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Dissipation and Mobility of the Pyrazol Herbicide JV 485 in the Soil of Winter Wheat Crops

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The assay herbicide JV 485 (5-[4-bromo-1-methyl-5-(trifluoromethyl)-1H-pyrazol-3-yl]-2-chloro-4-fluoro-benzoic acid isopropyl ester) is applied preemergence at the rate of 125-175 g ha^{-1} in winter wheat crops (Prosch et al., 1997; Ambolet et al., 1998; Figure 1). JV 485 gives an excellent herbicide protection throughout the growing season against a large number of important grass weeds *(Alopecurus myosuroides, Lolium* spp., *Apera spica-venti, Poa annua,* and *Phalaris* spp.), and a large number of dicotyledonous weeds including *Galium aparine.* The weed control includes that of herbicide resistant *A. myosuroides* populations. JV 485 is taken up by shoots of plants as they pass through the soil surface. Susceptible species quickly exhibit necrotic symptomology and die within days of emergence. It is an inhibitor of the mitochondrial and chloroplast enzyme protoporphyrinogen oxidase. The inhibition of this enzyme leads to an excessive formation of the singlet oxygen generating protoporphyrin IX (PPIX). In the presence of light PPIX produces singlet oxygen which causes the rapid peroxidation of unsaturated membrane lipids and ultimately the destruction of plant cell membranes (Devine et al., 1993). The solubility of JV 485 in water is very low (0.053 mg kg-$^{-1}$). This suggests that its mobility in the soil of crops should be low. However, at our knowledge nothing has been published about the dissipation and mobility of JV 485 in the soil of winter wheat crops. In the present work, the dissipation and the mobility of JV 485 has been studied in the soil of three winter wheat crops. Two ones were grown on sandy loam soils, and the third one was grown on a clay soil. The three crops were treated in the autumn preemergence with 175 g JV 485 ha^{-1}.

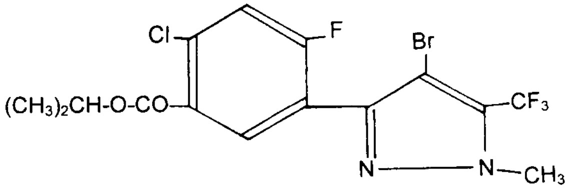

Figure 1. JV 485

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MATERIALS AND METHODS

A winter wheat crop was made on sandy loam soil at Melle with sowing and JV 485 application in the autumn. A field (150 x 350 m) at Melle (clay 7%, loam 38%, sand 55%, organic matter 1.8%, pH(H_2O) 6.6) was tilled and sown with winter wheat (cv. Castell) on the whole field on 3- 12- 1998 (day-month-year). Four 6 x 10 m replicate plots were located at random points in the field. On 17- 12- 1998, the replicate plots were treated pre-emergence with 175 g JV 485 ha^{-1} by spraying the emulsion of JV 485 (assay liquid formulation containing 500 g JV 485 L-1, Monsanto, Belgium) in water (400 L ha^{-1}). Winter wheat harvest was made at the end of July 1999. At intervals after the JV 485 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, S-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. 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.

At Melle, on a field next to the preceding one and with the same soil composition, a second trial was made in the same way except the following. JV 485 was applied in autumn and the wheat was sown in the spring. The field was tilled and made ready as for sowing on 3-12-1998. On the same day, 175 g JV 485 ha^{-1} was applied on 4 replicate plots, and the soil remained bare until April 1999, simulating the failure of the winter wheat crop. On 26-4-1999, the 0- 10 cm surface soil layer was rotary-tilled, and spring wheat (cv. Minaret) was sown. Other replacement and sensitive crops (sugar beet, turnip...) were also sown on separate bands, and their sensitivity to possible JV 485 soil residue was observed. At intervals after JV 485 application and till the wheat harvest at the end of July 1999, 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). 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.

A third trial was made on a clay soil at Zevekote (clay 36%, loam 45%, sand 19%, organic matter 2.1%, pH 7.1) in the same way as the first winter wheat trial at Melle with sowing and JV 485 application in autumn. On 29-10-1998, the field was tilled and winter wheat (cv. Castell) was sown. On 10-l 1-1998, 175 g JV 485 ha^{-1} was applied preemergence. At intervals after JV 485 application and till the wheat harvest at the end of July 1999, soil samples were taken in the O-10, O-2,2-4,4-6, 6-8, S-10, 10-15 and 15-20 cm surface soil layers (Table 3).

The analysis of JV 485 in soil was made in the following way. The mixture of soil (100 g) in acetone/water (8/2 vol./vol., 200 ml) was stirred at room temperature during 1 hr. The mixture was filtered, and the extraction was repeated during 30 mm. The filtrates were gathered and water (100 ml) was added. The acetone was removed in a vacuum rotary evaporator (30°C). NaCl(15 g) was added, and the aqueous solution was extracted two tunes with ethyl acetate (2 x 200 ml). The ethyl acetate extract was dried with Na_2SO_4 and concentrated in a vacuum rotary evaporator successively to 40 and 15 ml (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 at 20°C. The extract 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, along with the

Table 1. Dissipation and mobility of JV 485 in the soil of the winter wheat crop made on sandy loam soil at Melle with sowing and JV 485 application in autumn 1998.

Sampling date, day-month-year	Days after JV 485 application	Cumulative rainfall, mm	Surface soil layers depth, cm				
			0-10	0-2	2-4	4-6	6-8
			JV 485 concentrations (µg kg^{-1} dry soil) in the surface soil layers[a]				
21-12-1998	4	5	151±8				
22-1-1999	36	107	112±6	358±18	83±4	7±1	nd
26-2-1999	71	176	90±5	274±14	80±4	6±1	nd
12-3-1999	85	217	75±4	219±11	76±4	5±1	2±1
15-4-1999	119	278	55±3	154±8	58±3	8±1	nd
12-5-1999	146	326	43±2	117±6	46±2	6±1	3±1
3-6-1999	168	369	27±1	71±4	28±1	7±1	2±1
8-7-1999	203	461	7±1	18±1	9±1	1±1	nd
23-7-1999[b]	218	468	5±1				

[c]Corr. coeff.: -0.9847; slope, $days^{-1}$: -0.0098653; JV 485 half-life: 70.2±3.5 days

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[a] During the winter wheat crop, in the 0- 10 cm surface soil layer, means of 4 replicates ± SD. In the 0-2, 2-4, 4-6, 6-8 surface soil layers, means of 2 replicates ± SD. nd = Not detected. JV 485 was not detected in the 8- 10, 10-15 and 15-20 cm surface soil layers.

[b] Only the 0-10 cm surface soil layer was analyzed.

[c] In the 0-10 cm surface soil layer, and for the 168 days period following the JV 485 application.

JV 485 standard in a separate lane. Elution with dichloromethane/hexane (1/0.8 vol./vol.) gave a band corresponding to JV 485 at R_f= 0.52 which was scraped off. The silica gel was extracted with acetone (40 ml) in a small glass column. 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) and was applied onto a second TLC plate. Elution with ethyl acetate/hexane (0.1/1 vol./vol.) gave a band corresponding to JV 485 at R_f = 0.61 which was scraped off, and 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 JV 485 by gas-liquid chromatography (GLC) and, for several samples, by combined GC-mass spectrometry (GC-MS).

GLC was carried out with ^{63}Ni electron capture detection. Injector and detector at 280 and

Table 2. Dissipation of JV 485 in the soil of the winter wheat crop made on sandy loam soil at Melle with JV 485 application in autumn 1998, and sowing in April 1999.

Sampling date, day-month-year	Days after JV 485 application	Cumulative rainfall, mm	JV 485 concentrations (µg kg^{-1} dry soil) in the 0-10 cm surface soil layer[a]
5-12-1998	2	10	147±7
15-12-1999	12	45	142±7
22-1-1999	50	153	99±5
26-2-1999	85	222	73±4
29-3-1999	116	289	55±3
15-4-1999	133	324	49±3
12-5-1999	160	372	32±2
3-6-1999	182	415	11±1
8-7-1999	217	507	8±1
23-7-1999	232	514	7±1

[b]Corr. coeff.: -0.9923; slope, days^{-1}: -0.0093141; JV 485 half-life: 74.4±3.7 days

[a]Means of 4 replicates ± SD. JV 485 was not detected in the 10-15 and 15-20 cm surface soil layers.

[b]In the 0-10 cm surface soil layer, and for the 160 days period following the JV 485 application.

255°C respectively. Glass column 1.80 m x 2 mm i.d. containing 5% SE 30 on Chromosorb W-HR SO-100 mesh, 200°C isothermal. Nitrogen gas at 50 ml min“. The JV 485 retention time was 2.6 min. Mass spectra were recorded at 70 eV in the electron impact (EI) or chemical ionization (CI, NH_3) modes. At the levels of 10, 5 and 1 (sensitivity limit) µg JV 485 kg^{-1} dry soil, recoveries were 87-102, 83-94 and 76-89%, respectively.

The linear regression ln y = kt + b was applied between the naperian logarithms of the JV 485 soil concentrations (y = µg kg^{-1} dry soil) in the O-10 cm soil layer and the time t (days) following the JV 485 application. The period during which the linear regression was applied was 168 days in the trial at Melle with winter wheat sowing and JV 485 application in autumn, 160 days in the trial at Melle with JV 485 application in autumn and sowing in the spring, and 183 days in the trial at Zevekote with sowing and JV 485 application in autumn. The JV 485 soil half-lives with their 95% confidence intervals were obtained using the SAS Logical 6.12 (1997, SAS Institute Inc., Cary, NC 275 13).

The JV 485 analysis standard was prepared by recrystallization of the technical product (98% JV 485, Monsanto, Belgium) in dichloromethane/hexane (1/3 vol./vol.), giving >99.5% pure JV 485. IR (KBr, cm^{-1}): 2989, 1726 (CO), 1619, 1574, 1534, 1455, 1342, 1297, 1246, 1190, 1150, 1116, 1020, 947, 907, 868, 783, 659, 625. ^{1}H-NMR(300 MHz; σ, ppm relative to tetramethylsilane in $CDCl_3$): 1.39 (t, 6H, CH($CH_3)_2)$; 4.12 (s, 3H, NCH_3); 5.29 (m, 1H, $CH(CH_3)_2$; 7.32 (m, lH, benzene-6-H); 8.07 (m, 1H, benzene-3-H).

Table 3. Dissipation and mobility of JV 485 in the soil of the winter wheat crop made on clay soil at Zevekote with sowing and JV 485 application in autumn 1998.

Sampling date, day-month-year	Days after JV 485 application	Cumulative rainfall, mm	Surface soil layers depth, cm				
			0-10	0-2	2-4	4-6	6-8
			JV 485 concentrations (μg kg^{-1} dry soil) in the surface soil layers[a]				
12-11-1998	2	6	159±8				
21-12-1998	41	143	103±5	330±17	72±4	6±1	4±1
22-1-1999	73	246	78±4	234±12	68±3	7±1	3±1
26-2-1999	108	309	52±3	150±8	53±3	3±1	nd
12-3-1999	122	338	42±2	118±6	45±2	4±1	1±1
15-4-1999	156	404	32±2	87±4	32±2	6±1	3±1
12-5-1999	183	450	22±1	57±3	23±1	5±1	3±1
5-6-1999	207	556	5±1	12±1	6±1	2±1	nd
23-7-1999[b]	255	622	4±1				

[b]Corr. coeff.: -0.9965; slope, days^{-1}: -0.010694; JV 485 half-life: 64.8±3.2 days

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[a,b] As in Table 1.

[c] In the 0-10 cm surface soil layer, and for the 183 days period after the JV 485 application.

MS (70 eV, electron impact; m/e; relative abundance, %): 444.0 (M$^+$, 87); 442 (444-2, 67); 446 (444+2, 22); 428.9 (M-CH$_3$, 12); 426.9 (9); 430.9 (3); 401.9 (M-CH(CH$_3$)$_2$+ H, 84); 399.9 (65); 403.9 (21); 384.9 (M-OCH(CH$_3$)$_2$, 100); 382.9 (77); 386.9 (25); 357.9 (M-COOCH(CH$_3$)$_2$+ H, 28); 355.9 (22); 359.9 (7).

RESULTS AND DISCUSSION

For the three trials, there was a linear relationship 1n y = kt + b between the naperian logarithms of the JV 485 soil concentrations (y = μg kg^{-1} dry soil) in the O-10 cm surface soil layer and the time t (days) elapsed since the JV 485 application (first order kinetics)(Tables 1-3). This occurred during the main crop period following the JV 485 application, that is during about the six months which followed the JV 485 application, i.e. until the end of May 1999. Several parameters changed during each crop trial: seasons, temperature, rains, etc. The apparent kinetics of the JV 485 dissipation in soil thus had no fundamental chemical meaning but was a mathematical means to analyze statistically the results. On the other hand, rainfalls were similar and normal (about 69 mm month^{-1}) in the three trials. In the two trials made on sandy-loam soil at Melle, the JV 485 soil half-lives were similar, i.e. about 72 days (Tables 1 and 2). The presence or not of the winter wheat crop had no influence on the persistence of JV 485 in soil. The organic matter secreted by the wheat roots in soil should have no influence on the JV 485 persistence. This also suggests that the amount of JV 485 absorbed by the winter wheat was very low relative to the dose applied on soil.

In the trial on clay soil at Zevekote, the JV 485 soil half-life (65 days) was not significantly different from the ones in both crops at Melle (Table 3). At Melle, 40 tons cow slurry ha^{-1} was applied in November 1998 before sowing. At Zevekote, no organic fertilizer was applied before sowing. In previous work, it appeared that the recent organic fertilizer treatments increase the herbicide soil persistences (Rouchaud et al., 1993). On the other hand, the herbicide soil persistences are usually lower in sandy soil than in clay soil (Savage, 1976). The similar soil persistences of JV 485 in the three trials thus could result from compensation between the opposite effects of the organic fertilizer treatments and of the soil texture. Results also suggest that the JV 485 soil persistence does not much change with the soil parameters.

JV 485 has a low solubility in water (0.053 mg L^{-1}). This explains its high adsorption onto soil (K_d = 140-290 ml g^{-1}) and its organic matter (K_{oc}, = 0.7 10^4- 1.7 10^4 ml g^{-1})(Prosch et al., 1997). These adsorption constants indeed should be compared to the ones of other herbicides; for instance, the isoxazol-benzamide isoxaben (solubility in water: 1.4 mg L^{-1} at pH 7; K_d = 6-13 ml g^{-1}), the triazine atrazine (solubility in water: 33 mg L^{-1} at pH 7; K_d = 0.2- 18 ml g^{-1}; K_{oc} = 39- 173 ml g^{-1}), and the triazolo-pyrimidine flumetsulam (solubility in water: 49 mg L^{-1} at pH 2.5, and 5600 mg L^{-1} at pH 7 ; K_d = 0.14-1 .05 ml g^{-1}; K_{oc} = 5-75 ml g^{-1}) (Lehmann et al., 1992; Tomlin, 1997). The high adsorption of JV 485 onto soil should be related to its perhalogenated benzoic acid ester-pyrazol chemical structure. The adsorption of JV 485 onto the soil organic matter was so high that a little change in the soil organic matter concentration or chemical structure (relative to the usual important effect of the recent organic fertilizers onto the herbicide adsorption onto soil and the soil persistence) probably had a low influence onto the JV 485 soil persistence in the trial at Zevekote relative to both trials at Melle made on bare or cropped soil (Weerts, 1998).

JV 485 was not detected in the 10-15 and 15-20 cm surface soil layers during the three trials made on sandy-loam and clay soils, the analysis sensitivity limit being 1 µg JV 485 kg^{-1} dry soil. During the winter wheat crops at Melle and Zevekote with application of JV 485 preemergence in the autumn 70 to 80% of the JV 485 residue remained in the O-2 cm surface soil layer since the treatment until May 1999. The JV 485 concentration in this thin surface soil layer was high giving there a high herbicide efficiency. JV 485 thus had a very low mobility in soil, remaining at the surface within a very thin soil layer and at a high concentration. It is only after May 1999 that JV 485 slowly moved down in the 2-4 cm surface soil layer. The low mobility of JV 485 in soil should be related to its high adsorption onto soil and its organic matter.

Like JV 485, the pyridine-carboxamide herbicide diflufenican has a low solubility in water (less than 0.050 mg L^{-1} at pH 7), and does not move significantly below the O-15 cm surface layer in winter wheat crops (Rouchaud et al., 1991; Conte et al., 1998). The diflufenican soil concentrations were measured in the O-15, O-30, 30-60 and 60-90 cm soil depths in winter wheat (main crop) and maize (rotational crop) crops made alternately for a four-year period. In the present work, soil was sampled in each of the 2 cm thick surface soil layers. In this way, it has ben observed that JV 485 really remained at a high concentration at the near soil surface during about the whole winter wheat crop. Same if it is known that the herbicide mobilities in the soil of field crops are frequently lower than the ones predicted by laboratory assays (soil columns, soil thin-layer chromatography...), the very low mobility of JV 485 in field soils is unusual (Murphy and Shaw, 1997; Shaw and Murphy, 1997; Trubey et al., 1998). It is advantageous that an herbicide does'nt move at depths lower than 20-30 cm. At greater soil depths the persistence and the mobility of the herbicides are greater than in the surface soil layers. Indeed, at greater depths, the soil organic matter and oxygen concentrations, and the herbicide adsorption onto soil are lower, the temperature decreases and the soil microbial activity and the rates of herbicide metabolism are lower (Thirunarayanan et al., 1985; Walker et al., 1989; McDowell et al., 1997; Cranmer et al., 1999; Sarmah et al., 1999).

At the harvest of the winter wheat, the JV 485 remaining in the 0- 10 cm surface soil layer was low and corresponded to 2.5 to 4.8% of the applied dose. The tilling at a depth of 25 to 30 cm which followed the harvest diluted this residue in soil. During the period between the wheat harvest and the sowing of the next crop in October or in April of the next year, the low JV 485 soil residues should be further metabolized at the fast rate corresponding to the warm and humid summer and early autumn seasons in August, September and October. The results of the measurement of the JV 485 dissipation in soil thus indicated that there is no concern about a possible phytotoxicity toward the following crop due to persistent JV 485 soil residues. Moreover, no movement of JV 485 was observed toward deeper depths in soil and toward the ground water.

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REFERENCES

Ambolet B, De Keyzer A, Grogna R (1998) JV 485: A new herbicide for preemergence broad spectrum weed control in winter wheat. 17th Columa Conf. Dijon, France, 9 to 11 December 1998, p473-480

Conte E, Morali G, Galli M, Imbroglini G, Leake CR (1998) Long-term degradation and potential plant uptake of diflufenican under field conditions. J Agric Food Chem 46: 4766-4770

Cranmer BK, Westra P, Zimdahl RL (1999) Sorption, dissipation, and leaching of metsulfuron in Colorado soils. Weed Sci 47: 353-359

Devine DD, Duke SO, Fedtke C (1993) Inhibitors of protoporphyrinogen-oxidase. In: Physiology of Herbicide Action, p152-181. Prentice Hall, NJ

Lehmann RG, Miller JR, Fontaine DD, Laskowski DA, Hunter JH, Cordes RC (1992) Degradation of a sulfonamide herbicide as a function of soil sorption. Weed Res 32: 197-205

McDowell RW, Condron LM, Main BE, Dastgheib F (1997) Dissipation of imazapyr, flumetsulam and thifensulfinon in soil. Weed Res 37: 38 l-389.

Murphy GP, Shaw DR (1997) Field mobility of flumetsulam in three Mississipi soils. Weed Sci 45: 564-567

Prosch SD, Ciha AJ, Grogna R, Hamper BC, Feucht D, Dreist M (1997) JV 485: A new herbicide for preemergence broad spectrum weed control in winter wheat. 1997 Brighton Crop Prot Conf -Weeds 2-5: 45-50

Rouchaud J, Gustin F, Van Himme M, Bulcke R, Benoit F, Maddens K (1991) Metabolism of the herbicide diflufenican in the soil of field wheat crops. J Agric Food Chem 39: 968-976

Rouchaud J, Gustin F, Van Himme M, Bulcke R, Sarrazyn R (1993) Soil dissipation of the herbicide isoxaben after use in cereals. Weed Res 33: 205-212

Sarmah AK, Kookana RS, Alston AM (1999) Degradation of chlorsulfuron and triasulfuron in alkaline soils under laboratory conditions. Weed Res 39: 83-94

Savage KE (1976) Adsorption and mobility of metribuzin in soil. Weed Sci 24: 525-528.

Shaw DR, Murphy GP (1997) Adsorption and relative mobility of flumetsulam. Weed Sci 45: 573-578.

Thirunarayanan K, Zimdahl RL, Smika DE (1985) Chlorsulfuron adsorption and degradation in soil. Weed Sci 33: 558-563

Tomlin CDS (1997) In: The Pesticide Manual. 11th Edit. Brit Crop Protect Council. Farnham, Surrey, UK

Trubey RK, Bethem RA, Peterson B (1998) Degradation and mobility of sulfometuron-methyl (Oust herbicide) in field soil. J Agric Food Chem 46: 2360-2367

Walker A, Cotterill EG, Welch SJ (1989) Adsorption and degradation of chlorsulfuron and metsulfuron-methyl in soils from different depths. Weed Res 39: 281-287

Weerts J (1998) Director. Research and Development Department, Ministry of Middle Classes and Agriculture, Brussels, Belgium.