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Flufenacet Soil Persistence and Mobility in Corn and Wheat Crops

J. Rouchaud,[1] O. Neus,[1] K. Cools,[2] R. Bulcke[2]

[1] Phytopharmacy Laboratory, Catholic University of Louvain, 3, Place Croix du Sud, SCI, 15D, 1348 Louvain-la-Neuve, Belgium
[2] Weed Research Center, University of Gent, Coupure Links 653, 9000 Gent, Belgium

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Flufenacet (N-4-fluorophenyl)-N-(1-methylethyl)-2-[(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetamide) is a new oxyacetanilide herbicide having an excellent activity against major annual grasses and certain small-seeded dicotyledonous weeds (Figure l)(Deege et al., 1995; Förster et al., 1997). It is applied pre- or post-emergence in cereals (240 to 320 g flufenacet ha^{-1} in winter wheat) and in corn (600 g flufenacet ha^{-1}). Flufenacet is most effective when soil applied. It inhibits cell division and growth of weeds. Flufenacet being mainly active against grass weeds, it is applied in mixture with a broadleaf herbicide (e.g. diflufenican, metosulam...)(Dahmen et al., 1996). The corn selectivity of flufenacet is due to its metabolism catalyzed by glutathione S-transferases which is 3-4 times faster in the corn seedlings than in weeds (Bieseler et al., 1997).

Flufenacet is an oxyacetanilide. Mefenacet is the only oxyacetanilide herbicide commercially available. It is a cell division inhibitor used in rice at 1.0-l .6 kg ha^{-1} against grass weeds, and has a soil half-life of about three weeks (Schmidt et al., 1984). However, several α-chloroacetanilide herbicides are commercially available: propachlor, alachlor, dimethachlor, metazachlor and metolachlor. They are used in corn and several vegetable crops at rates between 1.5-2.5 kg a.i. ha^{-1} (but propachlor at 2.5-3.5 kg ha^{-1}; metazachlor at 0.6-l kg ha^{-1} in vegetable crops) for protection mainly against grass weeds. Like flufenacet, these acetanilides are cell division inhibitors.

A soil half-life of 34 days has been reported when flufenacet was first presented (Deege et al., 1995). At our knowledge, no study has been published about the soil persistence and mobility of flufenacet in the soil of field crops, This has been done in the present work in spring and summer corn crops grown on sandy loam soil, and after application in the autumn in wheat.

MATERIALS AND METHODS

A spring corn crop was made in 1998 with flufenacet pre-sowing application. In a field at Melle, Belgium (clay 7%, silt 38%, sand 55%, organic matter 2.2%, pH 6.2, sandy loam soil) four 6 x 10 m replicate plots were located at random points. The field was tilled on 20-11-1997 (day-month-year). On 24-3-1998, the field was rotary-tilled to 10 cm depth, and made ready as for sowing, and 600 g flufenacet ha^{-1} was applied by spraying the emulsion of flufenacet (assay liquid formulation containing 500 g L^{-1} flufenacet, Bayer, Belgium) in water (300 L ha^{-1}). Corn (cv. Aviso) was sown on 7-5-1998, and harvested at

Correspondence to: J. Rouchaud

the middle of October 1998. At intervals after flufenacet application, soil samples were taken separately (and analyzed separately) in the 0-10 cm surface soil layer of each of the four replicate plots (Table 1). Soil samples were also taken from the 10-15 and 15-20 cm surface soil layers, with samples at each depth from two replicate field plots being mixed to give duplicate samples for analysis. For each soil sample, 15 cores (2.5 cm diameter) were taken from each replicate plot at random points, the cores from each replicate plot were bulked together and then stored at -25°C until analyzed.

A summer corn crop was made in 1998 on a field located next to the one of the spring crop and of the same soil composition, and with flufenacet pre-sowing application. The summer corn crop trial was made in the same way as the spring one. The field was tilled on 20-ll-1997. On 28-5-1998, the field was rotary-tilled to 10 cm depth, and was made ready as for sowing, and 600 g flufenacet ha^{-1} was applied. Corn was sown on 8-6-1998, and harvested at the middle of October 1998 (Table 1).

Flufenacet has been applied in autumn 1997 at the dose used for winter wheat. The soil remained bare till May 1998, simulating the failure of the winter wheat crop. Spring wheat and other replacement crops were sown in May 1998, and their sensitivity to possible flufenacet soil residue was observed. Four 6 x 10 m replicate plots were located at random points in a field located next to the ones of the spring and summer corn crops, and of the same soil composition. The field was tilled on 20-11-1997, and was made ready as for sowing. On 21-1l-1997, 240 g flufenacet ha^{-1} was applied, which is the dose used in winter wheat. The soil remained bare until the 7-5-1998, date at which the field was rotary-tilled to 10 cm depth, and spring wheat and other replacement crops (corn, sugar beet, oat.. .) were sown as separate bands. At intervals after flufenacet application and till mid August 1998, soil samples were taken separately (and analyzed separately) in the 0-10 cm surface soil layer of each of the four replicate plots (Table 2). After flufenacet application and till the 7-5-1998, soil samples were also taken from the 0-2, 2-4,4-6, 6-8, 8-10, 10-15 and 15-20 cm surface soil layers, with samples at each depth from two replicate field plots being mixed to give duplicate samples for analysis. After the 7-5-1998, additional soil samples were taken only in the 10-15 and 15-20 cm surface soil layers, the 0-10 cm soil layer having been mixed by the rotary-tilling before sowing.

For the flufenacet soil analysis, soil (100 g) was stirred with acetone/water (8/2 vol./vol., 200 ml, 20°C, 1 hr). The mixture was filtered, and the extraction was repeated during 30 min. The filtrates were gathered, water (100 ml) was added, and the acetone removed in a vacuum rotary evaporator (30°C). NaCl (15 g) was added, the aqueous solution was extracted two times with ethyl acetate (2 x 200 ml), the ethyl acetate solution was dried (stirring during 1 hr at 20°C with Na_2SO_4), concentrated in a one litre flask to 40 ml in a vacuum rotary evaporator at 30°C, further concentrated to 15 ml in a 50 ml flask in a vacuum rotary evaporator at room temperature, and then further concentrated to 0.5 ml under a slow stream of nitrogen (20°C). The concentrate was applied as a band to a first silica gel 60 F 254 20 x 20 cm, 0.2 mm thick, thin-layer chromatography (TLC) plate. The flufenacet standard was applied on another part of the TLC plate, next to the band of the sample solution. Elution with ethyl acetate/hexane (l/3 vol./vol.) gave the enlarged TLC band containing the two flufenacet isomers at R_f= 0.14-0.33. This band was scraped off, the silica gel was extracted with acetone (40 ml) in a small glass column, the extract was concentrated successively to 15 ml in a vacuum rotary evaporator at room temperature, and to 0.5 ml under a slow stream of nitrogen (20°C), and was applied onto a second TLC

plate. Elution with acetone/hexane/acetic acid l/6/0.5 vol./vol./vol. gave the mixture of the flufenacet stereoisomers in the band at R_f = 0.32-0.56. This band was scraped off, the silica gel extracted with acetone (40 ml), the extract was concentrated successively to 15 ml in a vacuum rotary evaporator (20°C) and to 1 ml under a slow stream of nitrogen (20°C). The extract was analyzed for flufenacet by gas-liquid chromatography (GLC) and, for several samples, by combined GC-mass spectrometry (GC-MS).

GLC conditions were the following. Electron capture detection. Injection and detection at 280 and 255°C, respectively. Glass column 1.80 m x 2 mm i.d. containing 5% SE30 on Chromosorb W-HP 80-100 mesh. Nitrogen gas at 50 ml min^{-1}. With column oven at 190°C, the flufenacet retention time was 3.2 min (one peak with a very slight deformation). Mass spectra were recorded at 70 eV in the electron impact (EI) or chemical ionization (CI, NH_3) modes. At the 20 and 5 µg flufenacet kg^{-1} level in soil, recoveries were 86-97 and 78-88%, respectively. The analytical limit of sensitivity was 3 µg flufenacet kg^{-1} dry soil.

The linear regression ln y = kt + b was made between the naperian logarithms of the flufenacet soil concentrations (y = µg kg^{-1} dry soil) in the 0-10 cm surface soil layer and the time (days) following the flufenacet treatment. The period following the treatment and during which the linear regression was applied was 126, 117 and 203 days in the spring and summer corn crops, and after the autumn treatment, respectively. The flufenacet soil half-lives with their 95% confidence intervals were obtained using the SAS logicial CMS SAS 5.18 (1984, 1986, SAS Institute Inc., Cary, NC 27512).

For preparation of the flufenacet analysis standard, the formulation Terano (water dispersible granules containing 60 % flufenacet and 2.5% metosulam, Bayer Belgium; 50 g) was stirred in acetone (1 L; 20 min). The mixture was filtered and the acetone was evaporated in a vacuum rotary evaporator. The solid was dissolved in dichloromethane, the solution was washed four times with 0.1 M $NaHC0_3$ in water (4 x 400 ml). The washings were discarded, the dichloromethane solution was dried (Na_2S0_4) and concentrated to dryness giving flufenacet (26.2 g, 87%) of a purity greater than 99.8%. Spectra of flufenacet: IR (FTIR; KBr, cm^{-1}): 3075,2986,1655 (CO), 1508, 1487, 1427, 1329, 1312, 1254, 1223, 1155, 1121, 1099, 1036, 1005, 954, 848, 742. ^{1}H-NMR ($CDCl^3$, 300 MHz): 1.12 (d, 6H, CH_3); 4.74 (s, 2H, OCH_2); 4.98 (m, lH, C*H* $(CH_3)_2$); 7.17-7.35 (m, 4H, benzene-H). MS (CI, NH_3; relative abundance, %): 364 (M+l, 79); 235 (M-$CF_3C(S)$=NH, 22); 194 (M-CF_3(CNNCS)-O, 100); 152 ($(CH_3)_2CHNC_6H_4F$, 32).

RESULTS AND DISCUSSION

During the main crop period of the spring and summer corn crops -i.e. the 4 months following the application of flufenacet-, there was a linear relationship between the naperian logarithms of the flufenacet soil concentrations in the 0-10 cm surface soil layer and the time elapsed since its application (first order kinetics) (Table 1). When flufenacet was applied in autumn, the first order kinetics was followed during the 7 months following treatment, i.e. till the end of July 1998 at the wheat harvest (Table 2). During the latest one month period of each of the three trials, the rate of dissipation of the low residue of flufenacet remaining in soil became greater than the one predicted by the first order kinetics. Such an increase at crop end of the rate of the herbicide soil dissipation was previously observed with other herbicides, and the effect was more pronounced in soils

Table 1. Flufenacet soil persistence and mobility in the spring and summer corn crops.

Sampling date in 1998, day-month	Days after flufenacet treatment	Cumulative rainfall, mm	Surface soil layers depths, cm		
			0-10	10-15	15-20
			Flufenacet concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]		
1. Spring corn crop (flufenacet treatment on 24-3-1998):					
25-3	1	0	483±24	nd	nd
1-4	8	7	465±23	nd	nd
23-4	30	71	397±20	nd	nd
13-5	50	98	312±16	5±3	nd
28-5	65	123	258±13	nd	nd
12-6	80	214	227±11	7±3	nd
8-7	106	258	195±10	nd	nd
28-7	126	294	152±8	nd	nd
14-8	143	303	103±5	nd	nd
2-9	162	363	51±3	nd	nd
22-9	182	466	nd	nd	nd
Corr. coeff.: -0.9921; slope, $days^{-1}$: -0.009333; flufenacet soil half-life in the 0-10 cm surface soil layer: 74±3.7 days[b].					
2. Summer corn crop (flufenacet treatment on 28-5-1998)::					
28-5	0	0	524±26	nd	nd
12-6	15	91	415±21	nd	nd
8-7	41	135	317±16	nd	nd
28-7	61	171	240±14	5±3	nd
14-8	78	180	197±10	7±3	nd
2-9	97	240	154±8	5±3	nd
22-9	117	343	120±6	nd	nd
12-10	137	391	68±4	nd	nd
12-11	168	544	nd	nd	nd
Corr. coeff.: -0.9968; slope, $days^{-1}$: -0.01244; flufenacet soil half-life in the 0-10 cm surface soil layer: 56±2.8 days.[b]					

[a]In the 0-10 cm surface soil layer, means of 4 replicates ± SD. In the 10-15 and 15-20 cm soil layers, means of 2 replicates ± SD. nd = Non detected.

[b]In the 0-10 cm surface soil layer, flufenacet soil half-life with its 95% confidence interval

Table 2. Flufenacet soil persistence and mobility in the wheat crop after application in autumn on 21-11-1997.

Sampling date, day-month-year	Days after flufenacet treatment	Cumulative rainfall mm	Surface soil layers depths, cm						
			0-10	0-2	2-4	4-6	6-8	8-10	10-15
			Flufenacet concentrations (µg kg^{-1} dry soil) in the surface soil layers[a]						
22-11-1997	1	2	193 ±10	nd	nd	nd	nd	nd	nd
12-12-1997	21	67	187±9	514 ±26	421 ±21	nd	nd	nd	nd
13-1-1998	53	173	161±8	177±9	564 ±28	64±4	nd	nd	nd
18-2-1998	89	204	108±5	97±5	368 ±18	59±4	16±2	nd	nd
17-3-1998	116	269	91±5	82±4	273 ±14	77±4	23±3	nd	nd
23-4-1998	153	341	68±3	51±4	167±8	78±4	37±4	7±2	nd
13-5-1998	173	368	65±3						5±3
12-6-1998	203	484	49±3						nd
28-7-1998	249	564	32±3						nd
14-8-1998	266	573	nd						nd
Corr. coeff.: -0.9912; slope, $days^{-1}$: -0.007077; flufenacet soil half-life in the 0-10 cm surface soil layer: 98±4.9 days[b]									

[a]In the 0-10 cm surface soil layer, means of 4 replicates ± SD. In the 0-2, 2-4, 4-6, 6-8, 8-10, 10-15 and 15-20 cm surface soil layers, means of 2 replicates ± SD. nd = Non detected. Flufenacet was never detected in the 15-20 cm surface soil layer.
[b]In the 0-10 cm surface soil layer, flufenacet soil half-life with its 95% confidence interval.

containing greater concentrations of organic matter (Rouchaud et al., 1993). At the wheat and corn harvests, flufenacet was no more detected in the 0-10 and l0-15 cm surface soil layers. During the whole crops and after their harvests, flufenacet was not detected in the 15-20 cm surface soil layer.

In the wheat, and in the spring and summer corn crops, the flufenacet soil half-lives were 98, 74 and 56 days, respectively (Tables 1 and 2). The trials were done in neighbouring fields of the same soil compositions and history as to the crops and organic fertilization. In another winter wheat trial made on loam soil, flufenacet was applied at the rate of 300 or 600 g ha^{-1} (trial not described here); the flufenacet soil half-life in the 0-10 cm surface soil layer was the same at both doses. Between 300 and 600 g flufenacet ha^{-1}, the dose thus has no influence on the flufenacet soil half-life. The decreasing soil half-lives observed in the trials described here thus corresponded to the higher temperatures and soil microbial activities in summer and spring, relative to winter.

Flufenacet had greater soil half-lives than most of the α−chloroacetanilides (soil half-lives in days at 15°C and with 12% w/w soil moisture): propachlor 9, alachlor 17, dimethachlor 14, metazachlor 29, and metolachlor 47 (Walker and Brown, 1985). The hydrolysis of the amide bond in soil occurs in acid conditions, especially at the surface of the soil micelles. In such conditions, the steric hindrance around the amide bond due to the phenyl and thiadiazol rings, and the N-alkyl substituents, should protect it against hydrolysis, explaining the high persistence of flufenacet in soil (Ingold, 1953). The electron withdrawing fluorine and trifluoromethyl substituents on the phenyl and thiadiazol rings should less contribute to the low reactivity of the amide bond of flufenacet toward hydrolysis.

During the spring and summer corn crops, flufenacet remained in the 0-10 cm surface soil layer (Table 1). This occurred in spite of the heavy rains of this crop season, especially in June, September, October and November 1998. Unsignificant traces of flufenacet were sometimes detected in the l0-15 cm surface soil layer during the 2 to 3 months period after the treatment of the spring and summer corn crops. Flufenacet was never detected in the 15-20 cm surface soil layer of both corn crops.

In the wheat trial with flufenacet application in autumn, flufenacet also was measured in the 0-10, l0-15 and 15-20 cm surface soil layers (Table 2). But, during the 5 months following treatment, i.e. till the end of April 1998, flufenacet was further measured in the 0-2, 2-4, 4-6, 6-8 and 8-10 cm surface soil layers. After the application, flufenacet was mainly in the 0-2 cm surface soil layer. One month after the treatment, it moved down in the 2-4 cm surface soil layer which contained the maximum flufenacet soil concentration till April 1998. During this period small amounts of flufenacet progressively moved down in the 4-6, 6-8 and 8-10 cm surface soil layers in decreasing concentrations in each of these soil layers. The analysis of each 2 cm-thick soil layer in the 0-10 cm surface soil layer indicated the very low mobility of flufenacet in soil, same when the soil remained nake; the wheat and the other replacement crops indeed were sown at the beginning of May 1998. Flufenacet remained in high concentrations in the 0-2 and 2-4 cm surface soil layers, where it gave a high herbicide protection. This is at the opposite of a uniform diffusion of flufenacet in the surface soil layers, which should dilute the herbicide in soil and decrease its efficiency against weeds. At the beginning of May 1998, the 0-10 cm surface soil layer was mixed by the rotary-tilling before sowing of the spring wheat and the other replacement crops. Thereafter (and in the same way as from the flufenacet application), no significant concentration of flufenacet was detected in the 10-15 and 15-20 cm surface soil layers until the harvest at the mid of August 1998. The low solubility of flufenacet in water

(56 mg L^{-1} between pH 4 and 9) and its high adsorption onto soil (K_{oc} = 354 on sandy loam) explain the low mobility of flufenacet in soil (Deege et al., 1995; Weerts, 1997).

At the wheat harvest after application of flufenacet in autumn, and at the spring and summer corn harvests in September or October, no flufenacet residue was detected in the 0-10, 10-15 and 15-20 cm surface soil layers. There is thus no concern for possible persistent flufenacet soil residue which could be phytotoxic to the next crop.

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