Bull. Environ. Contam. Toxicol. (1998) 61:669-476
© 1998 Springer-Verlag New York Inc.

Bulletin of Environmental Contamination and Toxicology

Sulcotrione Soil Metabolism in Summer Corn Crops

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

[1] Laboratory of Phytopharmacy, 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

Received: 3 July 1998/Accepted: 13 October 1998

Sulcotrione (2-(2-chloro-4-(methylsulfonyl)benzoyl)-1,3-cyclohexanedione) is widely used in Europe for the efficient protection of corn crops against grass and broad-leaved weeds. It is applied post-emergence at the 4 to 6 leaves growth stage of the corn. Sulcotrione is absorbed both by the leaves and the roots of the weeds. Sulcotrione is adsorbed onto the soil organic matter (Wilson and Foy, 1992). Sulcotrione generates several isomers by ketone enolization. A procedure for the analysis of sulcotrione in soil has been described (Rouchaud et al., 1996). Sulcotrione soil dissipation and mobility has been compared in one summer corn crop grown in 1996 on sandy loam , and in winter wheat crops made in several sites of different soil textures with sulcotrione application in November 1996 (Rouchaud et al., 1997). Sulcotrione soil persistence was greater in the winter crops than in the summer one. Mobility of sulcotrione in soil always was low. However, in the winter wheat crops, sulcotrione penetrated to a lower depth than in the summer corn crop, in spite of the fact that the rains were lower in winter than in summer. At our knowledge, nothing so far has been published about sulcotrione soil metabolism. In the present work, sulcotrione metabolism has been studied in the soil of summer corn crops grown in 1996 and 1997 on sandy loam soil.

MATERIALS AND METHODS

Summer corn crops grown in 1997 in four different sites

Summer corn crops were grown in 1997 in four sites having different soil types. Sulcotrione was applied pre-emergence at the same date (except at Zingem where the sulcotrione treatment was made one week later than at the 3 other sites) on four corn crops (about 130 x 145 m each) located in 4 sites with differing soil textures and compositions, and located about 40 km apart in Belgium : 1. Melle: clay 7%, silt 38%, sand 55%, organic matter 1.71%, pH 5.6, sandy loam; no organic fertilizer was applied in spring 1997 nor in September 1996; in the past, 40 tons of cow manure ha^{-1} (or alternately 40 tons of cow slurry ha^{-1}) was applied once every 3 years. 2. Zingem: clay 10%, loam 11%, sand 79%, organic matter 1.72%, pH 7.0, loamy sand, in April 1997 (one month before sulcotrione treatment) 30 tons of cow manure ha^{-1} was applied; in the past, this treatment was applied once every 4 years. 3. Koksijde: clay 34%, loam 47%, sand 19%, organic matter 2.06%, pH 7.6, clay loam; in September 1996 (8 months before sulcotrione treatment), 30 tons of cow slung ha^{-1} was applied, winter wheat was the preceding crop; in the past, 30 tons of cow slurry ha^{-1} was applied once every 3 years. 4. Zarlardinge: clay 14%, loam 51%, sand 35%, organic matter 1.72%, PH 6.3, loam; in April 1997 (one month before sulcotrione treatment) 30 tons of cow manure ha^{-1} was applied; sugar beet was the preceding crop; in the past, corn and sugar beet crops alternated, and 30 tons of cow manure ha^{-1} was applied every year in the spring. The fields were tilled at the beginning of May 1997 ; some days later, corn (cv. Aviso) was sown. On 12-5-1997, 450 g sulcotrione ha^{-1} was applied preemergence on the fields at Melle, Koksijde and Zarlardinge, by spraying the emulsion of Mikado (30 g% sulcotrione, Zeneca, Belgium) in water (300 1 ha^{-1}). On 20-5-1997, the same sulcotrione treatment was applied pre-emergence on

---

Correspondence to: J. Rouchaud

the field at Zingem. Four 10 x 12 m replicate plots were localized at random in each field. At intervals after sulcotrione application, in each field and at the same date soil samples were taken in the 0-10 cm surface soil layer separately (and analyzed separately) in each of the 4 replicate plots (Table 1). For each soil sample, 15 cores (2.5 cm diameter) were taken at random points, the cores from each replicate plot were bulked together and then stored at -25°C until analyzed. In the 0-2, 2-4, 4-6, 6-8, 8-10, 10-15 and 15-20 cm surface soil layers, soil samples were taken in each replicate field plots, but the samples from two replicate field plots were mixed, giving a total of 2 separate replicates -for each surface soil layer- which were analyzed separately. At Melle, the sampling dates (day-month in 1997), the days after sulcotrione treatment, and the cumulative rainfall (mm) respectively were : 12-5, 0, 0; 21-5, 9, 40; 17-6, 36, 110; 8-7, 57, 178; 28-7, 77, 218; 20-8, 99, 225; 20-9, 130, 281; 10-10, 150, 347. At Zingem, these values respectively were : 21-5, 1, 0; 31-5, 10, 2; 17-6, 28, 72; S-7, 49, 140; 28-7, 69, 180; 20-8, 92, 187; 20-9, 123,243; 10-10, 143, 309. At Koksijde, these values respectively were : 12-5, 0, 0; 21-5, 9, 33; 17-6, 36, 92; 8-7, 57, 226; 28-7, 77,244; 20-8, 99, 253; 20-9, 130,338; 10-10, 150, 395. At Zarlardinge, these values respectively were : 12-5, 0, 0; 21-5, 9, 47; 17-6, 36, 100; 8-7, 57, 171; 28-7, 77, 228; 20-8, 99, 240; 20-9, 130, 286; 10-10, 150, 324.

A summer corn crop was grown and treated with sulcotrione in 1996 at Melle in the same way as in 1997, and at the same site (Rouchaud et al., 1997). In the present work, the concentrations of sulcotrione metabolites were measured in the 0-10 cm surface soil layer of the summer corn crops grown at Melle in 1996 and 1997 (Table 2).

Thin-layer chromatography (TLC) was made by using silica gel 60F 254 20 x 20 cm, 0.2 mm thick plates. The samples were applied as a band. Standards were applied on another part of the TLC plate, next to the band of the sample solution, Column chromatography was made using silica gel 60 (0.063-0.2 mm). Gas liquid chromatography (GLC) of sulcotrione and its soil metabolites was made in the following conditions. Electron capture detection. Injection and detection at 280°C. Glass column 1.80 m x 2 mm i.d. containing 5% SE30 on Chromosorb W HP SO-100 mesh. Nitrogen carrier gas at 50 ml min^{-1}. With the column oven at 200°C, the retention times of the methyl derivatives of sulcotrione and of compound **2** (5,7-diketo-7-(2-chloro-4-methylsulfonylphenyl)-heptanoic acid) respectively were 3.1 and 2.3 min. With column oven at 180°C, the retention times of compound **3** (1-acetyl-2-chloro-4-methylsulfonylbenzene; analyzed as such by GLC) and of the methylated compound **4** (methyl 2-chloro-4-methylsulfonyl-benzoic acid ester **4'**) respectively were 2.4 and 3.7 mm. In several cases, the GLC samples were further analyzed by combined GLC-mass spectrometry (GC-MS): 70 eV, electron impact EI if nothing else mentioned; otherwise, chemical ionization CI (NH_3) relative abundance, %. Infra red (IR) FTIR spectra were recorded in KBr discs, cm^{-1}. ^{1}H and ^{13}C Nuclear magnetic resonance spectra (NMR) were recorded at 300 MHz; δ, ppm, relative to tetramethylsilane in $CDCl_3$.

The sulcorione standard for analysis was prepared from its formulation Mikado (Rouchaud et al., 1996). 2-Chloro-4-methylsulfonylbenzoic acid **4** was obtained from Acros, Belgium. For preparation of 5,7-diketo-7-(2-chloro-4-methylsulfonylphenyl)-heptanoic acid **2,** sulcotrione (2.3 g, 7.0 mmole) in 3 M HCI in water was heated to reflux (5 hr) with stirring. The mixture was cooled to -20°C. The solid was filtered, recrystallized in methanol and purified by column chromatography (acetone/dichloromethane 1/3, vol./vol.), giving compound **2** (1.48 g, 4.27 mmole, 61%). IR: 3400-3017 (OH), 2934, 1696 (CO), 1618, 1414, 1383, 1310, 1213, 1150, 1098, 963, 793, 758. ^{1}H-NMR: 2.09 (2H, q,); 2.53 (4H, q); 6.08 (1H, s, COH=*CH*); 7.70 (1H, d, 6-H-phenyl); 7.93 (1H, d, 5-H-phenyl); 8.07 (1H, s, 3-H-phenyl). MS-EI: 346 (M^+, 18); 348 (346+2, 6); 328 ($M-H_2O$, 15); 330 (328+2, 5); 311 (M-Cl, 82); 259 ($M-CO_2HCH_2CH_2CH_2$, 100); 261(259+2, 33); 251 ($311-CO_2HCH_2-H$, 36); 217 ($M-CO_2HCH_2CH_2CH_2COCH_2$, 78); 219 (217+2, 27). MS-CI (NH_3): 364 ($M+NH_3+1$, 15); 366 (364+2, 5); 347 (M+1, 100); 349 (347+2, 33); 329 ($M-H_2O+1$, 29); 331 (329+2, 11); 311 (M-Cl, 58); 313 (M+2-Cl, 19).

The standard of methyl methoxy-keto-7-(2-chloro-4-methylsulfonylphenyl)-heptenoate (**2';** one of the isomers of the dimethyl derivative of compound **2**) was prepared by addition to compound **2** (0.5 g, 1.44 mmole) in ethyl acetate (100 ml), of a solution of diazomethane in ether until persistence of the yellow color. After 24 hr at 20°C, the solvent was evaporated under vacuum, and the solid was applied onto a chromatography column (ether/hexane 1/1, vol./vol.), giving compound **2’** (0.512 g, 1.37 mmole, 95%). IR: 3021, 2951, 2926, 1723 (CO), 1642, 1626, 1589, 1456, 1377, 1316, 1215, 1152, 1086, 970, 818, 750, 669. ^{1}H-NMR: 1.98 (2H, q); 2.42 (2H, t); 2.82 (2H, t); 3.14 (3H, s, SO_2CH_3); 3.62 (3H, s, CH=CO*CH_3*); 3.69 (3H, s, CO_2CH_3); 5.28 (1H, s, *CH*=COCH_3); 7.60 (1H, d, 6-H-phenyl); 7.93 (1H, d, 5-H-phenyl); 8.08 (1H, s, 3-H-phenyl). MS: 374 (M^+, 27); 376 (M+2, 9); 356 (M-H_2O, 43); 358 (356+2, 14); 339 (M-Cl, 100); 273 (M-$CO_2CH_2CH_2CH_2CH_2$ 83); 275 (273+2, 28); 265 (339-$CO_2CH_3CH_2$-H, 26).

For preparation of the standard of 1-acetyl-2-chloro-4-methylsulfonyl-benzene **3,** sulcotrione (2.3 g, 7.0 mmole) in 3 M HCl in water (100 ml) was heated to reflux (38 hr) with stirring. The mixture was cooled to -20°C and filtered. The solid was purified by column chromatography (acetone/hexane 1/4, vol./vol.) giving compound **3** (1.40 g, 6.02 mmole, 86%). IR: 3082, 3023, 3001, 1703 (CO), 1372, 1304, 1150, 1105, 1044, 966, 824, 754, 635. ^{1}H-NMR: 2.72 (3H, s, CH_3O), 3.13 (3H, s, SO_2CH_3); 7.71 (1H, d, 6-H-phenyl); 7.94 (1H, d, 5-H-phenyl); 8.08 (1H, s, 3-H-phenyl). ^{13}C-NMR 30.7 (CH_3CO); 44.2 (SO_2CH_3); 76.6, 77.1, 125.8, 129.7, 131.9, 143.9, 199.2 (CO). MS: 232 (M^+, 22); 234 (232+2, 7); 217 (M-CH_3, 100); 219 (217+2, 32); 155 (M-SO_2CH_3+2H, 62); 157 (155+2, 21); 139 (M-SO_2CH_3-CH_3+H, 86); 141 (139+2, 28).

The standard of methyl 2-chloro-4-methylsulfonylbenzoic acid ester **4’** was prepared by addition of a solution of diazomethane in ether, to compound **4** (0.5 g, 2.14 mmole) in ethyl acetate (100 ml), until persistence of the yellow color. After 24 hr at 20°C, the mixture was evaporated to dryness, and the solid was applied onto a chromatography column (dichloromethane/hexane l/l, vol./vol.), giving compound **4’** (0.515 g, 2.08 mmole, 97%). IR: 3077, 3005, 2961, 1728 (CO), 1431, 1373, 1319, 1260, 1154, 1049, 972, 895, 845, 791, 750, 685.^{1}H-NMR: 3.10 (3H, s, SO_2CH_3); 3.99 (3H, s, OCH_3); 7.87-8.08 (3H, m, H-aromatic). MS: 248 (M^+, 55); 250 (M+2, 18); 217 (M-OCH_3, 100); 219 (217+2, 33); 186 (M-CH_3SO+H, 21); 188 (186+2, 7); 169 (M-CH_3SO_2, 32); 171 (169+2, 11).

Soil analysis of sulcotrione was made according to a described procedure (Rouchaud et al., 1996) which was modified. Soil (100 g) was stirred in methanol/water (8/2 vol./vol.; 200 mL) at room temperature (1 hr). The mixture was filtered, and the extraction repeated. The filtrates were combined, water (100 ml) was added, and the methanol removed in a vacuum rotary evaporator (35°C). The volume of the water extract was adjusted to 180 ml by addition of water and was made HCl 0.24 M by addition of 12 M HCl (3.6 ml). NaCl (15 g) was added and the acidified aqueous solution was extracted two times with ethyl acetate (2 x 200 ml). The ethyl acetate solution was dried (Na_2SO_4), concentrated to 40 ml in a vacuum rotary evaporator at 30°C and further to 15 mL in the vacuum rotary evaporator at room temperature, and then concentrated to 0.5 ml under a slow stream of nitrogen (20°C). The concentrate was applied to a TLC plate. The sulcotrione standard was applied on another part of the TLC plate, next to the band of the sample solution. A first elution with ethyl acetate moved most of the yellow and green pigments in the solvent front, and sulcotrione at R_f=0-0.25. The plate was taken off the bath, quickly air dried, and placed in a second TLC bath made up of ethyl acetate/acetic acid (10/1, vol./vol.). When the solvent front reached R_f=0.50 (relative to the first elution front) the plate was taken off the TLC bath. The mixture of isomers of sulcotrione was in the band at R_f=0.15-0.45. 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 at room temperature, and then further to 1 ml under a slow stream of nitrogen (20°C). The extract was methylated by successive addition of ethyl acetate (4 mL) and a solution of diazomethane in ether (3 to 5 ml) until a persistent yellow color. After 2 hr at room temperature, the methylated extract was concentrated to 1 ml under a stream of nitrogen (20°C), and applied onto a second TLC plate. A first elution with ethyl acetate/hexane (1/3, vol./vol.) moved the solvent as far as the top of the TLC plate, and methylated sulcotrione in the band at R_f=0-0.25. The plate was taken off the bath, quickly air dried, and placed in a second TLC bath made up of ethyl acetate. When the solvent reached R_f=0.60 (relative to the first elution solvent front), the plate was taken off the TLC bath. The mixture of isomers of methylated sulcotrione was at R_f=0.43-0.53. This band was separated, and extracted with acetone. The extract was concentrated and analyzed by GLC and, for several samples, by combined GC-MS. At the 100 and 50 µg sulcotrione kg^{-1} level in soil, the recovery was 82-96%. The analytical limit of sensitivity was 5 µg sulcotrione kg^{-1} dry soil. For the 3 months period following the sulcotrione application, the linear regression ln y = kt + b was made between the naperian logarithms of the sulcotrione soil concentrations (y = µg kg^{-1} dry soil) in the 0-10 cm surface soil layer and the time t (days) elapsed after the sulcotrione soil application (first order kinetics; Table 1). The sulcotrione 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).

The soil analysis of the sulcotrione metabolites was made in the same way as for sulcotrione, except the following. Soil (100 g) was stirred in methanol/water 8/2, vol./vol. (200 ml, 20°C, 1 hr). The mixture was filtered, and the extraction repeated. The filtrates were gathered, water (100 ml) was added, the methanol was removed, the volume of the aqueous phase was adjusted to 180 ml, and made 0.24 M HCl. NaCl was added, the aqueous phase was extracted two times with ethyl acetate, the ethyl acetate solution was dried (Na_2SO_4), and concentrated successively to 40, 15 and 0.5 ml. The concentrate was applied onto a TLC plate. The standards of sulcotrione and compound **3** were applied on another part of the TLC plate, next to the band of the concentrate. Elution with ether/methanol/hexane/acetic acid 9/1/10/0.5, vol./vol., gave Band 1 at R_f= 0.1-0.25 containing sulcotrione and compound **2,** and Band 2 at R_f = 0.45 containing compounds **3** and **4.** Bands 1 and 2 were separately scraped off, the silica gel was extracted with acetone, giving respectively Extract 1 (sulcotrione + compound **2**) and Extract 2 (compounds **3** + **4**), which were concentrated to 0.5 ml. Extract 1 was applied onto a TLC plate, with the standards of sulcotrione and compound **2.** Elution with ethyl acetate/ acetic acid/hexane 5/2/6, vol./vol., gave Band 3 containing sulcotrione at R_f= 0.40, and Band 4 at R_f= 0.69 containing compound **2.** Band 4 was separated and extracted with acetone, giving Extract 4 containing compound **2.** Extract 4 was concentrated to 1 ml. Ethyl acetate (4 ml) and a solution of diazomethane in ether (5 ml) were successively added (persistence of the yellow color). After 2 hr at 20°C, the mixture was concentrated and applied onto a TLC plate. A first elution was made with ethyl acetate/hexane 1/3, vol./vol., as far as the top of the plate. The plate was taken off the bath, quickly air dried, and put into a second TLC bath made up of ethyl acetate. When the solvent reached R_f = 0.60 (relative to the first elution solvent front), the plate was taken off the bath. The main isomer of methylated compound **2** was in the band at R_f = 0.48-0.52. This band was separated, extracted with acetone, the acetone extract was concentrated and analyzed for methylated compound **2** by GLC and, in several cases, by GC-MS. Extract 2 was concentrated and analyzed for compound **3** by GLC and, for several samples, by GC-MS. Thereafter, Extract 2 was methylated and applied onto a TLC plate. Elution with chloroform gave a band containing compound **3** at R_f= 0 (**3** was not methylated by diazomethane), and a band containing methylated compound **4** at R_f= 0.45. The band at R_f = 0.45 was separated, extracted with acetone, the extract was concentrated and analyzed for methylated compound **4** by GLC and, in several cases, by GC-MS. At the levels of 50 and 10 µg kg^{-1} dry soil, as equivalents of sulcotrione, recoveries of compounds **2, 3** and **4** respectively were 78-92%, 83-97%, and 76-91%. For each of the compounds **2, 3** and **4,** the sensitivity limit was 4 µg kg^{-1} dry soil, as equivalents of sulcotrione.

RESULTS AND DISCUSSION

During the 3 months period following the application of sulcotrione in the summer corn crops grown in 1997, the sulcotrione soil half-life was 43 days in the sandy loam soil at Melle, 62 days in the loamy sand at Zingem, 31 days in the clay-loam at Koksijde, and 74 days in the loam at Zarlardinge (Table 1). In these trials made in 4 different sites, several parameters differed from site to site, namely the soil texture, pH, organic matter concentration, and recent organic fertilization. The relationships between the sulcotrione soil persistences and the soil compositions thus are made tentatively. In the soils of the same pH, and containing a low organic matter concentration (lower than 1.5%), the rate of herbicide dissipation generally depends on the soil texture, and is in the increasing order: clay < loam < sand (Savage, 1976). Results obtained here

Table 1. Sulcotrione soil dissipation and mobility in the summer corn crops made in 1997 on sandy loam (Melle), loamy sand (Zingem), clay loam (Koksijde), and loam soil (Zarlardinge).

Days after sulcotrione treatment	Surface soil layers depths, cm						
	0-10	0-2	2-4	4-6	6-8	8-10	10-15
	Sulcotrione concentrations (µg kg^{-1} dry soil) in the surface soil layers[a]						
1. Melle (sandy loam):							
0	371±19	1855±93					
9	330±17	1320±66	286±17	44±5	nd	nd	nd
36	233±16	465±33	580±29	92±5	28±5	nd	nd
57	144±7	146±7	432±22	98±5	30±5	14±5	nd
77	115±7	47±5	123±9	305±18	72±5	28±5	15±5
99	75±5	18±5	52±5	205±10	63±5	37±5	21±5
130	31±5	nd	19±5	60±5	45±5	31±5	12±5
150	nd	nd	nd	nd	nd	nd	nd
Corr. coeff.: -0.9938; slope, $days^{-1}$: -0.016207; sulcotrione half-life in the 0-10 cm soil layer: 42.8±2.1 days							
2. Zingem (loamy sand):							
1	353±18	1765±88					
10	324±16	1263±63	330±17	27±5	nd	nd	nd
28	290±15	609±37	792±40	28±5	21±5	nd	nd
49	246±15	368±18	730±51	93±5	27±5	12±5	nd
69	175±12	191±10	525±26	102±5	28±5	29±5	12±5
92	125±6	16±5	129±7	401±20	54±5	25±5	18±5
123	43±5	nd	62±5	130±5	43±5	15±5	16±5
143	nd	nd	nd	16±5	nd	nd	nd
Corr. coeff.: -0.9763; slope, $days^{-1}$: -0.011196; sulcotrione half-life in the 0-10 cm soil layer: 61.9±3.1 days.							
3. Koksijde (clay loam):							
0	394±19	1970±99					
9	295±15	818±41	605±36	52±5	nd	nd	nd
36	182±11	231±16	538±27	110±6	31±5	nd	nd
57	115±6	28±5	122±6	347±21	53±5	25±5	nd
77	71±5	15±5	44±5	211±11	62±5	23±5	18±5
99	40±5	nd	26±5	47±5	78±5	49±5	23±5
130	10±5	nd	nd	22±5	28±5	12±5	14±5
150	nd	nd	nd	nd	nd	nd	nd
Corr. coeff.: -0.9966; slope, $days^{-1}$: -0.022437; sulcotrione half-life in the 0-10 cm surface soil layer: 30.9±1.6 days.							
4. Zarlardinge (loam):							
0	356±18	1780±89					
9	342±17	1030±52	388±19	292±15	nd	nd	nd
36	290±15	597±36	573±29	226±11	54±5	nd	nd
57	251±15	248±17	752±38	163±10	65±5	27±5	nd
77	190±13	102±5	548±33	196±10	74±5	30±5	13±5
99	135±7	72±5	345±17	138±7	92±5	28±5	15±5

Table 1. contd.

130	**42±5**	**13 ±5**	**80±5**	**67±5**	**23±5**	**17±5**	**12±5**
150	n d	n d	n d	12±5	n d	n d	n d

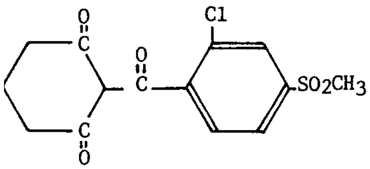
Corr. coeff. : -0.9675; slope, days-^{1}: -0.0094348; sulcotrione half-life in the 0-10 cm surface soil layer: 73.5±3.7 days

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 and 10-15 cm surface soil layer, means of 2 replicates ± SD. Sulcotrione was not detected in the 15-20 cm surface soil layer.

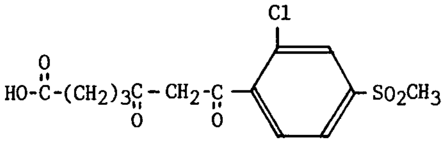
indicate that the soil texture is not the main parameter determining the sulcotrione soil persistence. The fast dissipation in the clay-loam soil at Koksijde could be related to its high pH 7.6. Previous trials indeed indicated that sulcotrione dissipation was faster in neutral or slightly basic soils than in acidic ones (Rouchaud et al., 1997). The recent application of organic fertilizer slows down the herbicides soil dissipation (Rouchaud et al., 1993). The trial made at Koksijde suggests that the application of cow slurry 8 months before the sulcotrione treatment only slightly reduced the rate of sulcotrione soil dissipation. In spite of the loamy sand texture and the soil pH 7.0 at Zingem, the sulcotrione soil persistence there was high; this is probably due to the application of cow manure one month before the sulcotrione treatment. At Zarlardinge, the application of cow manure one month before the sulcotrione treatment -this organic fertilizer treatment being repeated every year-, the acid soil pH 6.3 and the loam texture simultaneously contributed to the high sulcotrione soil persistence. After the first 3 months period following the sulcotrione application, the rates of sulcotrione soil dissipation increased, and became greater than the ones forecasted by the first order kinetics. At corn harvest, sulcotrione generally was no longer detected in the analyzed soil layers (0-2, 2-4, 4-6, 6-8, 8-10, 10-15 and 15-20 cm).

There was a soil layer containing the highest sulcotrione concentration (Table 1). This soil layer slowly moved deeper with time. During the first month after sulcotrione treatment, in the 4 sites the maximum residue was in the 0-2 and 2-4 cm surface soil layers. Two months after treatment, it still was in the 0-2 and 2-4 cm surface soil layers at Melle, Zingem and Zarlardinge, but in the 4-6 cm one at Koksijde. During the third and fourth months after application, sulcotrione remained concentrated in the 6-8 cm surface soil layer at Koksijde, the 4-6 cm one at Melle and Zingem, and the 2-4 cm one at Zarlardinge. The factors which reduced the moving down of sulcotrione in soil probably were the same as the ones which slowed down its soil dissipation: the recent organic fertilization, the acid soil pH and, to a lesser extent, the clay texture relative to the sandy one. Thus there was no homogeneous diffusion of sulcotrione in soil which would dilute the herbicide and reduce its efficiency. On the contrary, one soil layer contained a highest sulcotrione concentration, where the herbicide efficiency was high. At the 4 sites, in the 10-15 cm surface soil layer only small amounts of sulcotrione were detected, and sulcotrione was never detected in the 15-20 cm soil layer. Most of the sulcotrione residue thus remained in the higher soil surface layers. To it contributed the moving up movement of water in soil during summer due to the water evaporation and absorption by corn, and the high organic matter soil concentration given by the corn root system (*Weerts, 1998*).

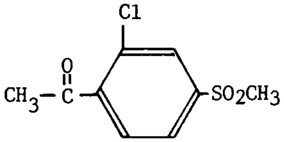
Sulcotrione soil metabolism initially generated compound **2** (5,7-diketo-7-(2-chloro-4-methylsulfonylphenyl)-heptanoic acid) by the unexpected opening of the cyclohexanedione ring through hydrolysis (Figure 1, Table 2). 1,3-Cyclohexanedione and 2-chloro-4-methylsulfonylbenzoic acid **4** indeed were expected from the hydrolysis of sulcotrione, which would have been the reverse of the sulcotrione synthesis process, i.e. benzoylation at the carbon-2 of 1,3-cyclohexanedione, this carbon bearing two active hydrogen atoms (Chin, 1988). For GLC detection, compound **2** must be methylated. Like sulcotrione, methylation of compound **2** generates several isomers. These are dimethylated. This is at the opposite of sulcotrione which is transformed by diazomethane into monomethyl isomers, during the sulcotrione analysis procedure. When the amount of compound **2** was equal to or lower than 10 mg, methylation of



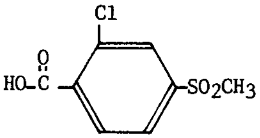
SULCOTRIONE



2



3



4

Figure 1. Sulcotrione and its soil metabolites.

Table 2. Sulcotrione soil metabolism in the 0-10 cm surface soil layer of the summer corn crops made on sandy loam soil at Melle in 1996 and 1997.

Days after sulcotrione treatment	Concentrations of sulcotrione and of its metabolites **2-4** (μg kg^{-1} dry soil, as equivs of sulcotrione) in the 0-10 cm surface soil layer[a]			
	Sulcotrione	**2**	**3**	**4**
1. Crop of 1996:				
0	373±19			
14	316±18	16	8	nd
31	252±13	25	18	10
47	185±8	39	25	21
66	131±9	53	24	22
80	110±6	60	14	16
98	83±5	48	10	14
110	50±5	15	8	11
2. Crop of 1997:				
0	371±19			
9	330±17	20	nd	nd
36	233±16	37	15	nd
57	144±7	41	28	22
77	115±7	36	22	17
99	75±5	51	19	20
130	31±5	21	17	22
150	nd	nd	nd	nd

a. Means of 4 replicates ± SD. For compounds **2**, **3** and **4**, ± SD = ±3 μg kg^{-1} dry soil, as equivs of sulcotrione.

the soil extracts (or of compound **2** produced by synthesis) generated one major dimethyl isomer which was analyzed by GLC and GC-MS. Compound **2** is a carboxylic acid and as such should be strongly adsorbed onto soil. However the herbicide activity of compound **2** was about 75% of that of sulcotrione. R Bulcke and H. Eelen measured the herbicide activity of compounds **2, 3** and **4,** by means of bioassays made in the greenhouse, and using sugar beet and yellow mustard as test plants. Metabolites **3** and **4** have no herbicide activity. At least two ketone functions therefore are required for herbicide activity.

In the trial made at Melle in 1997, two months after the sulcotrione treatment, the metabolite **2** soil concentration was 28% of that of sulcotrione; three months after the sulcotrione application, this percentage was 68% (Table 2). In the trial made at Melle in 1996, these percentages respectively were 41 and 55%. Metabolite **2** thus significantly extended the herbicide protection given by sulcotrione. At the end of October 1996 and 1997, at the harvest of both corn crops at Melle, metabolite **2** could no longer be detected in the soil.

Metabolite **2** was further transformed in soil into metabolite **3** (1-acetyl-2-chloro-4-methylsulfonyl-benzene) by hydrolytic cleavage between the C-5 and C-6 carbon atoms of metabolite **2.** Compound **3** was stable as indicated by its accumulation during its synthesis starting from sulcotrione. Metabolite **3** was generated in significant concentrations in soil (10 to 20% of the sulcotrione residue, after the first two months period following treatment), starting from metabolite **2.** Metabolite **3** has no herbicide activity.

Attempts were made to oxidize ketone **3** into 1-acetoxy-2-chloro-4-methylsulfonylbenzene **5** with 3-chloroperbenzoic acid (Baeyer-Villiger reaction). Compound **3** remained unchanged in spite of heating and acid catalysis by p-toluenesulfonic acid. Also, 2-chloro-4-methylsulfonylphenol **6** -which could have been generated by hydrolysis of compound **5-** has not been detected in the soil of the corn crops.

In the soil of the summer corn crops, sulcotrione thus was transformed into the herbicide metabolite **2,** and thereafter successively into ketone **3** and acid **4.** This corresponded to the progressive transformation in soil of the parent herbicide into non-toxic common compounds. At corn harvest, sulcotrione and its metabolites **2, 3** and **4** were no longer detected in soil.

Acknowledgments. Mass spectra were recorded by C. Moulard (Université Libre de Bruxelles, Brussels, Belgium). The authors thank J. Weerts, Director of the Research and Development Department, Ministry of Agriculture, Brussels, for interesting discussions. The research was supported by the Research and Development Department of the Ministry of Middle Classes and Agriculture, Brussels, Belgium.

REFERENCES

Chin HLM (1988) 2-(2-Substituted benzoyl)-4-(substituted)-1,3-cyclohexanediones, a process for their production and a herbicidal composition containing them. Stauffer Chemical Co. Eur Pat Appl EP 264, 859, 27 Apr 1988. US Appl 919, 277, 16 Oct 1986.

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.

Rouchaud J, Thirion A, Callens D, Bulcke R (1996) Soil dissipation of the post-emergence herbicide sulcotrione in maize crops treated with organic fertilizers. Bull Environ Contam Toxicol 57: 398-405.

Rouchaud J, Neus O, Callens D, Bulcke R (1997) Soil mobility of sulcotrione in corn and winter wheat crops. Mededelingen Fac. Landbouww. Univ. Gent, 62/3a: 815-823.

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

Wilson JS, Foy CL (1992) Influence of various soil properties on the adsorption and desorption of ICIA-0051 in five soils. Weed Technol 6: 583-586.