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Soil Persistence and Mobility in Corn Fields of Flumetsulam Applied at Low Doses

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The triazolopyrimidine sulfonanilide herbicide flumetsulam **1** (N-(2,6-difluorophenyl)-5-methyl[1,2,4]triazolo[1,5-a]pyrimidine-2-sulfonamide) is used efficiently in the U.S. at the rate of 60 to 80 g a.i. ha^{-1} for the efficient control of broad-leaved weeds and grasses in corn (*Zea mays* L.) and soybean (*Glycine max* L.) (Kleschick et al. , 1992). The solubility of flumetsulam in water is 49 mg/L at pH 2.5 and increases with pH (Tomlin, 2000); its pKa is 4.6. Like the sulfonylureas, flumetsulam is an (ALS) inhibitor of the biosynthesis of the branched chain amino acids (leucine, isoleucine and valine). It is absorbed by roots and leaves of plants. When flumetsulam was incorporated in clay soil at a concentration corresponding to 79 g a.i. ha^{-1}, and incubated in the laboratory, its soil half-life was 246 days at 7.5°C, 115 days at 15°C and 49 days at 26°C (Lehmann et al., 1993). During incubation of a loam soil containing flumetsulam at a concentration corresponding to 40 g ha^{-1}, the flumetsulam soil half-life was 88 days at 15°C, the concentrations being measured by a plant bioassay (Mc Dowell et al., 1997). The application of 50 to 100 g flumetsulam ha^{-1} on corn crops gave persistent flumetsulam residues in soil which gave injury symptoms to sensitive cabbage crops planted one year later (O' Sullivan et al., 1999). In the soil of a soybean field in the Mississipi (warm and humid region), after its application at the rate of 224 g ha^{-1}, the flumetsulam soil half-life measured by plant bioassay was between 20 and 46 days (Shaw and Murphy, 1997).

Much different soil persistences have thus been reported for flumetsulam on account of the different conditions of the experiments. Flumetsulam being not yet in use in Belgium and Europe, this work studied the persistence and the mobility of flumetsulam in the soil of corn fields treated pre- or post-emergence with 20 g of flumetsulam ha^{-1}.

A method has been described for the analysis of flumetsulam in soil using HPLC (high pressure liquid chromatography) after purification of the soil extracts by gel permeation chromatography (Baskaran et al., 1996). The detection limit of this method was 4 µg kg^{-1} dry soil. It was too high for the analysis of flumetsulam applied in this work at 20 g ha^{-1}, which gives an initial concentration of about 18 µg flumetsulam kg^{-1} dry soil in the 0-8 cm surface soil layer. The residues of

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flumetsulam in soil have been measured by GC (gas chromatography) with a detection limit of 2.5 µg kg^{-1} after derivatization of flumetsulam with methyl iodide (Enge et al., 1999). Using liquid chromatography combined with tandem mass spectrometry (LC-MS/MS), flumetsulam was measured in soil with a detection limit of one µg kg^{-1} (Lagana et al., 2000). In water, the detection limit of flumetsulam measured by LC-MS/MS was 0.1 µg kg^{-1} (Furlong et al., 1999).

In the present work, a sensitive method was developed for the analysis of flumetsulam in soil using GC and GC-MS (GC combined with mass spectrometry) after its methylation by diazomethane into flumetsulam-methyl **2** (N-(2,6-difluorophenyl)-N-(methyl)-5-methyl-[1,2,4]triazolo[1,5-a]pyrimidine-2-sulfonamide) and cleaning of the soil extracts by repeated TLC (thin-layer chromatography). The method was applied to the measurement of flumetsulam in the soil of several corn crops grown on sandy-loam or loamy-sand soils and treated with 20 g flumetsulam ha^{-1}.

MATERIALS AND METHODS

Corn crops were made in 2000 in two sites in Belgium having different soil textures: 1. Melle (clay 7%, silt 38%, sand 55%, pH(H_2O) 6.4, organic matter (%OC x 1.72) 1.39%, sandy-loam); no organic fertilizer was applied during the spring 2000; the latest organic fertilization (40 tons cow slurry ha^{-1}) was applied in March 1999, i.e. 1.5 years before the application of flumetsulam. 2. Zingem (clay 10%, silt 11%, sand 79%, pH 6.6, organic matter 1.51%, loamy-sand); no organic fertilizer was applied during the spring 2000; the latest organic fertilization (40 tons pig slurry ha^{-1}) was applied in April 1999, i.e. 1.4 years before the application of flumetsulam. The fields were tilled at the beginning of May 2000. Some days later, corn (cv. Aviso) was sown. Four 6 x 10 m replicate plots were located at random points in each field. 20 g Flumetsulam ha^{-1} was applied pre-emergence by spraying the emulsion in water (300 L ha^{-1}) of the formulation Python (granulates containing 80 weight % flumetsulam, Dow AgroSciences) on May 19, 2000 at Melle, and on May 25, 2000, at Zingem. The corn was harvested at the end of September 2000. At several delays after the application of flumetsulam, in each field and at the same date, soils samples were taken in the 0-8 cm surface soil layer, separately (and analyzed separately) in each of the 4 replicates (Table 1). In the 8-15 and 15-20 cm surface soil layers, the soil samples were taken in each of the replicate plots, but the samples from two replicate plots were mixed, giving a total of two separate replicates -for each soil layer- which were analyzed separately. For each soil sample, 15 cores (2.5 cm diameter) were taken in each replicate plot at random points, the cores from each replicate plot were mixed and kept at -25°C until analysis.

In 2001, the corn crop and its treatment with flumetsulam was repeated at Melle on the same field as in 2000 (pH 6.5, organic matter 1.41%). No organic fertilizer was applied between the two crops. 20 g Flumetsulam ha^{-1} was applied post-emergence on May 30, 2001 (Table 2).

Table 1. Flumetsulam dissipation and mobility in the soil of the corn crops made in 2000 on sandy loam soil at Melle and on loamy sand at Zingem, after 20 g flumetsulam ha^{-1} post-emergence application in May 2000.

Melle (sandy loam)					Zingem (loamy sand)				
Sampling date, day-month in 2000	Days after flumetsulam application	Cumulative rainfall, mm	Flumetsulam concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]		Sampling date, day-month in 2000	Days after flumetsulam application	Cumulative rainfall, mm	Flumetsulam concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]	
			0-8 cm	8-15 cm				0-8 cm	8-15 cm
19-5	0	0	18.1 ±0.9	nd	25-5	0	0	17.4 ±0.9	nd
6-6	18	77	15.7 ±0.8	nd	6-6	12	42	13.9 ±0.7	nd
29-6	41	86	10.8 ±0.5	0.5 ±0.3	29-6	35	51	9.2 ±0.5	0.4 ±0.3
23-7	65	166	6.1 ±0.3	0.8 ±0.3	23-7	59	109	5.8 ±0.3	0.6 ±0.3
10-8	83	229	5.9 ±0.3	0.4 ±0.3	10-8	77	194	2.4 ±0.3	0.5 ±0.3
28-8	101	269	3.5 ±0.3	nd	28-8	95	234	2.2 ±0.3	nd
22-9	126	340	2.3 ±0.3	nd	22-9	120	292	1.6 ±0.3	nd

[a] In the 0-8 cm surface soil layer, means of 4 replicates ± SD; ± 95% confidence intervals. In the 8-15 cm surface soil layer, means of 2 replicates ± SD. nd = Not detected. For the periods of 101 days at Melle and 95 days at Zingem following the flumetsulam application, in the 0-8 cm surface soil layer: (1) at Melle: corr. coeff.: -0.9821; Y intercept: 5.28; slope, days^{-1}: -0.016200; flumetsulam half-life: 42.8±2.1 days. (2) at Zingem: corr. coeff.: -0.9808; Y intercept: 5.23; slope, days^{-1}: -0.023077; flumetsulam half-life: 30.0±1.5 days. Flumetsulam was not detected in the 15-20 cm surface soil layer.

For the analysis of flumetsulam in soil, the soil extraction and the clean-up of the extract was made in a way similar to the one used previously with flupyrsulfuron (Rouchaud et al., 1999). Soil (100 g) was stirred with 0.1 M $NaHCO_3$ in water (200 ml, 20 min, 20°C, pH 8.1), the mixture was centrifuged (3000 rpm, 15 min), and the supernatant was removed. The extraction was repeated, and the supernatants were combined and washed with dichloromethane (2 x 150 ml). The dichloromethane washings were discarded, the aqueous phase was brought to pH 2.2 with 1 M HCl, and extracted two times with ethyl acetate (2 x 200 ml). The ethyl acetate solution was dried (Na_2SO_4), concentrated successively to 40 and 15

Table 2. Flumetsulam dissipation and mobility in the soil of the corn crops made in 2001 on sandy loam soil at Melle, after 20 g flumetsulam ha^{-1} post-emergence application in May 2001.

Sampling date, day-month in 2001	Days after flumetsulam application	Cumulative rainfall, mm	Flumetsulam concentrations (µg kg^{-1} dry soil) in the surface soil layers[a]	
			0-8 cm	8-15 cm
30-5	0	0	18.9±1.0	nd
5-6	7	6	16.3±0.8	nd
21-6	23	18	12.5±0.6	nd
9-7	41	61	8.6±0.4	0.5±0.3
27-7	59	126	7.4±0.4	0.7±0.3
10-8	73	162	6.2±0.3	0.6±0.3
31-8	94	181	3.3±0.3	nd
26-9	120	373	2.2±0.3	nd

[a] As in Table 1. However, for the period of 94 days following the flumetsulam application, in the 0-8 cm surface soil layer: corr. coeff.: -0.9844; Y intercept: 5.23; slope, $days^{-1}$: -0.017131; flumetsulam half-life: 40.5±2.0 days.

ml in a vacuum rotary evaporator (at 30 and 20°C, and in 1 L and 50 ml flasks, respectively), and then concentrated further to 0.5 ml under a slow stream of nitrogen (20°C). The extract was applied as a band to a TLC plate (20 x 20 cm, 0.2 mm layer, silica gel 60 F254, Merck) along with the flumetsulam **1** analysis standard applied as a spot in a separate lane (the lowest amount to make the spot visible at the fluorescence, i.e. ≈5 µg). Elution with diethyl ether/ethyl acetate 1/1 vol./vol. gave flumetsulam in a band at Rf = 0.54. The band was scraped off; the silicagel was extracted with acetone (40 ml) in a small column, and the extract was concentrated to 15 ml in a vacuum rotary evaporator at 20°C and then concentrated further to 0.5 ml under a slow stream of nitrogen (20°C). Ethyl acetate (4 ml) was added, and then a solution of diazomethane in ether (≈ 4 ml) was added until the yellow color persisted. After 20 min at 20°C, the solution was concentrated to 0.5 ml under a slow stream of nitrogen (20°C) and applied to a second TLC plate together with the standard of flumetsulam-methyl **2** in a separate lane. Elution with hexane/acetone 2/1 vol./vol. gave flumetsulam-methyl **2** in a band at Rf = 0.39. The band was separated, extracted with acetone, the extract was concentrated (between 0.08 and 0.3 ml) and analyzed by GC. Several samples were further analyzed by GC-MS for confirmation.

The GC conditions were the following. ^{63}Ni Electron capture detection, injector and detector at 260°C, and a glass column 0.9 m x 2 mm i.d. (treated with Glass-Prep before filling; Alltech) containing 1% SE30 on Chromosorb W-HP 80-100 mesh. Nitrogen was used as carrier gas at 50 ml min^{-1}. With the column at 225°C during 1 min, and thereafter increased to 240°C at 20°C min^{-1}, the retention time of flumetsulam-methyl **2** was 3.1 min. GC-MS analysis was made with a 15 m capillary column, 0.45 mm i.d., containing SE54 at 1.0 µm film thickness; column oven temperature program was 50°C (3 min) increasing to 250°C at 20°C min^{-1}. Electron impact ionization (EI) was at 30 eV, and the source temperature was 200°C. The MS spectrum of the analysis standards were obtained by direct introduction in the MS apparatus (70 eV; m/e; relative abundance, %). Chemical ionization (CI) was with NH_3. At the levels of 5, 1 and 0.3 (sensitivity limit) µg flumetsulam kg^{-1} dry soil, the recoveries were 86-102, 81-93 and 72-86% in the sandy-loam soil at Melle (4 repetitions for each concentration). The linear regression ln y = kt + b was applied between the naperian logarithms of the flumetsulam concentrations in the 0-8 cm surface soil layer (y = (µg kg^{-1} dry soil) x 10) and the time t (days) following flumetsulam treatment; this was made for the periods of 101, 95 and 94 days after the application of flumetsulam respectively at Melle and Zingem in 2000, and at Melle in 2001. The soil half-lives of flumetsulam -with their 95% confidence intervals- in the 0-8 cm surface soil layer were obtained by means of the logicial SAS 6.12 (Jan 2, 1997; SAS Institute Inc., Cary NC 27513).

The standard of analysis of flumetsulam **1** (purity of 99.5%) was obtained from DowAgroSciences, Belgium. Spectra of **1**: IR (infra red, KBr, cm^{-1}): 3441 (NH), 3037, 2847, 2797, 1617, 1600, 1534, 1477, 1419, 1295, 1237, 1171, 1006, 923, 808, 775, 676. ^{1}H-NMR ($CDCl_3$, low solubility of **1**, 300 MHz): 2.82 (s, 3H, pyrimidine CH_3); 6.51-7.23 (m, 4H, aromatic H); 8.72 (d, 1H, aromatic H). MS (EI): 325 (M^+, 100); 261 ($M-SO_2$, 18); 242 (261-F, 37); 197 ($(SO_2)(C_5H_2N_4)(CH_3)$, 8); 134 ($(C_5H_3N_4)CH_3$, 31); 128 ($(C_6H_3)(F_2)(NH)$, 83).

For the preparation of flumetsulam-methyl **2**, to flumetsulam **1** (0.5 g, 1.54 mmole) in ethyl acetate (375 ml) was added a solution of diazomethane in ether (≈15 ml) until the yellow color persisted. After 20 min at 20°C, the mixture was concentrated in vacuo to dryness. Column chromatography (silica gel 60F254, 70-230 mesh, Merck; hexane/acetone 4/1 vol./vol.) gave **2** (496 mg, 1.46 mmole, 95%). Spectra of **2**: IR (KBr, cm^{-1}): 3086, 2954, 1625, 1592, 1526, 1493, 1477, 1427, 1369, 1295, 1188, 1155, 1072, 1047, 998, 890, 783, 758, 659. ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.78 (s, 3H, pyrimidine CH_3); 3.51 (s, 3H, SO_2NCH_3); 6.81-6.95 (m, 2H, aromatic H); 7.13-7.35 (m, 2H, aromatic H); 8.79 (d, 1H, aromatic H). MS (EI): 338 (M-1, 3); 275 ($M-SO_2$, 8); 247 ($(C_6H_3F_2)(C_5H_2N_4)(CH_3)+H$, 16); 255 (275-F-H, 8). MS (CI): 340 (M+1, 58); 144 ($(C_6H_3)F_2(NHCH_3)+H$, 68); 135($(C_5H_3N_4)(CH_3)+H$,100).

RESULTS AND DISCUSSION

The extraction of flumetsulam from soil by 0.1 M $NaHCO_3$ in water (pH 8.1) was based on the acidity of flumetsulam (pKa = 4.6)(Tomlin, 2000). In an aqueous basic solution, flumetsulam was ionized and soluble. The washing of this solution with dichloromethane eliminated natural contaminants from soil. The aqueous solution thereafter was brought to pH 2.2, bringing flumetsulam in its acid form, which then was extracted with ethyl acetate. Two successive TLC -first of flumetsulam **1**, then of flumetsulam-methyl **2**- gave an extract generally sufficiently clean for the GC and GC-MS analyses; a supplementary TLC was made if necessary.

Flumetsulam has a low vapour pressure: 3.7 10^{-7} mPa at 25°C. For comparison, the vapour pressures of isoxaben and diflufenican are respectively 5.5 10^{-4} and 4.3 10^{-3} mPa at 25°C (Tomlin, 2000). When directly introduced in the MS apparatus, flumetsulam gave a molecular ion having a relative abundance of 100%, showing the high stability of this molecule. However, in the GC and GC-MS apparatus, flumetsulam **1** injected at the analytical amounts of 10^{-9} to 10^{-8} g, either was irreversibly adsorbed or decomposed. The high adsorption of flumetsulam on the GC column was due to the 5 nitrogen atoms of the molecule and the acidity of the sulfonamide group. On the other hand, flumetsulam-methyl **2** was analyzed with a high sensitivity by GC and GC-MS, but in severely controlled conditions in order to avoid adsorption and decomposition. These were cancelled by repeated injections of the standard of analysis **2** and of the purified soil extracts. At the opposite of what we observed previously with the sulfonylureas (metsulfuron, flupyrsulfuron...), the reaction time of diazomethane with flumetsulam **1** must be limited to 20 min, after which time the methylation was quantitative (Rouchaud et al., 1999); greater reaction times generated from flumetsulam an unextractable mixture of further transformation products.

The dissipation of flumetsulam in the 0-8 cm surface soil layer followed a first order kinetics in all the trials. The soil half-lives of flumetsulam in the corn crops made on sandy-loam soil at Melle in 2000 and 2001 were similar, i.e. about 41 days (Tables 1 and 2). In the corn crop made at Zingem on loamy sand soil in 2000, the flumetsulam soil half-life was 30 days. Except the soil textures, the soil parameters at Melle and Zingem were similar: 1. soil pH; 2. concentration of the old organic matter (humus) in soil; 3. the absence of recent organic fertilization in the spring 2000; 4. in the past, the application of high doses of organic fertilization (40 tons cow or pig slurry, or cow manure ha^{-1}) every two years; 5. the crop rotation practized in the past; 6. the cumulative rains during the trials. The comparison of the trials thus suggests that the loamy-sand texture explained the lower persistence of flumetsulam in the soil at Zingem, relative to the sandy-loam texture and the flumetsulam soil persistence at Melle. Indeed, it has been observed that the persistence of herbicide in soil is lower in sandy soil than in loamy or clay soils, when all the other soil parameters are similar, especially the concentration of organic matter in soil (Sanchez-Martin and Sanchez-Camazano, 1991). The greater soil half-lives observed for flumetsulam by Lehmann et al. (1993) and McDowell et al. (1997) should be due to different trial conditions (incubation of soil in the laboratory, higher doses of flumetsulam...).

At the harvest of corn at the end of September, only 9 to 13% of the applied dose of flumetsulam remained in soil (Tables 1 and 2). The heavy rains and the soft temperatures of the autumn certainly should dissipate the low residues of flumetsulam in soil within one or two months after the harvest. The results thus indicate that, when applied at the rate of 20 g ha^{-1}, the persistence of flumetsulam in soil was moderate, and should not give phytotoxicity problems to the following crop, especially as it is preceded by a tilling. H. Eelen and R. Bulcke (2001) made biological observations in agreement with the chemical results obtained here. Sensitive crops (sugar beet, lettuce...) were sown 5 months (at the end of August) after the application of 20 g flumetsulam ha^{-1}. No or only very light phytotoxicity symptoms were observed with the sensitive plants.

In each of the trials, in the 8-15 cm surface soil layer, low concentrations of flumetsulam at the limit of the analytical sensitivity were observed temporarily. In the 15-20 cm surface soil layer, flumetsulam was never detected. The mobility of flumetsulam in soil is thus very low, probably on account of its high adsorption onto the soil and its organic matter.

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