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Persistence, Mobility, and Adsorption of the Herbicide Flufenacet in the Soil of Winter Wheat Crops

J. Rouchaud,[1] O. Neus,[1] H. Eelen,[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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The new oxyacetanilide herbicide flufenacet (N-4-fluorophenyl)-N-(1-methylethyl)-2-[(5-trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetamide) was first applied in North Europe for the effective protection of corn crops against major annual grass weeds (Bloomberg, 1997; Förster et al., 1997; Figure 1). In order to extend the protection to dicotyledonous weeds, flufenacet at 600 g ha^{-1} was applied pre- or post-emergence in mixture with 25 g metosulam ha^{-1}. More recently, flufenacet was used effectively at the rate of 240 g ha^{-1} for the protection of winter cereals (winter barley, winter wheat...) against grass weeds (such as *Alopecurus myosuroides* and *Apera spica venti*), the best application being made post-emergence at the one- to three-leaf growth stage after autumn sowing. The protection against grass weeds lasts for a season, no new herbicide treatment being necessary in the spring. For simultaneous protection against broad-leaved weeds, flufenacet at 240 g ha^{-1} was applied mixed with 120 g diflufenican ha^{-1}. We previously studied the persistence of flufenacet in the sandy loam soil of corn crops after a pre-emergence application of 600 g a.i. ha^{-1} (Rouchaud et al., 1999). In the present work, the persistence, mobility and adsorption of flufenacet in soil was studied in winter wheat crops simultaneously at four sites with different soil textures. Flufenacet was applied post-emergence in the autumn at the rate of 240 g a.i. ha^{-1} . Moreover, in two of these fields, some plots -which had not been treated in the autumn with flufenacet- were treated with flufenacet in the spring of the following year.

MATERIALS AND METHODS

The trials were made in Belgium on fields located in four sites having different soil textures. Three of them (Melle, Zingem and Zevekote) were located 40 km apart, and Cortil-Noirmont was at 100 km from Melle. At Melle [clay 7%, silt 38%, sand 55%, pH (H_2O) 7.0 , organic matter (%OC x 1.72) 1.51%, sandy loam] and Zevekote (clay 36%, loam 45%, sand 19%, pH 6.6, organic matter 2.12%, clay loam), no organic fertilizer was applied in 1999; in the past, one year out of two, 40 tons cow slurry or alternately 40 tons cow manure ha^{-1} was applied in the spring at Melle, and 40 tons pig slurry or alternately 40 tons cow manure ha^{-1} was applied in September at Zevekote. At Zingem (clay 10%, silt 11%, sand 79%, pH

Correspondence to: J. Rouchaud

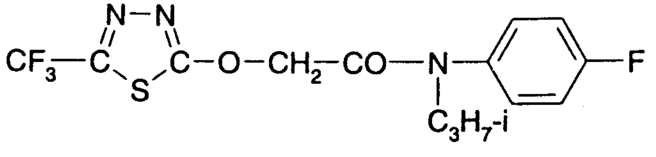

Figure 1. Flufenacet chemical structure

6.4, organic matter 1.60%, loamy sand), 40 tons cow manure ha^{-1} was applied in October 1999; in the past, one year out of two, 40 tons cow manure or alternately 40 tons pig slurry ha^{-1} was applied. At Cortil-Noirmont (clay 14%, silt 75%, sand 11%, pH 6.7, organic matter 1.2%, silt loam), the leaves of the sugar beet (the preceding crop) were incorporated into soil in October 1999; in the past, one year out of four, 40 tons cow manure ha^{-1} was applied. The fields were tilled in November 1999, and winter wheat (cv. Castell) was sown. In each field, four 6 x 10 m replicate plots were located at random points. 240 g Flufenacet ha^{-1} was applied by spraying the emulsion of flufenacet (assay liquid formulation containing 500 g flufenacet L^{-1}, Bayer, Belgium) in water (300 L ha^{-1}). At Melle and Zingem, flufenacet was applied on November 25, 1999; at Zevekote and Cortil-Noirmont, flufenacet was applied on November 26 and December 1, 1999, respectively. In the same fields at Melle and Zingem, flufenacet was applied in the same way in the spring on 4 other replicate plots not treated previously with flufenacet: on March 17 at Melle and on April 4, 2000 at Zingem. Winter wheat was harvested at the end of July 2000. 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 0-2, 2-4, 4-6, 6-8, 8-10, 10-15 and 15-20 cm surface soil layers of the field plots treated in autumn, 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.

The flufenacet analysis in soil was made as described previously (Rouchaud et al., 1999). The soil extracts were cleaned by repeated thin-layer chromatography (TLC). The cleaned extracts were analyzed by gas chromatography (GC; injection temperature was at 240°C, the degradation of flufenacet occurring at higher temperature) and by combined gas chromatography-mass spectrometry (GC-MS). For the 5 months period which followed the application of flufenacet in autumn, the linear regression $\ln y = kt + b$ was applied between the naperian logarithms of the flufenacet soil concentrations (y = µg flufenacet kg^{-1} dry soil) in the 0-10 cm surface soil layer and the time t (days) following flufenacet treatment. The same linear regression was applied for the 3.5 months period which followed the flufenacet application in the spring. The flufenacet soil half-lives with their 95% confidence intervals were obtained using the SAS logicial 6.12 (Jan 2, 1997) (SAS Institute Inc., Cary, NC 27513).

Table 1. Concentration of flufenacet in the soil of the winter wheat fields at the four sites after flufenacet treatment in autumn (at Melle and Zingem, on November 25, 1999; at Zevekote, on November 26, 1999; at Cortil-Noirmont, on December 1, 1999).

Sampling date	Days flufenacet treatment	Cumulative rainfall, mm	Surface soil layers depths, cm							
			0-10	0-2	2-4	4-6	6-8	8-10	10-15	15-20
			Flufenacet concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]							
1. Melle (sandy loam): sampling date: day-month-year 1999:										
26-11	1	0	198±10							
23-12	28	88	129±7	564±28	41±3	28±2	12±1	nd	nd	nd
Day-month-year 2000:										
13-1	49	177	102±5	279±14	90±5	71± 4	49±3	22±1	nd	nd
7-2	74	216	91±5	109±6	216±11	78± 4	43±3	18±1	nd	nd
24-2	91	273	79±4	83±4	136±7	94± 5	55±3	20±1	5±1	nd
22-3	117	308	61±3	58±3	55±3	127±6	36±2	25±2	11±1	nd
3-5	159	387	32±2	22±1	34±2	51±3	30±2	23±1	15±1	10±1
29-5	185	494	16±1	11±1	15±1	18±1	21±1	13±1	11±1	8±1
28-6	216	520	5±1	nd	nd	8±1	10±1	5±1	5±1	nd
23-7	241	604	nd	nd	nd	nd	4±1	3±1	nd	nd
Corr. coeff.: -0.9841; slope, $days^{-1}$: -0.010552; flufenacet soil half-life in the 0-10 cm surface soil layer: 66±3.3 days[b]										
2. Zevekote (clay loam): day-month-year 1999:										
26-11	0	0	202±10							
23-12	27	114	131±7	579±29	51±3	13±1	12±1	nd	nd	nd
Day-month-year 2000:										
13-1	48	190	103±5	140±7	208±10	101±5	47±3	17±1	nd	nd
7-2	73	230	90±5	125±6	191±10	73±4	44±2	18±1	nd	nd
24-2	90	282	82±4	110±6	174±9	78±4	34±2	14±1	nd	nd
22-3	116	302	56±3	67±4	131±7	47±3	19±1	13±1	10±1	nd
3-5	158	399	32±2	20±1	51±3	46±2	25±2	16±1	11±1	5±1

Table 1, continued

Sampling date	Days flufenacet treatment	Cumulative rainfall, mm	Surface soil layers depths, cm: 0-10	0-2	2-4	4-6	6-8	8-10	10-15	15-20
			Flufenacet concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]							
29-5	185	503	13±1	5±1	12±1	17±1	18±1	13±1	11±1	7±1
28-6	216	546	9±1	nd	5±1	11±1	14±1	10±1	8±1	5±1
23-7	241	599	nd	nd	nd	nd	5±1	3±1	nd	nd
Corr. coeff.: -0.9868; slope, $days^{-1}$: -0.010853; flufenacet soil half-life in the 0-10 cm surface soil layer: 64±3.2 days[b].										
3. Zingem (loamy sand): day-month-year 1999:										
26-11	1	0	189±10							
23-12	28	88	148±7	526±26	106±5	71±4	33±2	nd	nd	nd
Day-month-year 2000:										
13-1	49	177	126±6	198±10	233±12	105±5	68±3	25±1	nd	nd
7-2	74	216	115±6	129±7	230±12	110±6	73±4	23±1	nd	nd
24-2	91	273	104±5	99±5	237±12	91±5	64±3	24±1	nd	nd
22-3	117	308	80±4	62±3	116±6	147±7	48±3	28±2	14±1	5±1
3-5	159	387	58±3	31±2	47±2	96±5	91±5	26±1	21±1	10±1
29-5	185	494	31±2	16±1	22±1	47±3	43±2	25±1	14±1	11±1
28-6	216	520	13±1	9±1	16±1	17±1	16±1	10±1	6±1	7±1
23-7	241	604	nd	nd	nd	4±1	5±1	nd	nd	nd
Corr. coeff.: -0.9887; slope, $days^{-1}$: -0.0071803; flufenacet soil half-life in the 0-10 cm surface soil layer: 97±4.9 days[b].										
4. Cortil-Noirmont (silt loam): day-month-year 1999:										
1-12	0	0	209±11							
23-12	23	118	124±6	321±16	256±13	34±2	12±1	nd	nd	nd
Day-month-year 2000:										
13-1	44	193	91±5	134±7	195±10	55±3	49±3	24±1	nd	nd
7-2	69	226	71±4	70±4	153±8	57±3	46±3	23±1	nd	nd
25-2	87	287	52±3	36±2	121±6	52±3	31±2	14±1	12±1	5±1

Table 1, continued

Sampling date	Days flufenacet treatment	Cumulative rainfall, mm	Surface soil layers depths, cm							
			0-10	0-2	2-4	4-6	6-8	8-10	10-15	15-20
			Flufenacet concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]							
22-3	112	326	42±2	34±2	37±2	89±5	25±1	24±1	24±1	12±1
3-5	154	404	26±1	13±1	24±1	27±2	41±2	26±2	25±1	11±1
29-5	185	479	10±1	nd	5±1	8±1	15±1	16±1	16±1	11±1
28-6	216	521	nd	nd	nd	nd	nd	5±1	8±1	5±1
23-7	241	611	nd	nd	nd	nd	nd	nd	nd	nd
Corr. coeff.: -0.9869; slope, $days^{-1}$: -0.012865; flufenacet soil half-life in the 0-10 cm surface soil layer: 54±2.7 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. b. In the 0-10 cm surface soil layer, flufenacet soil half-life with its 95% confidence interval.

Table 2. Adsorption Freundlich constants K (equal to K_d) and K_{oc} of flufenacet to the four field soils.

Soil	K (= K_d, ml g^{-1})[a]	1/n	K_{oc}
Melle (sandy loam)	16	0.89	1802
Zevekote (clay loam)	15	0.93	1231
Zingem (loamy sand)	43	0.91	4602
Cortil-Noirmont (silt loam)	9	0.94	1257

[a] Means are compared within soils with Fisher's protected LSD test at the 5% level. LSD between 0.02 and 0.05.

For the analysis of flufenacet in water, the 0.01 M $CaCl_2$ solution in water (200 ml) -from the adsorption assays- was extracted two times with ethyl acetate (2 x 300 ml), the ethyl acetate solution was dried (Na_2SO_4) and analyzed further in the same way as the ethyl acetate extract from the soil extraction. At the levels of 10, 5 and 0.3 μg flufenacet kg^{-1} water, the recoveries were 87-98, 81-94 and 77-89%, respectively. For the measurement of the adsorption of flufenacet to soil, one day before the application of flufenacet in autumn, soil samples were taken in the 0-10 cm surface soil layer of each field. 0.01 M $CaCl_2$ water solutions containing flufenacet at the initial concentrations of 200, 100, 50 and 20 μg flufenacet kg^{-1} water were made by repeated dilutions -with a 0.01 M $CaCl_2$ solution in water- of an initial solution of flufenacet in acetone. The mixture of each solution of flufenacet (200 ml) with each soil (100 g) was stirred at 20°C in the dark for 24 hr, a period that preliminary studies showed was sufficient to attain equilibrium. For each soil and each initial flufenacet concentration in water, there were three replicates. The mixture was centrifuged (3500 rpm, 10 min), and the soil and water were analyzed separately for flufenacet. The flufenacet adsorption was described by the Freundlich equation $X = K\,C^{1/n}$ where X = amount adsorbed on soil (µg flufenacet kg^{-1} soil), K and n = constants, and C equilibrium concentration in solution (µg flufenacet $litre^{-1}$ solution)(Table 2). The logarithmic form of the above equation was fitted by the method of least squares to the set of experimental data. Constants K and n were calculated, and linear regression analysis was performed to determine the degree of fit of the Freundlich equation to the observed data points.

RESULTS AND DISCUSSION

The degradation of flufenacet in the 0-10 cm surface soil layer of the fields followed a first order kinetics. After the application in autumn, the flufenacet half-life was 97 days at Zingem (loamy sand), about 65 days at Melle (sandy loam) and Zevekote (clay loam), and 54 days at Cortil-Noirmont (silt loam) (Table 1). The sites of the trials were chosen so that a minimum number of parameters changed from one site to another, and that a careful comparison of the results could be made (Weerts, 1998). On the fields at the four sites, in the past the same crop rotation was usually practized -with similar herbicide treatments-, i.e. two consecutive cereal crops followed by corn. The pH of the soils was similar at the four sites, i.e. varying between 6.4 (at Zingem) and 7.0 (at Melle). The cumulative rainfall was also similar at the four sites, and for applications in both autumn and spring. The main differences between the four sites were the soil textures, the organic matter concentrations (old humus), and the recent organic fertilization.

When the soil organic matter concentration is low, the herbicide persistence in soil is usually longer in clay than in sandy soil (Sanchez-Martin and Sanchez-Camazano, 1991). When the concentration of the organic matter (old humus) in soil is greater than about 1.2%, the persistence of the herbicides in soil lasts longer when the concentration of the organic matter in soil is greater (Lehmann et al., 1992). There was no relationship here between the soil texture and the old humus concentration in soil, and the persistence of flufenacet in soil after the application in autumn. The persistence of flufenacet in fact was shorter at Zevekote (clay loam, organic matter 2.12%) and Melle (sandy loam, organic matter 1.51%) than at Zingem (loamy sand, organic matter 1.60%); the flufenacet persistence was lower at Cortil-Noirmont (silt loam) than at the other three sites. As observed previously, the recent organic fertilization treatments -and especially cow manure compared to plant waste- appeared to have the greatest effect in slowing down the degradation of the herbicide in soil (Rouchaud et al., 1996). This was observed with flufenacet at Zingem, in spite of its loamy sand texture, and in spite of the clay loam and high humus concentration at Zevekote. A recent addition in soil of organic matter in fact is richer in bonding heteroatoms (oxygen, nitrogen...) than old humus (Stevenson, 1982). The humification of the soil organic matter (generating the old humus) leads to the decrease of the adsorbing groups containing heteroatoms, and to an increase in carbon content.

When flufenacet was applied in the spring, its soil half-life in the 0-10 cm surface soil layer was 66±3.9 days at Zingem and 44±2.2 days at Melle. The longer persistence of flufenacet in soil at Zingem than at Melle thus was maintained six months after the application of cow manure in October at Zingem. On the other hand, the flufenacet persistence in soil was shorter after a spring treatment than that after an autumn treatment, corresponding with the lower temperature and soil microbial activity during winter than those during the spring and summer seasons.

The Freundlich K_d adsorption coefficients of flufenacet in the field soils were in decreasing order (Table 2): Zingem (loamy sand) > Zevekote (clay loam) and Melle (sandy loam) > Cortil-Noirmont (silt loam). This is the same order as for the persistence of flufenacet in the field soils after application in autumn. The adsorption coefficients confirm the interpretation of the results suggested previously. The flufenacet adsorbed into the soil organic matter is in the solid phase, and thus is less reactive and more persistent than the flufenacet dissolved in the soil solution. Greer and Shelton (1992) in fact made a comparison of the rate of the 2,4-D degradation in the soil solution (the pore water was pressed from soil which contained the soluble 2,4-D which was then measured) against the rate of degradation of 2,4-D adsorbed in soil (the concentrations of adsorbed 2,4-D were measured by solvent extraction). Soluble 2,4-D was metabolized much faster than that adsorbed; this was followed by degradation of both adsorbed (after desorption) and soluble 2,4-D.

The chloroacetanilide herbicides contain the α-chlororoacetamide group disubstituted at the amido nitrogen. One of the nitrogen substituents is the phenyl ring bearing no (propachlor), or two ortho-alkyl groups. The second N-substituent is either an alkyl (propachlor), an alkoxyalkyl (alachlor, dimethachlor, metolachlor, butachlor) or an heterocyclic-methylene group (metazachlor, thenylchlor). The solubilities in water (mg/L, 25°C, pH 7) of propachlor (580), alachlor (170), dimethachlor (2300), metazachlor (430) and metolachlor (488) explain their moderate K_{oc} (the adsorption coefficients corrected for the concentration of organic carbon in soil: between 90 and 300). During incubation, their half-lives at 15°C in sandy loam soil containing 12 g% water were 9, 17, 14, 29 and 47 days, respectively (Walker and Brown, 1985). The lower solubilities in water (mg/L) of thenylchlor (11) and butachlor (23) corresponded with their greater K_{oc} (between 500 and 2900), and their soil half-lives of about one month. Flufenacet is an oxyacetamide substituted at the amido nitrogen by the 4-fluorophenyl ring and the isopropyl group, and by 5-trifluoromethyl-1,3,4-thiadiazol-2-yl at the oxyacetamide oxygen. The low solubility of flufenacet in water (56 mg/L) corresponded with its greater K_{oc} (between 1230 and 4600) and soil half-lives (between 54 and 97 days when applied in the autumn, and 44 to 66 days when applied in the spring).

During the month which followed the application of flufenacet in autumn, flufenacet remained at a high concentration in the 0-2 cm surface soil layer (Table 1). Thereafter, it moved slowly downwards, being at a high concentration -and thus with a high herbicide efficiency- in a 2 cm thick soil layer which moved down as a chromatographic band on a TLC plate. At the end of cultivation, the combination of the descending movement and of the degradation of flufenacet in soil, resulted in flufenacet being almost evenly distributed at low concentrations in all the 2 cm thick layers in the 0-10 cm surface soil layers. After the winter wheat harvest at the end of July, flufenacet was not detected in significant concentrations in soil. The slight movement of flufenacet in the 10-15 and 15-20 cm surface soil layers -in spite of its high adsorption coefficients- could be related to the rains (75 mm $months^{-1}$) which were 25% heavier than normal (60 mm $month^{-1}$) during the whole crop season, and 50% heavier during the 3 months which followed the treatment in autumn. However, because of the rate of the simultaneous flufenacet degradation in the arable 0-20 cm surface soil layer -especially during the warm and humid summer and autumn seasons- the results indicate that flufenacet does not move through soil layers more than 30 cm in depth.

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