Soil Metabolism of the Herbicide Rimsulfuron under Laboratory and Field Conditions

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Procedures were developed for soil analysis of rimsulfuron and its metabolites by means of GC−ECD, GC−FPD and GC−MS with a detection limit of 1 μg of rimsulfuron equivalents per kilogram of dry soil, after purification of the soil extracts by TLC. Soil containing an exaggerated rimsulfuron concentration was incubated in the laboratory, in order to adjust the analytical procedures. To evaluate the role of different manuring managements, rimsulfuron was applied postemergence (10 g ha^{-1} on a corn field in 1994 and 1995) on plots treated with (1) green manure, pig slurry applied in (2) November and (3) March, and cow manure applied in (4) November and (5) March and (6) untreated control plots without organic fertilizer. Neither rimsulfuron nor its metabolites were detected at soil depths lower than 8 cm. The results show that manure managements prolong rimsulfuron half-life in the 0−8 cm surface soil layer from a minimum of 14 days (control) to a maximum of 46 days (pig slurry in March). At corn harvest, rimsulfuron and its metabolites were not detected in soil. Similar soil degradation pathways were observed in the field as in the laboratory. *N*-(4,6-Dimethoxypyrimidin-2-yl)-*N*-[3-(ethylsulfonyl)-2-pyridinyl]urea **2** was a transient soil degradation product. *N*-[3-(ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine **3** attained a maximum soil concentration after 20 days of incubation and then progressively disappeared and could not be detected after 40 days. The high-molecular weight amine **3** did not accumulate in soil, eliminating the concern for potential formation of nitroso amino compounds. 2-Hydroxy-3-(ethylsulfonyl)pyridine **4** became the major rimsulfuron soil degradation product. The soil concentrations increased and attained a maximum after 40 days of incubation and then decreased; its isomerization into 2-pyridone, followed by hydrolysis, could transform it into low molecular weight nontoxic products. The concentrations of 2-amino-4,6-dimethoxypyrimidine **5** were somewhat lower than those of compound **4**.

Keywords: *Rimsulfuron; sulfonylureas; herbicide; soil; metabolism; cow manure; pig slurry; corn crop*

INTRODUCTION

The sulfonylurea herbicide rimsulfuron [*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide] is applied postemergence at the rate of 10−15 g of ai ha^{-1} on corn crops at the 2−6 leaves stage. It is absorbed by both plant leaves and roots. It efficiently controls a wide variety of perennial and annual grasses, and some broadleaf weeds (Palm et al., 1989). Rimsulfuron alone or in mixture with metribuzin gives also an efficient weed control in potato crops (Ackley et al., 1996).

The rimsulfuon application of 7.5 or 15 g ha^{-1} in March on bare soil inhibited the growth of several sensitive crops sown 5 weeks later such as sugar beet, lettuce, oat, rye-grass, clover, summer wheat and barley, flax, turnip, Savoy cabbage, and spinach (Callens and Bulcke, 1993). When sown 4.5 months after the rimsulfuron treatment, some of these sensitive crops (sugar beet, lettuce, and turnip) still were inhibited.

A trace level analytical method was developed for rimsulfuron and compound **2** by thermospray LC−MS in soil at levels down to 0.02 mg kg^{-1} (Shalaby et al., 1992). After monomethylation with diazomethane, trace analysis of the herbicide chlorsulfuron in soil was carried out by GC with electron capture detection, with a detection limit of 1 ng/g (Ahmad and Crawford, 1990). Soil and water residues of chlorsulfuron-methyl and metsulfuron-methyl are dimethylated in ethyl acetate by reaction with an excess of diazomethane; they were measured by GC with electron capture detection with detection limits below 1 ng/g (Klaffenbach and Holland, 1993). Primisulfuron-methyl and metsulfuron-methyl were measured in field soils using this GC technique, the detection limits being 0.4 and 2 ng/g, respectively (James et al., 1995). GC−MS indicated that the methyl derivatives of chlorsulfuron, metsulfuron-methyl and primisulfuron-methyl, generated according to these analytical procedures, are thermostable and detected as such by GC.

When incorporated at a concentration of 100 μg (kg of dry soil)$^{-1}$ in soil incubated in the laboratory, rimsulfuron was mainly transformed into the rearranged urea *N*-(4,6-dimethoxypyrimidin-2-yl)-*N*-[3-(ethylsulfonyl)-2-pyridinyl]urea (**2**) (Schneiders et al., 1993). Minor amounts of the high-molecular weight amino compound *N*-[3-(ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine (**3**) were also observed. Both compounds **2** and **3** are also generated by decomposition of rimsulfuron adsorbed on clay (Pantani et al., 1996). When rimsulfuron was applied in the field, compound **2** was the sole rimsulfuron metabolite observed, whereas no compound **3** was observed (Schneiders et al., 1993).

In the present work, (1) procedures were developed for the analysis of rimsulfuron and of its metabolites in soil, with a detection limit sufficiently low [1 μg of rimsulfuron equivalents (kg of dry soil)$^{-1}$] to allow their

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measurements in the fields after application at the normal rate (about 10 g of ai ha^{-1}). (2) The kinetics of rimsulfuron soil biodegradation were studied in soil containing an exaggerated concentration of rimsulfuron and incubated in the laboratory. This was done in order to identify the rimsulfuron soil metabolites and to adjust the analytical methods for measurements of rimsulfuron and its metabolites in field soils. The kinetics of rimsulfuron soil biodegradation were also studied in corn field trials after application of the normal rimsulfuron dose. Moreover, the influence of recent organic fertilizer treatments (applied on the field at normal rates) on rimsulfuron soil dissipation was studied. We previously observed that recent organic fertilizer treatments slow the herbicide soil dissipation (Rouchaud et al., 1993, 1996a). The problem here was to see if the organic fertilizer treatments would increase the soil persistence of rimsulfuron and its metabolites. (3) The degradation pattern of rimsulfuron (i.e. metabolite formation) was studied by laboratory and field trials.

EXPERIMENTAL PROCEDURES

Laboratory Studies. Rimsulfuron was incorporated in fresh soil samples (75% of the field moisture holding capacity) taken in March 1994 in the 0−8 cm soil surface layer of a bare and rimsulfuron-untreated field at Melle, Belgium (8% clay, 35% silt, 57% sand, sandy loam, and 1.9% organic matter, pH 6.2), at a concentration of 60 μg of ai (kg of dry soil)$^{-1}$, which corresponds to a field application rate of approximately 65 g of ai ha^{-1} in the 0−8 cm soil surface layer. The field into which the soil was taken for incubation was located about 150 m from the field on which the corn crop was made in 1994. The slight difference in soil composition between both fields does not reduce the significance of the results obtained with soil incubation in the laboratory at high rimsulfuron concentrations. This indeed was done in order to identify the rimsulfuron soil metabolites and to establish the analytical procedures for measurements of rimsulfuron and its metabolites in soil. A solution of the pure active ingredient rimsulfuron (4.2 mg) in acetone (100 mL) was further diluted in water (5 L). The aqueous solution was thoroughly mixed with the soil (70 kg; previously partially air-dried at 20 °C during 24 h), which then was allowed to evaporate for 2 h. Thirty-two open pots were then each filled with 2 kg of this soil and incubated at 20 °C in the dark. The soil moisture (75% of the field moisture holding capacity) was maintained by weighing and periodical addition of water to compensate for evaporation. On different times after starting incubation (0, 6, 14, 22, 29, 38, 45, and 61 days), four replicate pots were taken out according to a randomized block design (Figure 3); the soil content of each pot was mixed, and an aliquot (300 g) was taken as a separate sample. Soil samples were analyzed after having been stored at −25 °C.

Field Studies. An experimental field was set up in 1994 on a field (32 × 36 m) located at Melle, Belgium (7% clay, 38% silt, 55% sand, sandy loam, and 2.2% organic matter, pH 6.7). On September 2, 1993, the whole field was tilled and divided into 24 plots (6 m × 8 m each). To evaluate the role of manuring management, six treatments were used in the experiment: (1) green manure, (2) pig slurry in November, (3) pig slurry in March, (4) cow manure in November, (5) cow manure in March, and (6) control without manuring. Each treatment (control included) was performed on four plots (replicates) which were located according to a randomized blocks design. On September 2, 1993, yellow mustard (*Sinapis alba*, cv. Emergo) was sown as green manure, and on March 4, 1994, when its height reached 45−50 cm, it was incorporated into the soil by rotary-tilling at a depth of 15 cm. On November 12, 1993, either cow manure or pig slurry was applied at the normal rate of 50 tons ha^{-1}. On March 4, 1994, either cow manure or pig slurry was applied at the same rate on other plots. One organic fertilizer thus was applied per plot, and only once. The plots treated with cow manure or pig slurry were immediately rotary-tilled at a depth of 15 cm after treatment. On May 11, 1994, the whole field was rotary-tilled at a depth of 15 cm, and corn (cv. Solfege) was sown. On June 17, 1994, 10 g of rimsulfuron ha^{-1} was applied when corn was at the 4−6 leaves stage, by spraying the mixture of 40 g of Titus ha^{-1} (25% rimsulfuron; obtained from Du Pont, Belgium) in water (600 L ha^{-1}) containing the surfactant Trend at 1 mL L^{-1}. At intervals during the trial (Tables 1 and 3), soil samples were taken separately (and analyzed once separately) in the 0−8 cm surface soil layer of each of the four replicate plots, of each of the organic fertilizer treatments and control. Soil sampling was made outside the 0.5−1 m broad band nearest to the separation between plots. Each soil sample from each replicate plot was analyzed separately once. In addition, on July 15 and August 11, 1994, samples were taken from the 8−20 cm soil layer. For each soil sample, 15 cores (2.5 cm diameter) were taken from each replicate plot at random points; the cores from each plot were sliced, and then the slices correponding to each horizon were bulked together and then stored at −25 °C until they were analyzed.

The corn crop of 1994 was repeated in the same way in 1995 at Melle, on a field which was located near to the one on which the trial of 1994 was run, both fields having similar soil structures, pHs, and compositions. Green manure was sown on September 12, 1994. Cow manure and pig slurry were applied on November 14, 1994; on other plots, they were applied on March 10, 1995. Corn was sown on May 4, 1995, and rimsulfuron was applied on June 6, 1995. Soil sampling was carried out at the dates indicated in Tables 2 and 4.

Table 1. Field Studies (1994) Measuring Concentrations of Rimsulfuron and of Its Metabolites 2−5 in the 0−8 cm Soil Surface Layer in the Control Plots

days after rimsulfuron application[c]	concentrations of rimsulfuron and of its metabolites **2**−**5** [μg (kg of dry soil)$^{-1}$, as equivalents of rimsulfuron; means of four replicates ± SD][a]				
	rimsulfuron	**2**	**3**	**4**	**5**
3	8.6 ± 0.6	nd[b]	nd	nd	nd
10	5.6 ± 0.4	nd	2.4 ± 0.5	nd	nd
20	3.7 ± 0.3	nd	2.3 ± 0.5	1.6 ± 0.3	1.2 ± 0.2
28	2.3 ± 0.3	nd	1.2 ± 0.2	2.8 ± 0.6	2.4 ± 0.5
35	1.8 ± 0.3	nd	nd	3.2 ± 0.6	2.9 ± 0.6
45	1.0 ± 0.2	nd	nd	3.5 ± 0.7	2.1 ± 0.4
55	nd	nd	nd	1.2 ± 0.2	nd

[a] **2**, *N*-(4,6-dimethoxypyrimidin-2-yl)-*N*-[3-(ethylsulfonyl)-2-pyridinyl]urea; **3**, *N*-[3-(ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine; **4**, 2-hydroxy-3-(ethylsulfonyl)pyridine; **5**, 2-amino-4,6-dimethoxypyrimidine. [b] nd = not detected. [c] Sampling dates (day-month, year 1994), days after rimsulfuron treatment, and cumulative rainfall (millimeters) were, respectively, as follows: 20-6, 3, 0; 27-6, 10, 2; 7-7, 20, 19; 15-7, 28, 59; 22-7, 35, 59; 1-8, 45, 100; 11-8, 55, 118.

Table 2. Field Studies (1995) Measuring Concentrations of Rimsulfuron and of Its Metabolites 2−5 in the 0−8 cm Soil Surface Layer in the Control Plots

days after rimsulfuron application[c]	concentrations of rimsulfuron and of its metabolites **2**−**5** [μg (kg of dry soil)$^{-1}$, as equivalents of rimsulfuron; means of four replicates ± SD][a]				
	rimsulfuron	**2**	**3**	**4**	**5**
1	9.8 ± 0.7	nd[b]	nd	nd	nd
9	7.3 ± 0.5	nd	1.4 ± 0.3	nd	nd
17	5.5 ± 0.4	nd	1.8 ± 0.4	1.2 ± 0.2	1.0 ± 0.2
23	4.7 ± 0.3	nd	1.0 ± 0.2	2.0 ± 0.4	1.7 ± 0.2
31	3.8 ± 0.3	nd	nd	2.8 ± 0.6	2.3 ± 0.5
41	2.9 ± 0.3	nd	nd	3.2 ± 0.6	2.1 ± 0.4
48	1.7 ± 0.3	nd	nd	1.7 ± 0.3	nd

[a] As in Table 1. [b] As in Table 1. [c] Sampling dates (day-month, year 1995), days after rimsulfuron treatment, and cumulative rainfall (millimeters) were, respectively, as follows: 7-6, 1, 0; 15-6, 9, 35; 23-6, 17, 41; 29-6, 23, 41; 7-7, 31, 52; 17-7, 41, 73; 24-7, 48, 73; 11-8, 66, 78.

Table 3. Field Studies (1994) Measuring Concentrations of Rimsulfuron in the 0−8 cm Soil Surface Layer of the Corn Field Treated Postemergence with 10 g of Rimsulfuron ha^{-1} at Melle in 1994

days after rimsulfuron application[c]	concentrations of rimsulfuron [μg (kg of dry soil)$^{-1}$; means of four replicates ± SD][a]				
	green manure	pig slurry in November	pig slurry in March	cow manure in November	cow manure in March
3	8.4 ± 0.5	8.7 ± 0.6	8.3 ± 0.6	8.9 ± 0.6	8.1 ± 0.6
10	6.8 ± 0.5	7.1 ± 0.5	7.4 ± 0.5	6.8 ± 0.5	7.7 ± 0.5
20	4.1 ± 0.3	4.8 ± 0.3	6.0 ± 0.4	5.4 ± 0.4	5.8 ± 0.4
28	3.5 ± 0.3	4.0 ± 0.3	4.3 ± 0.3	4.3 ± 0.3	4.2 ± 0.3
35	2.5 ± 0.3	3.1 ± 0.3	3.6 ± 0.3	3.5 ± 0.3	3.6 ± 0.3
45	1.8 ± 0.3	2.1 ± 0.3	3.0 ± 0.3	2.8 ± 0.3	3.0 ± 0.3
55	nd[b]	nd	nd	nd	nd

[a] Rimsulfuron soil concentrations in the untreated control plots without organic fertilizers are reported in Table 1. [b] As in Table 1. [c] As in Table 1.

Table 4. Field Studies (1995) Measuring Concentrations of Rimsulfuron in the 0−8 cm Soil Surface Layer of the Corn Field Treated Postemergence with 10 g of Rimsulfuron ha^{-1} at Melle in 1995

days after rimsulfuron application[c]	concentrations of rimsulfuron [μg (kg dry soil)$^{-1}$; means of four replicates ± SD][a]				
	green manure	pig slurry in November	pig slurry in March	cow manure in November	cow manure in March
1	9.5 ± 0.7	9.3 ± 0.7	8.9 ± 0.6	9.1 ± 0.6	8.8 ± 0.6
9	8.1 ± 0.6	8.1 ± 0.6	8.6 ± 0.6	8.1 ± 0.6	8.5 ± 0.6
17	6.3 ± 0.4	6.8 ± 0.5	7.5 ± 0.5	6.8 ± 0.5	7.3 ± 0.5
23	4.9 ± 0.3	6.6 ± 0.5	6.8 ± 0.5	6.6 ± 0.5	6.7 ± 0.5
31	4.3 ± 0.3	5.2 ± 0.4	6.1 ± 0.4	6.0 ± 0.4	5.7 ± 0.4
41	3.4 ± 0.3	4.2 ± 0.3	4.9 ± 0.3	4.7 ± 0.3	4.8 ± 0.3
48	1.6 ± 0.3	1.8 ± 0.3	1.4 ± 0.3	1.8 ± 0.3	1.9 ± 0.3
55	nd[b]	nd	nd	nd	nd

[a] Rimsulfuron soil concentrations in untreated control plots without organic fertilizers are indicated in Table 2. [b] As in Table 1. [c] As in Table 2.

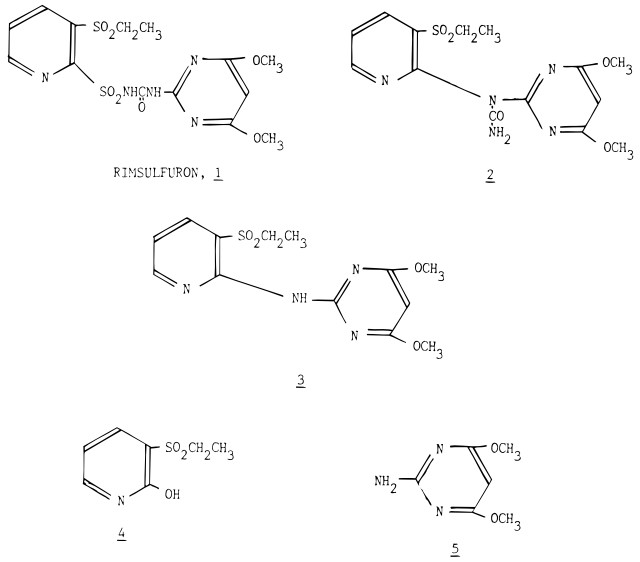

Figure 1. Rimsulfuron and its soil metabolites **2**−**5**.

Analytical Procedures. For rimsulfuron soil residue analysis, a separate soil extraction was made with 0.1 M $NaHCO_3$ in water. This extraction system was based on the low acidity of rimsulfuron and gave clean extracts, i.e. containing low quantities of natural compounds interfering with the GC−ECD and GC−MS analyses. The extract was washed with dichloromethane, brought to pH 2.8, and extracted with ethyl acetate. Metabolites **2**−**5** have no such acidic properties (Figure 1). They were separately extracted from a second soil sample, by means of the nonspecific but efficient 8/2 methanol/water (v/v) solvent. The extracts were cleaned by repeated TLC. Rimsulfuron and its metabolites in the soil extracts were located as TLC bands (which thereafter were separated and extracted) using synthetic standards applied on the TLC plate next to the soil extract. The standards and their structures were determined by IR, NMR, and mass spectrometries and, for metabolites **3** and **4**, by elemental analyses.

In the soil extracts, rimsulfuron and compounds **2** and **3** were first separated by TLC. Rimsulfuron soil residues were analyzed by GC and GC−MS after methylation with diazomethane. In the GC and GC−MS apparatus, the monomethyl derivative **1′** of rimsulfuron and compound **2** were transformed into amine **3** which was measured, as explained in Analysis of Rimsulfuron and Its Metabolites under Results and Discussion. Compounds **4** and **5** also were first separated by TLC in the soil extracts. Their GC and GC−MS analyses were made after methylation of compound **4** and trifluoroacetylation of compound **5**. After derivatization, the purified soil extracts were analyzed by GC−ECD or GC−FPD and, in several cases, by GC−MS.

Analytical Methods. TLC was carried out using silica gel 60F 254 (20 cm × 20 cm, 0.2 mm thick plates from Merck). The sample was applied as a band. Standards and samples were applied on different lanes of the TLC plate. Column chromatography, used for purification of the synthesized standards of the metabolites, was carried out on silica gel 60 HF 254 + 366 from Merck.

Diazomethane (toxic, explosive) was freshly prepared before use. Behind a safety shield, to a 250 mL flask was added a cooled solution of potassium hydroxide (6 g) in water (10 mL). Diethyl ether (80 mL) was added, and the stirred mixture was cooled in an ice bath. *N*-Methyl-*N*-nitrosourea (3 g; suspected to be carcinogenic) was added portionwise, after which the reaction mixture was stirred for an additional 15 min with ice cooling. The ether layer containing diazomethane was decanted and immediately used as such for methylation.

For GC analysis, rimsulfuron and compound **4** were analyzed after methylation with diazomethane, which transformed them into their monomethyl derivatives, **1′** [*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-*N*-methyl-3-(ethylsulfonyl)-2-pyridinesulfonamide] and **4′** [a mixture of 2-methoxy-3-(ethylsulfonyl)pyridine and 1-methyl-3-(ethylsulfonyl)-2-pyridone], respectively. The TLC-purified extracts (5 mL in ethyl acetate or methanol, respectively, for rimsulfuron and compound **4**) were treated at 20 °C with a solution (~3 mL) of diazomethane in ether until the yellow color persisted, and the mixture was stirred for 3 h at 20 °C (Rouchaud et al., 1996a). In the GC apparatus, monomethylrimsulfuron **1′** was transformed into compound **3** which was detected (electron capture), as indicated by the GC retention times and the GC−MS spectra. Unmethylated rimsulfuron also was transformed in the GC apparatus into compound **3** which was detected, but with a

GC signal 2 times lower than that of monomethylrimsulfuron **1′**. Monomethyl derivative **4′** of compound **4** was GC detected as such (flame photometry) and was made up of a mixture of *O*- and *N*-methyl derivatives (as shown by ^{1}H NMR) which were not separated by TLC and GC. Compounds **2** and **3** were injected directly into the GC apparatus. Compound **2** also was transformed in the GC apparatus into compound **3** which was detected; compound **3** was GC detected as such. For GC analysis of compound **5**, to its TLC-purified extract in ethyl acetate (2 mL) was added a solution of trifluoroacetic anhydride (Acros; 25%, v/v, in ethyl acetate; 2 mL), the mixture was carefully heated to boiling (∼5 min) until concentrated to 0.1 mL, ethyl acetate was added, and the mixture was analyzed by GC for trifluoroacetylated **5** [*N*-(trifluoroacetyl)-2-amino-4,6-dimethoxypyrimidine **5′**]. GC conditions were as follows: glass column with a 1.80 m × 2 mm internal diameter packed with 5% SE30 on Gas Chrom Q 80−100 mesh; nitrogen carrier gas at 40 mL min^{-1}; injection and detection temperatures of 275 °C for rimsulfuron and compounds **1′**, **2**, and **3** and of 250 °C for compound **5′**, and detection of each of these compounds by electron capture (GC Varian 2700 apparatus); for compound **4′**, injection at 250 °C and detection at 180 °C, and detection by flame photometry in the sulfur mode (GC Tracor 550 apparatus). Column temperature and retention times for each compound were as follows: compound **3** (from rimsulfuron and compounds **1′**, **2**, or **3**), 245 °C, 3.7 min; compound **4′**, 160 °C, 3.9 min; and compound **5′**, 170 °C, 2.7 min. The GC samples from soil extracts of rimsulfuron (as its monomethyl derivative **1′**) and of the rimsulfuron metabolites **2**−**4** (as its methyl derivative **4′**) and **5** (as its trifluoroacetyl derivative) were in many cases further analyzed by GC−MS.

IR spectra were recorded in KBr discs in cm^{-1} (Midac FTIR apparatus; 4000−400 cm^{-1}). ^{1}H NMR spectra were in parts per million (δ) in tetramethylsilane (Varian 250 MHz). MS and GC−MS (VG AutoSpec; Fisons GC 8065) spectra conditions were as follows: 70 eV, electron impact EI and (or) chemical ionization (CI) with NH_3; FAB-SIMS in glycerol for rimsulfuron; *m*/*e*, relative abundance, %.

Analytical Standards for Rimsulfuron and Its Metabolites. *Rimsulfuron.* The commercial formulation Titus (25 g; 25% rimsulfuron; Du Pont, Belgium) in ethyl acetate (200 mL) was heated to reflux (7 min, stirring); the hot mixture was filtered. The solid was reextracted in the same way two more times, and the filtrates were gathered and concentrated to dryness in a vacuum rotary evaporator. Recrystallization in 1/1 ethyl acetate/chloroform (v/v) gave rimsulfuron (5.94 g, 95%, purity greater than 99% as shown by TLC). IR: 3424, 3277, 3093, 2946, 2789, 1734, 1611, 1586, 1507, 1454, 1375, 1356, 1318, 1235, 1196, 1171, 1130, 1047, 990, 779, 718. ^{1}H NMR ($CDCl_3$): 1.33−1.38 (t, 3H, $SO_2CH_2CH_3$), 3.75 (q, 2H, SO_2CH_2 CH_3), 3.98 (s, 6H, OCH_3), 5.82 (s, 1H, pyrimidine H), 7.18 (br, 1H, N*H*-pyrimidine), 7.78, 8.62, 8.93 (m, 3H, pyridine-H), 12.98 (br, 1H, SO_2NH). MS (EI): 322 (compound **3** − 2H, 18), 231 [$C_4HN_2(OCH_3)_2NH(C_5H_3N)$, 36], 155 [$C_4HN_2(OCH_3)_2$-$NH_2$, 59], 137 [$C_4HN_2(OCH_3)_2$ − 2H, 18], 123 [$C_4HN_2(OCH_3)(O)$ − H, 14], 109 [$C_4HN_2(OCH_3)$ + H, 19]. MS FAB-SIMS (glycerol): 432 (M + 1, 100), 340 [M − $SO_2CH_2CH_3$ + 2H, 8), 299 (340 − CONH + 2H, 11), 199 [$C_4HN_2(OCH_3)_2NHCONH_2$ + H, 83], 182 [$C_4HN_2(OCH_3)_2NHCO$, 78], 156 [$C_4HN_2(NH_2)$-$(OCH_3)_2$ + H, 58].

*Monomethylrimsulfuron (**1′**).* Rimsulfuron (1.0 g, 2.32 mmol) in ethyl acetate (100 mL) was treated with a solution of diazomethane in ether until the yellow color persisted. The mixture was stirred for 20 h (20 °C), maintaining the yellow color by addition of the diazomethane ethereal solution when necessary. The solvent was evaporated under vacuum, and the residue was column chromatographed [10/1 dichloromethane/acetic acid (v/v)], yielding methylrimsulfuron (0.91 g, 2.04 mmol, 88%). IR: 3423, 3277, 3092, 2953, 1698, 1597, 1561, 1539, 1414, 1366, 1316, 1211, 1171, 1155, 1051, 955, 785, 750, 720. ^{1}H NMR ($CDCl_3$): 1.21−1.28 (t, 3H, $SO_2CH_2CH_3$), 2.99 (s, 3H, SO_2NCH_3), 3.25 (q, 2H, $SO_2CH_2CH_3$), 3.62 (s, 6H, OCH_3), 5.67 (s, 1H, pyrimidine H), 7.57, 8.42, 8.86 (m, 3H, pyridine H), 9.87 (br, 1H, N*H*-pyrimidine). MS (EI): 381 (M − SO_2, 3), 352 (M − SO_2NCH_3, 2), 338 (M − SO_2NCO − H, 32), 324 (compound **3**, 36), 260 (**3** − SO_2, 48), 245 (**3** − SO_2CH_3, 85), 231 (**3** − $SO_2CH_2CH_3$, 100). MS (CI): 382 (M − SO_2 + H, 100), 339 (M − SO_2NCO, 85), 325 (compound **3** + H, 95), 296 (**3** − CH_2CH_3 + H, 76), 245 (**3** − SO_2CH_3, 42), 231 (**3** − SO_2-CH_2CH_3, 72).

*N-(4,6-Dimethoxypyrimidin-2-yl)-N-[3-(ethylsulfonyl)-2-pyridinyl]urea (**2**) and N-[3-(Ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine (**3**).* Rimsulfuron (1.0 g, 2.32 mmol) in a mixture (1.4 N in HCl) of methanol (30 mL) and hydrochloric acid (12 N, 4 mL) was stirred (8 days, 20 °C). The solid rimsulfuron was first in suspension and at the end of the reaction was completely dissolved. Methanol was evaporated under vacuum and water (50 mL) added; the mixture was brought to pH 7.0 with NaOH and extracted with ethyl acetate. The ethyl acetate solution was dried (Na_2SO_4) and concentrated under vacuum to dryness. The product was column chromatographed [successively 1/2 ether/hexane (v/v) and 1/2 ethyl acetate/hexane (v/v)], giving successively compounds **3** (0.35 g, 1.08 mmol, 47%) and **2** (0.37 g, 1.0 mmol, 43%). ^{1}H NMR ($CDCl_3$) spectrum of compound **2**: 1.22−1.29 (t, 3H, $SO_2CH_2CH_3$), 3.27 (q, 2H, $SO_2CH_2CH_3$), 3.63 (s, 6H, OCH_3), 5.71 (s, 1H, pyrimidine H), 7.61, 8.44, 8.89 (m, 3H, pyridine H). Spectra of compound **3**: IR 3356, 3095, 2956, 1603, 1570, 1516, 1447, 1408, 1372, 1354, 1310, 1273, 1200, 1163, 1132, 1059, 1005, 801, 739. ^{1}H NMR ($CDCl_3$): 1.24 (t, 3H, $SO_2CH_2CH_3$), 3.17 (q, 2H, $SO_2CH_2CH_3$), 3.87 (s, 6H, OCH_3), 5.73 (s, 1H, pyrimidine H), 6.35 (br, 1H, NH). MS (EI): 324 (M$^+$, 45), 309 (M − CH_3, 4), 295 (M − CH_2CH_3, 9), 279 (M − OCH_2CH_3, 4), 277 (M − $HOCH_2CH_3$ − H, 3), 259 (M − SO_2H, 19), 245 (M − SO_2CH_3, 24), 231 (M − $SO_2CH_2CH_3$, 100), 216 (231 − CH_3, 42), 186 (216 − OCH_3 + H, 35).

*2-Hydroxy-3-(ethylsulfonyl)pyridine (**4**).* Rimsulfuron (4.0 g, 9.3 mmol) in 12 N HCl in water (50 mL) was heated to reflux (stirring, 3.5 h). The cooled mixture was brought to pH 7 by careful addition (cooling) of a 4 N NaOH solution in water, and the aqueous solution (∼80 mL) was repeatedly (4 × 300 mL) extracted with ethyl acetate; the ethyl acetate solution was dried (Na_2SO_4) and concentrated to dryness under vacuum, and the residue was column chromatographed [1/1ethanol/ether (v/v)], giving compound **4** (1.51 g, 8.07 mmol, 87%). IR: 3423, 3117, 2986, 1699, 1653, 1607, 1539, 1478, 1406, 1366, 1300, 1235, 1127, 976, 774, 737. ^{1}H NMR ($CDCl_3$): 1.27 (t, 3H, CH_2CH_3), 3.48 (q, 2H, CH_2CH_3), 6.53 (t, 1H, pyridine H), 7.79 (t, 1H, pyridine H), 8.32 (t, 1H, pyridine H). MS (EI): 187 (M$^+$, 71), 158 (M − CH_2CH_3, 17), 141 (158 − OH, 23), 123 (M − SO_2, 29), 111 (158 − SO + H, 32), 95 (C_5H_3NOH + H, 100).

*Mixture of 2-Methoxy-3-(ethylsulfonyl)pyridine and 1-Methyl-3-(ethylsulfonyl)-2-pyridone (**4′**).* 2-Hydroxy-3-(ethylsulfonyl)pyridine **4** (1 g, 5.3 mmol) in methanol (50 mL) was treated at 20 °C with an ethereal solution of diazomethane until the yellow color persisted. The mixture was stirred at 20 °C for 2 h and concentrated under vacuum to dryness, and the solid was purified by column chromatography [2/1 hexane/acetone (v/v)], giving the mixture of compounds **4′** (1.02 g, 5.1 mmol, 96%). ^{1}H NMR ($CDCl_3$): 1.19 (t, 3H, $SO_2CH_2CH_3$), 3.24−3.49 (m, 2H, $SO_2CH_2CH_3$), 3.57 (s, 1H, NCH_3), 3.67 (s, 2H, OCH_3), 6.31 (t, 1H, pyridine H), 7.02 (m, 0.5H, pyridine H), 7.63 (m, 0.5H, pyridine H), 8.12 (m, 1H, pyridine H). MS (EI): 201 (M$^+$, 43), 186 (M − CH_3, 21), 172 (M − CH_2CH_3, 24), 156 (M − OCH_2CH_3, 18), 142 (156 − CH_2, 31), 107 (M − HSO_2CH_2-CH_3, 78), 78 (C_5H_3N + H, 100).

*2-Amino-4,6-dimethoxypyrimidine (**5**).* To the stirred (20 °C) mixture of 2-amino-4,6-dihydroxypyrimidine (1 g, 7.87 mmol; Acros) in methanol (30 mL) was added an ethereal solution of diazomethane until the yellow color persisted. The mixture was stirred during 24 h (20 °C), maintaining the yellow color by addition of the diazomethane solution when necessary. The solvent was evaporated under vacuum, and the residue was column chromatographed [1/1 ethanol/hexane (v/v)], yielding compound **5** (1.05 g, 6.77 mmol, 86%). IR: 3431, 2932, 1653, 1622, 1539, 1466, 1418, 1252, 1213, 1165, 1034, 974. ^{1}H NMR (DMSO-d_6): 3.70 (s, 6H, OCH_3), 4.93 (s, 1H, pyrimidine H), 7.28 (br, 2H, NH_2). MS (EI): 155 (M$^+$, 100), 139 (M − NH_2, 4), 127 (M − HCN − H, 28), 125 (M − OCH_2, 21), 112 (M − NH_2CNH, 38).

Rimsulfuron Soil Analysis. Soil (100 g) was stirred with 0.1 M $NaHCO_3$ in water (200 mL, 20 min, 20 °C), and the mixture was centrifuged (3000 rpm, 15 min); the extraction was repeated, and the supernatants were combined and washed with dichloromethane (2 × 150 mL; contact time of lower than 5 min). The dichloromethane layer was discarded, and the aqueous phase was brought to pH 2.8 with 1 N hydrochloric acid and extracted two times with ethyl acetate (2 × 200 mL); the ethyl acetate solution was dried (Na_2SO_4), concentrated to 40 mL in a vacuum rotary evaporator (30 °C), and then concentrated further to 0.5 mL under a slow stream of nitrogen (20 °C). The extract was applied to a TLC plate with the standard of rimsulfuron. Elution with ethyl acetate gave a band containing rimsulfuron at $R_f = 0.20$ which was scraped off; the silica gel was extracted with ethyl acetate (40 mL) in a small column (internal diameter of 6 mm), and the extracts were concentrated further under a slow stream of nitrogen (20 °C) to 5 mL. A solution of diazomethane in ether (~3 mL) was added until the yellow color persisted, and the mixture was stirred for 2 h at 20 °C, concentrated to 0.5 mL under a slow stream of nitrogen (20 °C), and applied to a TLC plate, together with the standard of methylrimsulfuron **1′**. This second TLC was made to clean the extract from natural soil compounds interfering with the GC and GC−MS analyses to obtain a low sensitivity limit. Elution with 10/1 ethyl acetate/acetic acid (v/v) gave a band at $R_f = 0.38$ containing monomethylrimsulfuron **1′** which was scraped off and extracted with ethyl acetate, and the extract was concentrated under nitrogen and analyzed for methylrimsulfuron **1′** (detected as compound **3**) by GC. After the GC analyses, for about one of the four replicate samples, GC−MS analysis was done in order confirm the identity and the amount of rimsulfuron corresponding to the GC peak. When the final extract was not sufficiently clean, i.e. still contaminated too much by soil natural compounds interfering with the GC and GC−MS measurements, the second TLC was repeated.

Recoveries of rimsulfuron were measured by adding a dilute solution [rimsulfuron in ethyl acetate solution, 5 mL/(100 g of soil)] to samples taken from Melle (0−8 cm untreated with the herbicide). The soil was kept in an open pot at 20 °C in the dark, and the analysis was made between 0 and 48 h after rimsulfuron incorporation. Soil incorporations were made at levels of 5 and 1 (sensitivity limit) μg of rimsulfuron (kg of dry soil)$^{-1}$. Recoveries were 84−96 and 78−89%, respectively (four replicates at each level). Between 0 and 48 h, incubation time had no significant influence on recoveries. The gas chromatograms were free of interfering peaks close to that of compound **3**. At the 1 μg of rimsulfuron (kg of soil)$^{-1}$ level, the signal to noise ratio was 3.

Results were analyzed statistically according to the method described by Draper and Smith (1981), using the relationship $\ln y = kt + b$ of rimsulfuron soil concentrations (y = in micrograms per kilogram of dry soil) in the incubated soil, or in the 0−8 cm field surface soil layer, against time t (days) for the 45 day period following rimsulfuron incorporation in the soil incubated in the laboratory, or following its application in the corn fields. Determination coefficients R^2 are given in Table 5. The 95% confidence intervals for the soil half-lives were evaluated using the SAS logical CMS SAS 5.18 (1984, 1986, SAS Institute Inc., Cary, NC).

Soil Analysis with Metabolites 2−5. Soil (100 g) was stirred with 8/2 methanol/water (v/v) (200 mL, 30 min, 20 °C); the mixture was filtered and the extraction repeated (Figure 2). The filtrates were combined; water (100 mL) was added and the methanol removed in a vacuum rotary evaporator (30 °C). NaCl (15 g) was added to the aqueous solution, which was then extracted four times with ethyl acetate (4 × 200 mL). The ethyl acetate solution was dried (Na_2SO_4), concentrated to 40 mL in a vacuum rotary evaporator (30 °C), and then concentrated further to 0.5 mL under a slow stream of nitrogen (20 °C). The extract was applied to a TLC plate, together with the standards of rimsulfuron and compounds **2**−**5**. Elution with ether gave band A containing compound **3** at $R_f = 0.42$ and band B containing rimsulfuron and compounds **2**, **4**, and **5** at $R_f = 0$−0.25. Band A was isolated and extracted with ethyl acetate, and the extract was concentrated and analyzed for compound **3** by GC and, in several cases, by GC−MS (as with rimsulfuron); if the final extract was not sufficiently clean, the TLC with ether elution was repeated. Band B was scraped off and extracted with methanol, and the extract was concentrated and applied onto a second TLC plate, together with the standards of rimsulfuron and compounds **2**, **4**, and **5**. Elution with ethyl acetate gave band C containing compound **5** at $R_f = 0.13$, band D containing rimsulfuron at $R_f = 0.20$, and band E containing the mixture of compounds **2** and **4** at $R_f = 0.40$−0.42. Band C was scraped off and extracted with acetone. This extract was still contaminated too much by soil natural compounds, so a third TLC was needed. The acetone was concentrated and applied to a third TLC plate, together with the standard of compound **5**; elution with 1/1 acetone/hexane (v/v) gave band F at $R_f = 0.28$ containing compound **5** which was isolated and extracted with acetone. The acetone was evaporated to 0.1 mL; ethyl acetate (2 mL) was added, and the mixture was trifluoroacetylated and analyzed for compound **5′** by GC and, in several cases, by GC−MS. Band E was scraped off, extracted with ethyl acetate, which was concentrated (~0.1 mL), and analyzed for compound **2** (detected as compound **3**) by GC and, in several cases, by GC−MS; thereafter, to this extract were successively added methanol (5 mL) and a solution of diazomethane in ether (~3 mL), and the mixture was concentrated and applied onto a third TLC plate, together with the standard of compound **4′**. Elution with 1/1 acetone/hexane, (v/v) gave band G containing compound **4′** at $R_f = 0.35$, which was scraped off and extracted with acetone and concentrated and analyzed for compound **4′** by GC and, in several cases, by GC−MS.

Recoveries of compounds **2**−**5** were made by adding separately to rimsulfuron-untreated 0−8 cm surface soil from Melle a dilute solution of each compound in acetone [5 mL/(100 g soil)] and mixing. Soil was kept in an open pot at 20 °C and analyzed 24 h after incorporation. With 5 μg equivalents of rimsulfuron (kg of dry soil)$^{-1}$, recoveries of **2**−**5** were 82−93, 86−97, 78−91, and 75−91%, respectively (four replicates for each compound). With 1 μg equivalents of rimsulfuron (kg of dry soil)$^{-1}$ (sensitivity limit), recoveries were 73−88, 81−95, 79−88, and 64−81%, respectively (four replicates for each compound). The gas chromatograms were free of interfering peaks close to that of the analyzed compound, and at the 1 μg kg^{-1} level, the signal to noise ratio was 3.

Table 5. Comparison of Rimsulfuron Soil Half-Lives (Days) and Determination Coefficients (R^2) for the Field Degradation of Rimsulfuron in the 0−8 cm Surface Soil Layer as a Function of Organic Fertilizer Treatments

trials and organic fertilizer treatments	R^2	rimsulfuron soil half-lives (days) ± SD
(1) laboratory incubation (no organic fertilizer)	0.988	18 ± 1
(2) corn field at Melle in 1994		
no organic fertilizer	0.986	14 ± 1
green manure	0.984	19 ± 1
pig slurry in November	0.986	21 ± 2
pig slurry in March	0.968	27 ± 2
cow manure in November	0.979	26 ± 2
cow manure in March	0.962	27 ± 2
(3) corn field at Melle in 1995		
no organic fertilizer	0.979	23 ± 2
green manure	0.971	26 ± 2
pig slurry in November	0.949	35 ± 3
pig slurry in March	0.924	46 ± 3
cow manure in November	0.926	44 ± 3
cow manure in March	0.932	44 ± 3

[a] Coefficients of determination were all significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

Analysis of Rimsulfuron and Its Metabolites. Intramolecular nucleophilic substitution easily transforms rimsulfuron, its monomethyl derivative **1′**, and compound **2** into amine **3**. This occurs thermally in the

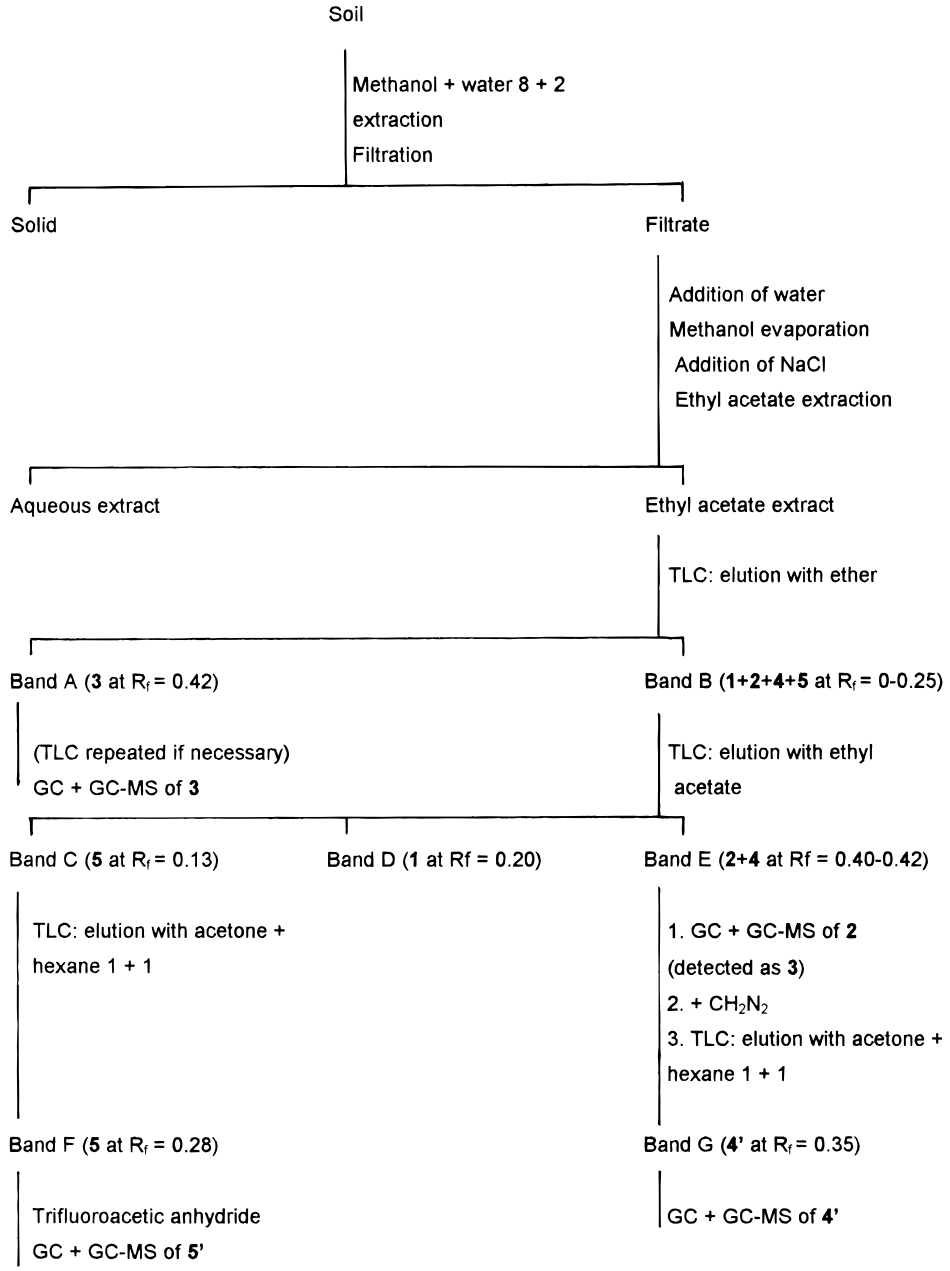

Figure 2. Flow chart of the metabolites **2**−**5** analysis procedure (rimsulfuron = **1**).

GC and GC−MS apparatus and also in the MS apparatus with direct introduction when operated in the EI (electron impact) and CI (chemical ionization) modes. The molecular ions of rimsulfuron and **1′** were observed in MS only with the FAB-SIMS direct injection at room temperature. This system however is not useful for soil residue analysis, as it does not include an initial GC separation. MS and GC−MS, thus, are insufficient for distinguishing unambiguously between rimsulfuron, **1′**, and **2**, relative to compound **3**. TLC of the soil residues with comparison to synthetic standards thus was needed. Identification of the synthetic standards also could not be carried out unambiguously by MS and GC−MS. For identification of synthesized compound **4**, MS and GC−MS alone were ambiguous. Simultaneous formation of 2-amino-3-(ethylsulfonyl)pyridine **6** during synthesis indeed was possible, and the difference between the molecular weights of **4** and **6** is only 1 unit. IR and ^{1}H NMR spectra were thus, needed, as were elemental analyses for compounds **3** and **4**. Metabolites **2**, **3**, and **5** (but not **4**) were previously identified by other authors, but their syntheses and spectra were not published (Schneiders et al., 1993).

Rimsulfuron soil residues were analyzed by GC after monomethylation with diazomethane. NMR and MS (FAB-SIMS in glycerol) indicated that diazomethane transformed rimsulfuron into its monomethyl derivative. GC retention times and GC−MS however indicated that monomethyl rimsulfuron **1′** was transformed into compound **3** in the GC and GC−MS apparatus. The same thing occurred when rimsulfuron was injected into the GC apparatus, but the yield of compound **3** and the sensitivity were lower. Separation of rimsulfuron and metabolite **3** in the soil extracts was carried out by TLC before the GC and GC−MS analyses. TLC using ether as eluent gave rimsulfuron and metabolite **3** at $R_f = 0$ and 0.42, respectively.

Recoveries of rimsulfuron were measured between 0 and 48 h after incorporation in rimsulfuron-untreated soil of Melle. Within 48 h, the incubation time had no significant influence on rimsulfuron recoveries, indicating no decrease of extractability in limited aged soils.

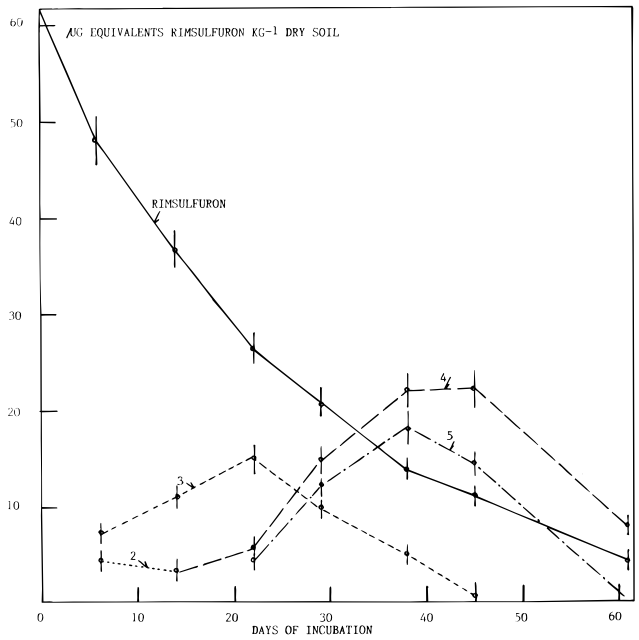

Figure 3. Concentrations of rimsulfuron and its metabolites **2**−**5** in soil incubated in the laboratory and containing an exaggerated concentration of rimsulfuron.

Residue values obtained were based on TLC, GC, and GC−MS, with comparison with authentic standards. Radiolabeled rimsulfuron coupled with HPLC has not previously been used, a method which should reveal all the rimsulfuron metabolites. The method used here is thus blind to unexpected degradation products. However, after 1 month of incubation of the soil containing rimsulfuron, the total amount of rimsulfuron plus its metabolites **2**−**5** was 71% of the incorporated dose (Figure 3). In the control plots of the 1994 and 1995 field crops at Melle, these percentages were 73 and 67%, respectively (Tables 1 and 2). If metabolites other than compounds **2**−**5** were formed in soil from rimsulfuron, their soil concentrations thus should be low.

Laboratory and Field Degradation of Rimsulfuron. The rimsulfuron soil half-life (18 days) during soil incubation at 20 °C in the laboratory was similar to the ones reported under the same conditions by Schneiders et al. (1993) (25 days; residue measurement by HPLC and ^{14}C-labeled rimsulfuron) and Vicari et al. (1994) (plant bioassay) but greater than those (5 days) observed at 30 °C by Palm et al. (1989).

Rimsulfuron and its soil metabolites **2**−**5** were not detected in the 8−20 cm soil layer, indicating that no apparent leaching of rimsulfuron or of its metabolites occurred in these soils. During the period of the first 45 days following the rimsulfuron treatment, the rate of rimsulfuron soil dissipation followed apparent first-order kinetics. There was a linear relationship between the logarithms of rimsulfuron soil concentrations and time following rimsulfuron treatment (Tables 1−4). In the 1994 corn crop, in the control plots not treated with organic fertilizers, and in the plots treated with green manure, with pig slurry applied in November or in March, or with cow manure applied in November or in March, the rimsulfuron soil half-lives were 14 ± 1, 19 ± 1, 21 ± 2, 27 ± 2, 26 ± 2 and 27 ± 2, days, respectively (Table 5). In the 1995 corn crop, the corresponding values were 23 ± 2, 26 ± 2, 35 ± 3, 46 ± 3, 44 ± 3, and 44 ± 3 days.

The rimsulfuron soil half-lives were greater in 1995 than in 1994. This was probably due to the cumulative rains which were lower in 1995 than in 1994, i.e. 73 and 118 mm, respectively, during the 2 month period following rimsulfuron application. The rimsulfuron soil half-lives observed in the field are in agreement with the inhibition observed for the growth of sensitive crops sown in soil treated with rimsulfuron 1.5 or 4.5 months before (Callens and Bulcke, 1993). The rimsulfuron soil half-lives observed here are also in agreement with the 81−91% *Sorghum halepense* (L.) Pers. control obtained during 90 days after application of 7.5, 10.0, and 12.5 g of rimsulfuron ha^{-1} to corn in a field overseeded with *S. halepense* at a height of 20−35 cm (Eleftherohorinos and Kotoula-Syka, 1995).

In the field, the rimsulfuron soil half-lives in the control plots not treated with organic fertilizers of corn fields (14 days with normal rains, 23 days during a dry season) were greater than those (about 6 days) observed by Schneiders et al. (1993) (HPLC and ^{14}C), Vicari et al. (1994, 1996) (plant bioassay), and Onofri (1996) (plant bioassay) in warmer climatic conditions, either with much rains or with the dry Mediterranean weather and simultaneous abundant irrigations. The lower rimsulfuron soil half-lives (6 days) observed by Schneiders et al. (1993) in soil cylinders driven into the ground in the field could possibly be due to the experimental device and the high rains (about 236 mm in 2 months) during their trial. In laboratory incubations at 25 °C in the dark, they however observed rimsulfuron soil half-life of 22 days, similar to the value obtained in the present work but greater than the ones reported by Palm et al. (1989).

In the field trials, during the 45 days period following rimsulfuron application, the organic fertilizer treatments slowed the rimsulfuron soil degradation. This most probably occurred by the increase of the rimsulfuron adsorption onto the organic soil matter, protecting the herbicide in the solid-adsorbed phase against soil degradation (Honnay, 1995; Rouchaud et al., 1996b,c).

Pig slurry application in March (3.5 months before rimsulfuron treatment) was more effective than the one in November (8 months before rimsulfuron treatment) in slowing the rimsulfuron soil biodegradation. For the March and November applications, the rimsulfuron soil half-lives were 27 and 21 days in 1994 and 46 and 35 days in 1995, respectively (Table 5). Such a difference was not observed with cow manure; the rimsulfuron soil half-lives for both March and November applications were about 27 days in 1994 and 44 days in 1995. This suggests that the recent soil organic matter from pig slurry was metabolized faster in soil than the one from cow manure.

Weed counting by D. Callens and R. Bulcke in the 1994 and 1995 field trials generally indicated better herbicide protection in the plots treated with one of each of the organic fertilizers than in the control plots not treated with organic fertilizers.

After the first 45 days following rimsulfuron application, the rates of rimsulfuron soil degradation increased. Two to two and one-half months after rimsulfuron application, rimsulfuron and its metabolites **2**−**5** were not detected in the soil of any of the untreated or organic fertilizer-treated plots.

Laboratory and Field Metabolism of Rimsulfuron. Laboratory incubation of rimsulfuron in soil at the initial concentration of 60 μg of ai (kg of dry soil)$^{-1}$ (which approximately corresponds to a field application rate 4 times greater than the normal one) allowed the identification of rimsulfuron soil degradation products

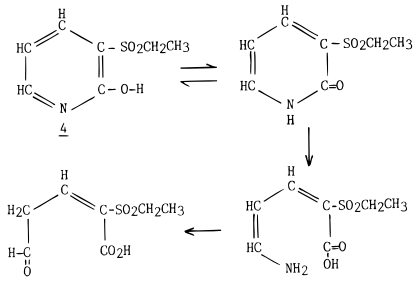

Figure 4. Isomerization of 2-hydroxypyridine **4** into 2-pyridone, which further could be hydrolyzed into low-molecular weight nontoxic products.

(Figures 1 and 3). Results indicate that compound **2** was a transient degradation product. It appeared in soil only at low concentrations [4 μg (kg of dry soil)$^{-1}$, as equivalents of rimsulfuron] during the first 15 days following soil incorporation and thereafter was not detected. Amino compound **3** corresponds to extrusion of the SO_2NHCO group from rimsulfuron or from compound **2**. Results indicate that compound **3** is an important rimsulfuron soil degradation product but that it does not accumulate in soil. Indeed, its maximum soil concentration occurred after 20 days of incubation; thereafter, it decreased, and amino compound **3** was below detection levels after 40 days of soil incubation. The 2-hydroxypyridine **4** then became the major rimsulfuron soil degradation product, its soil concentration becoming 2 times greater than that of rimsulfuron after 45 days of soil incubation. The concentrations of 2-amino-4,6-dimethoxypyrimidine (**5**) were somewhat lower than those of compound **4**. Formation of both compounds **4** and **5** corresponds to the cleavage in soil of the sulfonylurea bridge of rimsulfuron or to the hydrolysis of **3**. Results therefore indicate that the high-molecular weight amino compound **3** does not accumulate in soil, eliminating the concern of the potential formation in soil of nitroso compounds from amine **3**. The hydroxypyridine **4** was more stable in soil than the amino compound **3**, forming later and in greater soil concentrations. Compound **4** in soil should further isomerize into 2-pyridone, which consecutively could be hydrolyzed into low-molecular weight nontoxic products (Figure 4). Tautomerism of 2-hydroxypyridine into 2-pyridone is indeed known (Uff, 1984).

The rimsulfuron degradation products **3**−**5** observed in soil containing a high rimsulfuron concentration and incubated in the laboratory were also observed in the soil of the control plots not treated with organic fertilizers from corn fields treated postemergence with rimsulfuron at the normal rate of 10 g of ai ha^{-1} (Tables 1 and 2). Compound **2**, however, was not detected in the field soils. Compound **3** did not accumulate in the field soils. The 2-hydroxypyridine **4** appeared later and in greater concentrations in soil than compound **3**, becoming the main rimsulfuron soil degradation product. Thereafter, compound **4** also progressively disappeared.

Results suggest that the soil metabolism of rimsulfuron proceeds via two main pathways. In the first, rimsulfuron decomposes into compound **3**, after hydrolysis of the transient rearranged urea **2**. Compound **3** could further be transformed in soil into compound **4**. According to the second pathway, the sulfonyl bridge is broken after nucleophilic substitution by OH^- at the 2-pyridine carbon atom; this generates compounds **4** and **5**. Schneiders et al. (1993) already observed compounds **2** and **3** in soil incubated in the laboratory after rimsulfuron incorporation. In field soil, only compound **2** was observed. Results observed here indicate that the high-molecular weight amino compound **3** is not the final product of rimsulfuron soil decomposition and does not accumulate in soil.

The soil concentrations of rimsulfuron metabolites **3**−**5** were lower and nearer the detection limit in the plots treated with the organic fertilizers (results not indicated in the tables) than in the control plots (Tables 1 and 2) because the rimsulfuron soil degradation was slowed by the organic fertilizer treatments. However, 40 days after application, the soil concentrations of rimsulfuron metabolites were not greater in the plots treated with the organic fertilizers than in the control plots. At the time of harvest, neither rimsulfuron nor its metabolites **2**−**5** were detected in soil, the detection limit for each of these compounds being 1 μg of equivalent of rimsulfuron (kg of dry soil)$^{-1}$.

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