* **1992**, *32*, 137–142.

Sabadie, J. Dégradation du chlorimuron–ethyl déposé sur diverse support minéraux et sur acides humiques. *Weed Res.* **1995**, *35*, 295–302.

Schneiders, G. E.; Koeppe, M. K.; Naidu, M. V.; Horne, P.; Brown, A. M.; Mucha, C. F. Fate of rimsulfuron in the environment. *J. Agric. Food Chem.* **1993**, *41*, 2404–2410.

Smith, C. J. Hydrogeology with respect to underground contamination. In *Environmental fate of pesticides*; Hutson, D. H., Roberts, T. R., Eds.; John Wiley and Sons Ltd.: London, 1990; pp 47–99.

Tomlin, C., Ed. *Pesticide Manual*, 10th ed.; Crop Protection Publishers, 1994.

Vicari, A.; Catizone, P.; Zimdahl, R. L. Persistence and mobility of chlorsulfuron and metsulfuron under different soil and climatic conditions. *Weed Res.* **1994**, *34*, 147–155.

Vicari, A.; Zimdahl, R. L.; Cranmer, B. K.; Dinelli, G. Primisulfuron and rimsulfuron degradation in aqueous solution and adsorption in six Colorado soils. *Weed Sci.* **1996**, *44*, 672–677.