

ANNEX B

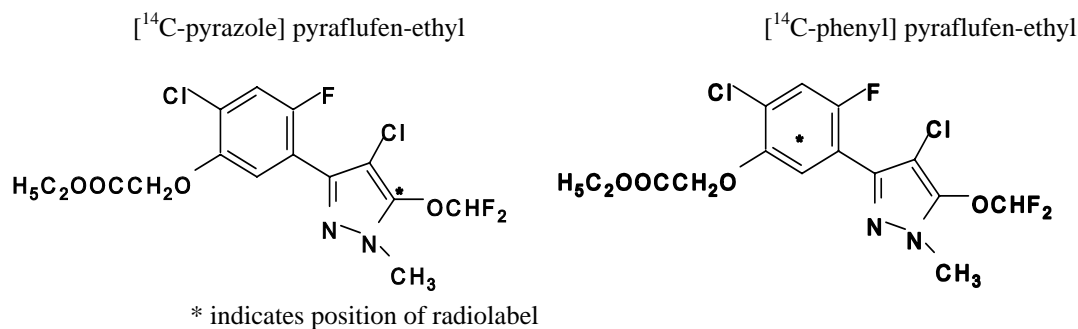
Pyraflufen-ethyl

B.7 Environmental fate and behaviour

B.7.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)

The fate and behaviour of pyraflufen-ethyl in soil has been investigated using [^{14}C -pyrazole] and [^{14}C -phenyl] pyraflufen-ethyl.

Figure B.7.1: Positions of radiolabelling in pyraflufen-ethyl used in soil degradation studies

**B.7.1.1 Route of degradation (Annex IIA 7.1.1.1)****B.7.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)**

(^{14}C)-ET-751: Aerobic soil metabolism (Purser, D. , 1996a)

Guidelines :

EC Directive 91/414/EEC, Section 7.1.1.1 (Draft, April 1993)

GLP :

Yes

Material and Methods :Test substance :

[^{14}C -phenyl] pyraflufen-ethyl, specific activity : 134.8 $\mu\text{Ci/mg}$, radiochemical purity = 98.4%

[^{14}C -pyrazole] pyraflufen-ethyl, specific activity : 145.7 $\mu\text{Ci/mg}$, radiochemical purity >99%

Soil :

Table B.7.1.1.1-1 : Characteristics of the soil - aerobic soil metabolism

Soil Type (UK Classification)	Sandy loam
Organic carbon (%)	2.0
Organic matter (%)	3.5
Cation exchange capacity (meq/100g)	14.7
Particle size distribution (%)	
63 μm to 2 mm	53
2 μm to 63 μm	37
< 2 μm	10
pH (1:2.5) in 1M KCl	5.8
pH in water	5.82
Maximum water holding capacity (%)	
pF 2.5	19.9
pF 2.3	23.0
pF 0	53.7
Microbial biomass ($\mu\text{g C/g soil}$)	
Pre-study	433.99
Post-study	291.70 - 341.84

Experimental design :

The aerobic degradation of [^{14}C -phenyl] and [^{14}C -pyrazole] pyraflufen-ethyl was investigated in a sandy loam soil over a period of 178 days. The test substances were applied to duplicate samples of the soil, with a moisture content pF value of 2.3, at rates equivalent to approximately 20 and 200 g a.s./ha (1 μg a.s./50 g soil and 10 μg a.s./ 50 g soil) and incubated in the dark at $20 \pm 2^\circ\text{C}$. Samples were taken at intervals of 0, 1, 3, 7, 14, 28, 64, 100 and 178 days for determination of radioactivity by combustion and liquid scintillation counting (LSC). Samples of the soils were extracted with acetonitrile/1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and two-dimensional thin layer chromatography (2D-TLC). The presence and structure of pyraflufen-ethyl and its 3 major degradation products (E-1, E-2, E-3) were confirmed by MS.

Findings :

Table B.7.1.1.1-2 : Distribution of applied radioactivity (mean %) after application of [^{14}C -phenyl] pyraflufen-ethyl at 20 g a.s./ha to soil under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	64	100	178
<u>Extractable</u>	102.63	100.40	100.86	99.20	97.62	92.82	91.11	89.62	83.01
Pyraflufen-ethyl	74.45	13.89	7.45	8.06	3.35	4.72	N.D.	2.16	N.D.
E-1	16.15	75.54	78.79	73.36	41.96	23.04	9.05	11.06	7.09
E-2	N.D.	1.23	5.93	6.85	15.54	15.55	14.15	11.79	N.D.
E-3	N.D.	N.D.	4.70	9.36	28.19	46.62	58.63	63.50	62.87
E-9	N.D.	N.D.	2.24	N.D.	1.57	1.39	1.00	N.D.	N.D.
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	9.69
Unresolved Background	0.69	1.74	1.36	1.80	1.09	1.21	1.46	1.82	1.43
$^{14}\text{CO}_2$	N.A.	N.D.	0.04	0.08	0.79	1.18	1.5	2.53	8.71
'Bound'	0	0.81	3.26	2.99	4.08	8.12	10.28	13.70	15.98
Recovery	102.63	101.20	104.15	102.26	102.48	102.12	102.88	105.84	107.69

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.1.1-3 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole] pyraflufen-ethyl at 20 g a.s./ha to soil under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	64	100	178
<u>Extractable</u>	103.54	102.86	103.29	101.97	100.01	96.59	92.43	88.81	86.74
Pyraflufen-ethyl	80.10	12.98	6.66	5.95	5.15	3.46	N.D.	N.D.	N.D.
E-1	22.57	84.10	88.15	74.91	44.59	23.56	8.97	7.78	2.57
E-2	N.D.	5.41	5.85	5.50	16.21	16.52	14.39	13.31	N.D.
E-3	N.D.	N.D.	5.21	8.49	24.91	48.24	58.46	61.07	68.96
E-9	N.D.	N.D.	N.D.	N.D.	N.D.	1.08	N.D.	N.D.	N.D.
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	10.34
Unknown 5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.22	N.D.
Unresolved Background	1.03	0.56	1.50	1.87	0.50	1.18	0.96	0.66	0.71
$^{14}\text{CO}_2$	N.A.	0.06	0.13	0.21	0.32	0.51	0.83	1.71	2.72
'Bound'	0	0	2.39	3.39	5.39	8.98	11.61	16.36	14.57
Recovery	103.54	102.92	105.80	105.56	105.71	106.08	104.86	106.87	104.02

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.1.1-4 : Distribution of applied radioactivity (mean %) after application of [^{14}C -phenyl] pyraflufen-ethyl at 200 g a.s./ha to soil under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	64	100	178
<u>Extractable</u>	109.95	108.90	107.33	104.51	98.28	93.90	87.33	83.25	81.71
Pyraflufen-ethyl	91.96	10.40	4.80	4.66	1.40	3.01	2.12	N.D.	N.D.
E-1	15.93	93.99	92.81	79.57	56.69	21.31	8.13	7.23	3.36
E-2	N.D.	2.40	8.51	5.21	14.11	18.95	15.10	11.02	N.D.
E-3	N.D.	N.D.	5.88	10.63	23.52	44.86	53.43	53.96	58.27
E-9	N.D.	N.D.	N.D.	1.05	2.93	2.78	1.76	N.D.	0.54
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.34	0.85	8.15
Unknown 5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.90	3.85	3.35
Unresolved Background	0.47	0.63	0.30	0.09	0.21	0.34	0.94	1.30	1.24
$^{14}\text{CO}_2$	N.A.	0.01	0.05	0.15	0.40	0.75	1.37	2.13	3.25
<u>'Bound'</u>	0	0.50	2.38	3.28	5.03	9.02	11.05	14.95	15.39
<u>Recovery</u>	109.95	109.40	109.76	107.94	103.70	103.66	99.79	100.32	100.34

A. : Not analysed, N.D. : Not detected

Table B.7.1.1.1-5 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole] pyraflufen-ethyl at 200 g a.s./ha to soil under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	64	100	178
<u>Extractable</u>	104.50	99.94	98.66	97.36	91.69	88.03	83.76	87.28	79.36
Pyraflufen-ethyl	71.73	6.82	4.40	2.62	1.51	0.65	3.93	N.D.	N.D.
E-1	27.68	85.48	81.23	75.35	39.35	15.44	5.17	4.16	3.17
E-2	N.D.	4.86	6.07	6.91	18.54	17.60	14.31	11.63	3.80
E-3	N.D.	0.45	3.69	9.84	32.29	46.51	44.44	56.13	55.89
E-9	N.D.	1.14	1.97	N.D.	0.89	2.63	1.72	1.09	0.60
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.52	1.32	5.43
Unknown 5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.93	N.D.	1.06
Unresolved Background	0.46	0.49	0.40	1.08	0.27	0.19	1.08	0.24	0.23
$^{14}\text{CO}_2$	N.A.	0.07	0.13	0.21	0.32	0.55	0.88	1.18	1.94
<u>'Bound'</u>	0.24	0.95	2.08	3.68	7.64	11.59	13.93	14.89	17.04
<u>Recovery</u>	104.73	100.95	100.87	101.25	99.65	100.17	98.59	103.34	98.33

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.1.1-6 : Rate of degradation of pyraflufen-ethyl and metabolite E-1 under aerobic conditions at 20°C

Label Position and Application Rate (Active Substance)	DT ₅₀		DT ₉₀	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
Phenyl label (20 g/ha)	< 0.5	20	2.1	67
Phenyl label (200 g/ha)	< 0.5	17	1.1	57
Pyrazole label (20 g/ha)	< 0.5	20	1.7	65

Pyrazole label (200 g/ha)	< 0.5	16	0.83	52
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Conclusions :

In soil under aerobic conditions, pyraflufen-ethyl is rapidly degraded by hydrolysis to E-1. (DT₅₀ a.s. <0.5 d, DT₉₀ a.s. = 0.83 - 2.1 days).

The primary metabolite E-1 is further degraded to E-2 (DT₅₀ E-1 = 16-20 d, DT₉₀ E-1 = 52-67 d) (E-2 : maximum of 14-19% of applied radioactivity after 14-28 days then declining) and E-3 (56-69% applied radioactivity after 178 days), respectively. Small quantities of E-9 are also formed along with other minor/insignificant unidentified degradation products.

Soil 'bound' residues increased with time (up to 17% of the applied radioactivity after 100 days). The mineralization is low (1.18 - 2.53% of the applied radioactivity after 100 days)

The unknown 2 metabolite reaching 10% of the applied radioactivity was partially identified by MS. This substance would contain in its structure the phenyl group and the pyrazole group.

Hydrolysis of pyraflufen-ethyl to E-1 was also observed under sterile conditions indicating that the initial degradation process included chemical decomposition. However, no E-2 was found under sterile conditions indicating that micro-organisms were necessary for this hydrolysis reaction.

B.7.1.1.2 Anaerobic degradation in soil (Annex IIA 7.1.1.1.2)

(¹⁴C)-ET-751: Anaerobic soil metabolism. Purser, D. (1996b).

Guidelines :

EC Directive 91/414/EEC, Section 7.1.1.1 (Draft, April 1993)

GLP :

Yes

Material and Methods :**Test substance :**

[¹⁴C-phenyl] pyraflufen-ethyl, specific activity : 134.8 µCi/mg, radiochemical purity = 98.4%

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 145.7 µCi/mg, radiochemical purity >99%

Soil - Experimental design:

The anaerobic degradation of [¹⁴C-phenyl] and [¹⁴C-pyrazole] pyraflufen-ethyl was investigated in a sandy loam soil over a period of 101 days. The characteristics of the soil are presented in Table B.7.1.1.1-1 with the difference that the microbial biomass of the soil at the end of the study was 342.66 - 433.63 µg C/g soil. Deionised water to a depth of 3 cm above the surface was added to samples of the soil which were pre-incubated for 32 days prior to application of the test substances at rates equivalent to approximately 20 and 200 g a.s./ha and incubated in the dark at 20 ± 2°C. Samples were taken at intervals of 0, 1, 3, 7, 14, 28, 63 and 101 days for determination of radioactivity by combustion and liquid scintillation counting (LSC). Samples of the soils were extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and two-dimensional thin layer chromatography (2D-TLC). Traps were used to collect volatile degradation products.

Findings :

Table B.7.1.1.2-1 : Distribution of applied radioactivity (mean %) after application of [^{14}C -phenyl] pyraflufen-ethyl at 20 g a.s./ha to soil under anaerobic conditions (HPLC) (*)

	Sampling Interval (Days)							
	0	1	3	7	14	28	63	101
Pyraflufen-ethyl								
Water	91.53	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-1								
Water	N.D.	92.55	82.03	64.34	42.14	30.91	27.00	25.70
Soil	N.A.	6.45	17.79	31.4	51.48	46.16	48.99	35.28
E-2								
Water	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil	N.A.	N.D.	N.D.	N.D.	3.25	8.87	22.25	34.54
Unresolved background								
Water	0.80	0.77	1.45	0.63	0.71	0.33	N.D.	0.20
Soil	N.A.	N.D.	0.23	0.26	0.37	0.47	0.38	1.27
'Bound'	N.D.	N.D.	N.D.	N.D.	1.66	1.68	1.53	0.97
$^{14}\text{CO}_2$	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.11	0.2
Recovery	95.76	96.16	94.47	96.26	98.23	91.21	98.78	95.69

A. : Not analysed, N.D. : Not detected

Table B.7.1.1.2-2 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole] pyraflufen-ethyl at 20 g a.s./ha to soil under anaerobic conditions (HPLC) (*)

	Sampling Interval (Days)							
	0	1	3	7	14	28	63	101
Pyraflufen-ethyl								
Water	92.68	5.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-1								
Water	N.D.	85.69	78.93	62.43	53.24	36.36	29.17	23.92
Soil	N.A.	11.87	23.07	33.47	45.83	55.62	64.22	42.54
E-2								
Water	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.66
Soil	N.A.	N.D.	N.D.	N.D.	2.37	9.13	8.49	30.90
Unresolved background								
Water	1.14	1.44	0.41	0.44	0.82	0.69	0.30	0.17
Soil	N.A.	0.08	0.41	0.36	N.D.	0.84	N.D.	0.92
'Bound'	N.D.	N.D.	N.D.	N.D.	N.D.	0.75	0.74	N.D.
$^{14}\text{CO}_2$	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Recovery	94.79	101.31	98.56	96.23	98.09	93.47	98.00	98.23

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.1.2-3 : Distribution of applied radioactivity (mean %) after application of [^{14}C -phenyl] pyraflufen-ethyl at 200 g a.s./ha to soil under anaerobic conditions (HPLC) (*)

	Sampling Interval (Days)							
	0	1	3	7	14	28	63	101
Pyraflufen-ethyl								
Water	83.75	12.88	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil	7.20	N.A.	0.18	N.D.	N.D.	N.D.	N.D.	N.D.
E-1								
Water	1.49	76.11	69.94	60.41	45.31	36.13	27.22	23.22
Soil	0.89	N.A.	21.77	33.61	46.05	51.31	45.21	30.58
E-2								
Water	N.D.	N.D.	N.D.	N.D.	N.D.	0.37	0.46	0.75
Soil	N.D.	N.A.	0.36	1.19	4.36	8.93	17.33	21.70
Unresolved background								
Water	0.23	0.51	0.52	0.61	0.84	0.62	0.13	0.46
Soil	0.08	N.A.	0.25	0.50	0.63	0.60	1.04	0.77
'Bound'	N.D.	N.D.	N.D.	0.31	0.63	1.18	2.12	2.04
$^{14}\text{CO}_2$	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	0.06	0.11
Recovery	96.65	93.42	94.99	98.32	99.48	91.19	95.42	96.87

A. : Not analysed, N.D. : Not detected

Table B.7.1.1.2-4 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole] pyraflufen-ethyl at 200 g a.s./ha to soil under anaerobic conditions (HPLC) (*)

	Sampling Interval (Days)							
	0	1	3	7	14	28	63	101
Pyraflufen-ethyl								
Water	88.91	4.95	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil	N.A.	2.30	0.06	0.11	N.D.	N.D.	N.D.	N.D.
E-1								
Water	0.56	85.07	77.84	65.14	49.95	25.12	24.23	21.77
Soil	N.A.	8.24	18.38	27.41	41.34	46.47	46.96	39.87
E-2								
Water	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.41	0.83
Soil	N.A.	N.D.	0.19	1.05	3.52	7.42	18.91	28.04
Unresolved background								
Water	0.26	0.52	0.39	0.63	0.65	0.25	0.23	0.69
Soil	N.A.	0.11	0.15	0.52	0.33	0.53	1.42	0.62
'Bound'	N.D.	N.D.	N.D.	0.08	0.47	1.07	1.88	1.81
$^{14}\text{CO}_2$	N.A.	N.D.	N.D.	N.D.	N.D.	0.01	0.05	0.07
Recovery	94.64	97.04	100.21	101.70	97.93	99.25	95.92	98.96

N.A. : Not analysed, N.D. : Not detected

(*) : % recovery of soil extracts, water and unit wash are present in the study report.

Table B.7.1.1.2-5 : Rate of degradation of pyraflufen-ethyl and metabolite E-1 under anaerobic conditions at 20°C

Label Position and Application Rate (Active Substance)	DT ₅₀		DT ₉₀	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
Phenyl label (20 g/ha)	< 1	147	< 1	487
Phenyl label (200 g/ha)	< 1	125	< 3	414
Pyrazole label (20 g/ha)	< 1	191	< 1	634
Pyrazole label (200 g/ha)	< 1	159	< 1	528

Conclusions :

In soil under anaerobic conditions pyraflufen-ethyl is rapidly degraded to its major degradation product E-1 (DT₅₀ a.s. and DT₉₀ a.s. < 1d). The major degradation product E-1 was found in both the water and soil (DT₅₀ E-1 = 125-191 d, DT₉₀ E-1 = 414-634 d). E-2 was a major degradation product in soil but was not found at significant levels in the aqueous phase. Degradation products E-3, E-11 or E-8, E-9 were found at very low levels (N.D. to 1.5% of the applied radioactivity) in either the soil or aqueous phase.

The mineralization is very low (up to 0.2% of the applied radioactivity after 101 days). The bound residue level is very low (up to 2.04% of the applied radioactivity after 101 days).

B.7.1.1.3 Soil photolysis (Annex IIA 7.1.1.1.2)

(¹⁴C)-ET-751: Photodegradation on a soil surface. (Lewis, C. J., 1996a)

Guidelines:

EC Directive 91/414/EEC, Section 7.1.1.1.2 (Draft, September 1994)

GLP :

Yes

Material and Methods :**Test substance :**

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 145.7 µCi/mg, radiochemical purity >99%

Soil :

Table B.7.1.1.3-1 : Characteristics of the soil - Photodegradation of the a.s.

Soil Type (UK Classification)	Sandy silt loam
Organic carbon (%)	2.1
Organic matter (%)	3.6
Cation exchange capacity (meq/100g)	17.4
Particle size distribution (%)	
63 µm to 2 mm	34
2 µm to 63 µm	54
< 2 µm	12
pH (1:2.5) in 1M KCl	5.8
pH in water	6.4
Maximum water holding capacity (%)	
pF 2.5	26.6
pF 0	61.7

Experimental design :

The photodegradation of [¹⁴C-pyrazole] pyraflufen-ethyl was investigated on a sandy silt loam soil over a period of 31 days. The test substance was applied to duplicate samples of the air dried soil at a rate equivalent to 200 g a.s./ha and continuously irradiated at 20 ± 3°C for up to the equivalent of 31 days sunlight exposure with a Hanau Suntest CPS accelerated exposure machine which had a spectral distribution close to that of natural sunlight. Control samples were kept in the dark at 20 ± 3°C. Traps were used to collect volatile degradation products. The soils were extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by liquid scintillation counting (LSC), HPLC and 2D-TLC. Radioactivity remaining in the soil was determined by combustion and LSC. DT₅₀ and DT₉₀ values of the dark controls were calculated by interpolation from the graphs of per cent remaining against time and for the irradiated samples were calculated by linear regression of log per cent remaining

against time.

Findings :

Table 7.1.1.3-1 : Distribution of applied radioactivity (mean %) after irradiation of [^{14}C -pyrazole] pyraflufen-ethyl applied to soil at 200 g a.s./ha (HPLC)

	Sampling Interval (Days)				
	0	3.4 - 3.5	9.7 - 9.9	16.1	30.9
Irradiated soil					
<u>Soil extract</u>	100.46	97.51	94.95	99.13	95.75
Pyraflufen-ethyl	99.15	93.69	92.23	95.65	89.72
E-1	N.D.	2.88	2.39	2.42	3.18
Unresolved background	1.31	0.27	0.32	1.06	1.28
<u>Soil residue</u>	0.20	0.45	0.84	1.19	1.08
$^{14}\text{CO}_2$	N.A.	0.30	0.89	1.72	3.44
<u>Recovery</u>	100.66	98.46	96.68	102.04	100.27
Dark controls					
<u>Soil extract</u>	100.46	100.94	99.16	101.44	100.15
Pyraflufen-ethyl	99.15	70.34	4.75	2.19	N.D.
E-1	N.D.	30.84	94.61	98.42	98.62
Unresolved background	1.31	-0.25	-0.20	0.82	0.42
<u>Soil residue</u>	0.20	0.26	0.53	0.89	0.59
$^{14}\text{CO}_2$	N.A.	N.D.	0.29	0.29	2.50
<u>Recovery</u>	100.66	101.20	99.98	102.61	103.47

N.A. : Not analysed, N.D. : Not detected

Conclusions :

No photodegradation of pyraflufen-ethyl occurred under the conditions of the test. The DT_{50} and DT_{90} values for photodegradation of pyraflufen-ethyl on a soil surface were calculated to be 299 and 993 days, respectively.

The DT_{50} and DT_{90} values for the dark control samples were approximately 6 and 9 days, respectively. Degradation in the dark control samples was a result of hydrolysis of pyraflufen-ethyl to E-1 caused by moisture present in the soil.

B.7.1.2 Rate of degradation (Annex IIA 7.1.1.2.1; Annex IIIA 9.1.1.1.1)**B.7.1.2.1 Aerobic degradation**

(¹⁴C)-ET-751: Soil degradation at 20°C (Purser, 1995a).

Guidelines:

EC Directive 91/414/EEC, Section 7.1.1.2.1 (Draft, July 1993)

GLP :

Yes

Material and methods :Test substance :

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 145.7 µCi/mg, radiochemical purity >99%

Soil :

Table B.7.1.2.1-1 : Characteristics of the soil - aerobic degradation rate study

Soil Type (UK Classification)	Sandy silt loam	Sandy loam	Clay loam
Organic carbon (%)	1.4	1.1	3.4
Organic matter (%)	2.4	1.9	5.9
Cation exchange capacity (meq/100g)	13.1	9.6	30.6
Particle size distribution (%)			
63 µm to 2 mm	46	70	28
2 µm to 63 µm	40	16	38
< 2 µm	14	14	34
pH (1:2.5) in 1M KCl	5.3	4.0	6.9
pH in water	6.34	4.94	7.81
Maximum water holding capacity (%)			
pF 2.5	16.7	12.1	35.1
pF 2.3	21.3	14.3	41.7
pF 0	49.5	44.6	88.8
Microbial biomass (µg C/g soil)			
Pre-study	77.9	117.11	1510.06
Post-study	118.35	147.20	1557.42

Experimental design :

The degradation rate of [¹⁴C-pyrazole] pyraflufen-ethyl was investigated in three soils under aerobic conditions at 20°C over a period of 179 days. The test substances were applied to duplicate samples of the soil, (10 µg a.s./50 g soil) with a moisture content pF value of 2.3, at rates equivalent to approximately 200 g a.s./ha and incubated in the dark at 20 ± 2°C. No attempt was made to determine volatiles and bound residues. Samples were extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and confirmed by two-dimensional thin layer chromatography (2D-TLC). Radioactivity in the extracts was measured by liquid scintillation counting (LSC). The DT₅₀ and DT₉₀ values for ET-751 were determined by inspection of the graphical presentation of the HPLC data and the values for E-1 were calculated from the HPLC using computer software assuming first-order reaction kinetics.

Findings:Table B.7.1.2.1-2 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole] pyraflufen-ethyl at 200 g a.s./ha to sandy silt loam under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	66	100	179
Pyraflufen-ethyl	91.55	19.73	11.46	6.55	3.82	2.39	N.D.	0.87	N.D.
E-1	1.56	71.94	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-2	N.D.	3.90	4.32	6.14	16.62	27.05	37.25	38.63	24.00
E-3	N.D.	N.D.	N.D.	3.02	11.19	21.85	26.67	32.29	38.36
E-9	N.D.	N.D.	N.D.	1.11	3.94	2.90	2.52	1.00	N.D.
Unknown 1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.59
Unknown 2	N.D.	0.79	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Unresolved Background	1.27	0.30	0.31	0.66	0.38	0.28	0.23	0.75	1.01
Soil extract	94.39	95.80	99.34	101.14	100.94	86.30	89.82	90.56	77.93

Table B.7.1.2.1-3 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole] pyraflufen-ethyl at 200 g a.s./ha to sandy loam under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	66	100	179
Pyraflufen-ethyl	88.79	21.24	4.21	2.97	3.58	0.63	N.D.	N.D.	N.D.
E-1	6.09	69.73	74.56	59.76	48.22	14.73	5.73	3.82	2.70
E-2	N.D.	4.65	14.60	15.56	26.10	35.98	31.09	29.61	30.60
E-3	N.D.	N.D.	0.85	3.27	9.44	20.60	23.78	23.38	19.95
E-9	N.D.	N.D.	N.D.	0.37	2.54	3.71	1.21	2.17	N.D.
Unknown 1	N.D.	N.D.	N.D.	N.D.	N.D.	0.69	4.37	4.44	3.76
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.63	4.10	3.55
Unresolved Background	0.49	0.43	0.28	1.25	0.39	0.13	0.13	0.42	0.47
Soil extract	95.36	96.06	94.49	83.18	90.27	76.48	69.95	67.94	61.03

Table B.7.1.2.1-4 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole] pyraflufen-ethyl at 200 g a.s./ha to clay loam under aerobic conditions (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	66	100	179
Pyraflufen-ethyl	55.63	6.71	1.90	1.30	0.91	N.D.	N.D.	N.D.	N.D.
E-1	25.51	84.34	76.23	74.80	63.70	47.02	10.72	6.49	2.74
E-2	N.D.	1.67	4.43	6.02	4.95	7.08	8.09	7.26	7.93
E-3	1.71	N.D.	3.63	8.52	15.95	30.48	52.35	54.68	52.79
E-11 or E-8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.08	7.00	6.43
E-9	N.D.	N.D.	N.D.	0.64	3.37	3.46	1.68	1.25	N.D.
Unknown 1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.28	4.15	3.44
Unresolved Background	0.58	0.45	0.18	0.73	0.39	0.27	0.39	0.20	0.74

Soil extract	83.44	93.17	86.38	92.01	89.26	88.30	80.60	81.05	74.06
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N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-5 : Degradation rates of pyraflufen-ethyl and its first metabolite E-1 in 3 soils under aerobic conditions at 20°C

Soil Type	DT ₅₀		DT ₉₀	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
Sandy silt loam	< 0.5	53	4.0	175
Sandy loam	< 0.5	22	1.9	73
Clay loam	< 0.5	25	0.8	84

Conclusions :

The patterns of the degradation products extracted from the 3 soils of this study (extractable) and from the aerobic metabolism study in 1 soil (extractable, bound residue and volatiles) are similar : Pyraflufen-ethyl is readily hydrolyzed to degradation product E-1 (DT₅₀ a.s. < 0.5 d).

The metabolite E-1 is further hydrolyzed to E-2 which reached a maximum plateau of 8-37% of applied radioactivity after 66 days then slightly declined . (DT₅₀ E-1 = 22-53 d, DT₉₀ E-1 = 73-175 d).

E-3 increased steadily throughout the incubation period accounting for between 20 and 53% of the applied radioactivity by the end of the study.

(¹⁴C)-ET-751: Soil degradation at 10°C. Purser, D. (1995b).

Guidelines:

EC Directive 91/414/EEC, Section 7.1.1.2.1 (Draft, July 1993).

GLP:

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 145.7 µCi/mg, radiochemical purity >99%

Soil :

Table B.7.1.2.1-6 : Characteristics of the soil - aerobic degradation rate study (10°C)

Soil Type (UK Classification)	Sandy silt loam
Organic carbon (%)	1.4
Organic matter (%)	2.4
Cation exchange capacity (meq/100g)	13.1
Particle size distribution (%)	
63 µm to 2 mm	46
2 µm to 63 µm	40
< 2 µm	14
pH (1:2.5) in 1M KCl	5.3
pH in water	6.34
Maximum water holding capacity (%)	
pF 2.5	16.7
pF 2.3	21.3
pF 0	49.5
Microbial biomass (µg C/g soil)	
Pre-study	170.72
Post-study	115.31

Experimental design :

The degradation rate of [¹⁴C-pyrazole] pyraflufen-ethyl was investigated in a sandy silt loam soil under aerobic conditions at 10°C over a period of 178 days. The test substances were applied to duplicate samples of the soil, with

a moisture content pF value of 2.3, at rates equivalent to approximately 200 g a.s./ha and incubated in the dark at $10 \pm 2^\circ\text{C}$. Samples were taken at intervals of 0, 1, 3, 7, 14, 28, 64, 100 and 178 days, were extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and confirmed by two-dimensional thin layer chromatography (2D-TLC). Radioactivity in the extracts was measured by liquid scintillation counting (LSC). No attempt was made to determine volatiles and bound residues. The DT_{50} and DT_{90} values for ET-751 were determined by inspection of the graphical presentation of the HPLC data and the values for E-1 were calculated from the HPLC using computer software assuming first-order reaction kinetics.

Findings :

Table B.7.1.2.1-7 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole] pyraflufen-ethyl at 200 g a.s./ha to sandy silt loam under aerobic conditions at 10°C (HPLC)

	Sampling Interval (Days)								
	0	1	3	7	14	28	64	100	178
Pyraflufen-ethyl	93.26	44.25	24.81	12.78	13.66	8.22	4.39	3.34	4.86
E-1	8.73	41.55	73.40	87.77	82.95	88.63	69.71	51.44	55.97
E-2	N.D.	N.D.	1.47	3.15	2.56	4.03	17.22	16.00	11.36
E-3	N.D.	N.D.	N.D.	1.69	N.D.	N.D.	4.49	3.93	5.46
E-9	N.D.	N.D.	0.99	1.09	2.40	0.75	N.D.	N.D.	N.D.
Unknown 2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	7.49
Unknown 3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.50
Unresolved Background	1.24	1.24	1.09	0.94	0.66	0.45	1.12	0.92	0.73
Soil extract	107.53	104.69	105.63	103.75	105.60	103.55	102.38	101.85	105.33

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-8 : Degradation rates of pyraflufen-ethyl and its first metabolite E-1 in 1 soil at 10°C

Soil Type	DT_{50}		DT_{90}	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
Sandy silt loam	1	328	22	1089

Conclusions :

Under aerobic conditions at 10°C pyraflufen-ethyl is readily hydrolyzed to degradation product E-1 (DT_{50} a.s. = 1 d). The metabolite E-1 is slowly degraded. (DT_{50} E-1 = 328 d, DT_{90} E-1 = 1089 d). The degradation followed the same pathways with formation of degradates E-2 and E-3.

(¹⁴C)-E-2 (ET-751 metabolite): Soil degradation at 20°C. (Yeomans, P., 1996a)

Guidelines :

EC Directive 91/414/EEC, Section 7.1.1.2.1 (Draft, September 1994) and FAO Annex to Revised Guidelines on Environmental Criteria for the Registration of Pesticides, Part 1, Section 1.1 (Draft August 1993).

GLP :

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenol (E-2), specific activity : 158.37 µCi/mg, radiochemical purity >98%

Soil :

Table B.7.1.2.1-9 : Characteristics of the soil - degradation rate of E-2 under aerobic conditions at 20°C

Soil Type (UK Classification)	Sandy silt loam	Sandy loam	Clay loam
Organic carbon (%)	2.1	1.2	3.7
Organic matter (%)	3.6	2.1	6.4
Cation exchange capacity (meq/100g)	17.4	11.5	31.8
Particle size distribution (%)			
clay	12	15	29
silt	54	15	38
sand	34	70	33
pH in KCl	5.8	4.3	6.9
pH in water	6.4	5.2	7.6
Maximum water holding capacity (%)			
pF 2.5	26.6	13.7	36.4
pF 0	61.7	49.3	86.7
Microbial biomass (µg C/g soil)			
Pre-study	294	121	1537
Post-study	232	84	1013

Experimental design :

The degradation rate of [¹⁴C-pyrazole] E-2 was investigated in three soils under aerobic conditions at 20°C over a period of 120 days. The test substance was applied to duplicate samples of the soil, with a moisture content of 45% the maximum water holding capacity at pF = 0, at a rate equivalent to approximately 200 g a.s./ha (10 µg/50 g soil) and incubated in the dark at 20 ± 2°C. Samples were taken at intervals of 0, 3, 7, 15, 29, 60, 90 and 120 days, extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and confirmed by two-dimensional thin layer chromatography (2D-TLC) (similar results for both methods). Radioactivity in the extracts was measured by liquid scintillation counting (LSC). Radioactivity remaining in the soils after extraction was determined by combustion and LSC (after 120 days : 30 to 50% RR as bound residue). The DT₅₀ and DT₉₀ values for E-2 were determined by inspection of the graphical presentation of the HPLC data and the values for E-1 were calculated from the HPLC using computer software assuming first-order reaction kinetics. No attempt was made to determine volatiles and bound residues.

Findings :

Table B.7.1.2.1-10 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole]E-2 at 200 g a.s./ha to sandy silt loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	15	29	60	90	120
E-2	91.46	59.04	47.49	25.06	9.20	4.62	2.24	1.84
E-3	N.D.	3.77	8.92	21.25	29.12	25.75	30.60	29.92
Unknown 1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Unknown 2	N.D.	N.D.	N.D.	2.07	5.10	8.27	7.34	8.05
Other unknown	2.62	1.08	2.12	0.44	0.00	1.59	0.00	0.48

Unresolved Background	0.31	1.00	0.98	0.82	0.50	0.18	0.42	0.37
Soil extract	94.40	64.89	59.50	49.64	43.93	40.41	40.60	40.66

Table B.7.1.2.1-11 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole]E-2 at 200 g a.s./ha to sandy loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	15	29	60	90	120
E-2	84.57	73.82	57.92	31.49	21.28	10.58	6.91	2.93
E-3	N.D.	4.34	6.53	15.49	18.59	19.97	18.72	19.30
Unknown 1	N.D.	N.D.	1.55	6.03	6.70	10.07	8.04	11.87
Unknown 2	N.D.	N.D.	N.D.	3.86	4.97	7.60	6.76	6.40
Other unknown	3.31	1.90	2.27	3.19	6.27	4.88	4.38	4.06
Unresolved Background	1.37	0.44	0.94	0.23	0.60	0.38	0.17	0.42
Soil extract	89.25	80.49	69.20	60.30	58.42	53.47	44.98	44.98

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-12 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole]E-2 at 200 g a.s./ha to clay loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	15	29	60	90	120
E-2	85.77	72.88	46.70	15.97	6.82	4.20	3.57	6.76
E-3	N.D.	10.68	23.45	39.91	41.15	35.79	30.16	24.92
Unknown 1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Unknown 2	N.D.	N.D.	N.D.	2.40	4.34	4.98	4.13	3.03
Other unknown	2.45	0.84	0.99	0.53	2.75	2.18	2.85	2.54
Unresolved Background	0.79	0.12	0.60	0.70	0.37	0.64	0.09	0.37
Soil extract	89.01	84.54	71.75	59.53	55.44	47.79	40.81	37.62

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-13 : Degradation rates of metabolite E-2 in 3 soils under aerobic conditions at 20°C (HPLC / 2D-TLC)

Soil Type	DT ₅₀	DT ₉₀
Sandy silt loam	9.07 / 8.74	30.13 / 29.04
Sandy loam	10.35 / 10.98	34.39 / 36.50
Clay loam	6.00 / 6.49	19.94 / 21.56

Conclusions :

The soil metabolite E-2 is degraded in soil under aerobic conditions initially following first-order reaction kinetics. The DT₅₀ = 6.00 - 10.98 days. The DT₉₀ = 19.94 - 36.54 days. The major initial metabolite was found to be E-3 which reached levels of 20 - 40% of the applied radioactivity during the course of the study. A significant proportion of the applied radioactivity remained as soil 'bound' residues at the end of the study. (30-50% applied radioactivity)

(^{14}C)-E-3 (ET-751 metabolite): Soil degradation at 20°C. (Yeomans, P., 1996b)

Guidelines :

EC Directive 91/414/EEC, Section 7.1.1.2.1 (Draft, September 1994) and FAO Annex to Revised Guidelines on Environmental Criteria for the Registration of Pesticides, Part 1, Section 1.1 (Draft August 1993).

GLP :

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] 4-chloro-3-(4-chloro-2-fluoro-5-methoxyphenyl)-5-difluoromethoxy-1-methylpyrazole (E-3), specific activity : 146.58 µCi/mg, radiochemical purity = 98.4%

Soil :

Table B.7.1.2.1-14 : Characteristics of the soil - degradation rate of E-3 under aerobic conditions at 20°C

Soil Type (UK Classification)	Sandy silt loam	Sandy loam	Clay loam
Organic carbon (%)	2.1	1.2	3.7
Organic matter (%)	3.6	2.1	6.4
Cation exchange capacity (meq/100g)	17.4	11.5	31.8
Particle size distribution (%)			
clay	12	15	29
silt	54	15	38
sand	34	70	33
pH in KCl	5.8	4.3	6.9
pH in water	6.4	5.2	7.6
Maximum water holding capacity (%)			
pF 2.5	26.6	13.7	36.4
pF 0	61.7	49.3	86.7
Microbial biomass (µg C/g soil)			
Pre-study	294	121	1537
Post-study	192	80	1558

Experimental design :

The degradation rate of [¹⁴C-pyrazole] E-3 was investigated in three soils under aerobic conditions at 20°C over a period of 120 days. The test substance was applied to duplicate samples of the soil, with a moisture content of 45% the maximum water holding capacity at pF 0, at a rate equivalent to approximately 200 g a.s./ha (10 µg/50 g soil) and incubated in the dark at 20 ± 2°C. Samples were taken at intervals of 0, 3, 7, 14, 28, 60, 91 and 122 days, extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and confirmed by two-dimensional thin layer chromatography (2D-TLC) (similar results for both methods). Radioactivity in the extracts was measured by liquid scintillation counting (LSC). No attempt was made to determine volatiles and bound residues.

Findings :

Table B.7.1.2.1-15 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole]E-3 at 200 g a.s./ha to sandy silt loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	14	28	60	91	122
E-3	92.99	89.50	N.A.	87.45	92.73	78.82	78.49	69.61
Unknown 1	N.D.	1.43	N.A.	1.66	3.65	3.89	4.24	4.55
Unresolved Background	0.20	0.66	N.A.	1.20	0.94	1.22	0.95	0.91
Soil extract	93.20	91.59	N.A.	90.31	97.33	83.92	83.68	75.07

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-16 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole]E-3 at 200 g a.s./ha to sandy loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	14	28	60	91	122

E-3	90.46	88.51	91.65	85.42	86.37	83.96	79.93	75.03
Unknown 1	N.D.	1.87	2.48	2.79	3.80	6.64	7.61	9.95
Unknown 2	N.D.	N.D.	0.28	N.D.	0.51	0.37	0.61	N.D.
Unknown 3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.48	N.D.
Unresolved Background	0.76	0.43	1.16	0.79	0.57	0.88	0.36	1.64
Soil extract	91.22	90.82	95.57	89.00	91.25	91.85	89.00	86.62

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-17 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole]E-3 at 200 g a.s./ha to clay loam under aerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	14	28	60	91	122
E-3	87.68	85.62	81.56	77.26	69.39	66.57	59.51	46.94
Unknown 1	N.D.	5.22	5.86	3.94	5.14	4.42	3.16	4.25
Unknown 2	N.D.	N.D.	N.D.	N.D.	0.77	2.46	2.52	3.63
Unknown 4	N.D.	N.D.	N.D.	N.D.	N.D.	0.90	1.99	3.01
Unresolved Background	0.59	0.78	1.04	0.48	0.25	0.27	0.76	0.80
Soil extract	88.27	91.62	88.46	81.68	75.55	74.62	67.94	58.63

N.A. : Not analysed, N.D. : Not detected

Table B.7.1.2.1-18 : Degradation rates of metabolite E-3 in 3 soils under aerobic conditions at 20°C (HPLC / 2D-TLC)

Soil Type	DT ₅₀	DT ₉₀
Sandy silt loam	321 / 318	1067 / 1056
Sandy loam	496 / 388	1648 / 1291
Clay loam	153 / 162	509 / 540

Conclusions :

The soil metabolite E-3 is slowly degraded in soil under aerobic conditions to unknown metabolites (<10 % not identified) and bound residue (not determined) (DT₅₀ = 153-496, DT₉₀ = 509-1648 d)

B.7.1.2.2 Anaerobic degradation

(^{14}C)-E-2 (ET-751 metabolite): Anaerobic soil degradation at 20°C. (Yeomans, P., 1996c).

Guidelines :

EC Directive 91/414/EEC, Section 7.1.1.2.1 (Draft, April 1995) and SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Section 1.2 (March 1995).

GLP :

Yes

Material and methods :

Test substance :

[^{14}C -pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenol (E-2), specific activity : 158.37 $\mu\text{Ci}/\text{mg}$, radiochemical purity >98%

Soil :

Table B.7.1.2.2-1 : Characteristics of the soil - degradation rate of E-2 under anaerobic conditions at 20°C

Soil Type (UK Classification)	Sandy loam
Organic carbon (%)	2.2
Organic matter (%)	3.8
Cation exchange capacity (meq/100g)	17.4

Particle size distribution (%)	
clay	11
silt	35
sand	54
pH in KCl	6.4
pH in water	6.7
Maximum water holding capacity (%)	
pF 2.5	21.9
pF 0	60.0
Microbial biomass ($\mu\text{g C/g soil}$)	
Pre-study	457
Post-study	176

The anaerobic degradation of [^{14}C -pyrazole] E-2 was investigated in a sandy loam soil over a period of 122 days. Deionised water to a depth of 3 cm above the soil surface was added to samples of the soil which were pre-incubated for up to 33 days prior to application of the test substance at rates equivalent to approximately 200 g a.s./ha (10 $\mu\text{g}/50\text{ g soil}$) and incubated in the dark at $20 \pm 2^\circ\text{C}$. Samples were taken at intervals of 0, 3, 7, 14, 28, 60, 90 and 122 days, extracted with acetonitrile, 1M aqueous ammonium chloride and acetonitrile/1M HCl and analysed by high performance liquid chromatography (HPLC) and two-dimensional thin layer chromatography (2D-TLC) (similar results for both methods). Radioactivity in the extracts was determined by LSC.

Table B.7.1.2.2-2 : Distribution of applied radioactivity (mean %) after application of [^{14}C -pyrazole]E-2 at 200 g a.s./ha to sandy loam under anaerobic conditions (HPLC)

	Sampling Interval (Days)							
	0	3	7	14	28	60	90	122
E-2								
Water	90.62	78.12	52.21	27.31	12.92	9.33	N.A.	N.A.
Soil	N.A.	16.43	42.01	65.20	78.75	78.23	79.52	75.49
E-3								
Water	N.D.	N.D.	N.D.	0.63	1.90	N.D.	N.A.	N.A.
Soil	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.06
Unresolved background								
Water	0.58	0.44	0.62	0.26	0.03	0.03	N.A.	N.A.
Soil	N.A.	0.28	0.36	0.51	0.74	0.75	0.16	1.14
Total extract								
Water	91.21	78.57	52.83	28.20	14.85	9.36	7.59	5.45
Soil	4.03	16.72	42.37	65.71	79.49	78.98	79.68	78.70

N.A. : Not applicable, N.D. : Not detected

(*) : % recovery of soil and water extracts are present in the study report.

Table B.7.1.2.2-3 : Degradation rate of metabolite E-2 in soil under anaerobic conditions at 20°C (HPLC)

Soil Type	DT_{50}	DT_{90}
Sandy loam	392	1304

Conclusions :

The soil metabolite E-2 is slowly degraded in soil under anaerobic conditions ($\text{DT}_{50} = 392$, $\text{DT}_{90} = 1304\text{ d}$)

B.7.1.3 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)**B.7.1.3.1 Soil dissipation testing**

ET-751 SC (Containing 20 g ET-751/L): Dissipation from four field soils following spring application. (Benwell, L. and Burden, A. N. 1997).

Guidelines :

EU Commission Directive 7171/VI/94 - EN rev 2, 06/12/94. The report complies with the SETAC recommendations (Lynch, 1995)

GLP :

Yes

Material and methods :*Test substance :*

SC formulation containing 20 g a./l

Soils :

Table B.7.1.3.1-1 : Characteristics of the soils from the field dissipation studies

Location	Senas (Provence, France)	Orgon (Provence, France)	Selling (Kent, U.K.)	Münster (Westphalia, Germany)
Soil Type (UK Classification)	Clay loam	Silt loam	Silt clay loam	Sandy clay loam
Organic matter (%)	3.1	1.2	1.4	1.7
Cation exchange capacity (meq/100g)	13.9	5.9	14.6	14.6
Bulk density	0.88	0.92	1.05	0.95
pH (KCl)	7.5	7.7	6.9	7.2
Maximum water holding capacity (% w/w)				
pF 2.5	22.5	21.9	24.7	20.8
pF 0	60.5	51.4	53.6	52.9
Microbial biomass (µg C/g soil)	311	157	199	302
Application date	23-05-95	24-5-95	16-06-95	23-06-95
Crop	bare soil (glyphosate applications to maintain the plots without vegetation)			
Design	3 replicates on plots 5 m x 7 m; 1 control plot	3 replicates on plots 5 m x 7 m; 1 control plot	3 replicates on plots 5 m x 7 m; 1 control plot	3 replicates on plots 5 m x 7 m; 1 control plot

Experimental design :

The test substance was applied to three plots at each location at a rate of 200 g a.s./ha. Soil cores were taken at intervals of 0, 1, 3 days, 1, 2, and 4 weeks and 2, 3, 6, 9 and 12 months following application. The initial soil cores (0 day) were 5 x 10 cm and subsequent samples were 2.5 x 30 cm. The samples were analysed for pyraflufen-ethyl and its major degradation products, E-1, E-2 and E-3 by high performance liquid chromatography with electrospray mass spectrometry (LC/MS-MS) with a limit of determination of 0.01 mg/kg. The DT₅₀ and DT₉₀ values for pyraflufen-ethyl at each site were calculated based on first order regression and the DT₅₀ and DT₉₀ values for E-1 were calculated using the Timme/Frehse model.

Weather conditions (air and soil temperatures, rainfall) were recorded. Irrigation was not necessary.

Findings :

Table B.7.1.3.1-2 : Mean field soil residues (mg/kg) of pyraflufen-ethyl and E-1 following spring application at a rate of 200 g a.s./ha.

Sampling Interval (Days)	Senas		Orgon		Selling		Münster	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
0								
0-5 cm	0.11-0.23	0.24-0.27	0.18-0.48	0.21-0.27	0.20-0.25	0.17-0.20	0.54-0.63	0.05-0.26
5-10 cm	<0.01	<0.01	<0.01	<0.01-0.01	<0.01	<0.01	<0.01	<0.01
1								
0-5 cm	0.11-0.20	0.14-0.22	0.46-0.65	0.19-0.25	0.31-0.51	0.19-0.29	0.35-0.51	0.13-0.25
5-10 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
3								
0-5 cm	<0.01-0.05	0.18-0.27	0.05-0.07	0.20-0.38	0.05-0.09	0.25-0.48	0.42-0.70	0.13-0.15
5-10 cm	<0.01	<0.01-0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
7								
0-5 cm	<0.01	0.17-0.22	0.02-0.05	0.32-0.46	0.04-0.11	0.19-0.38	0.09-0.16	0.11-0.14
5-10 cm	<0.01	<0.01-0.02	<0.01	<0.01	<0.01	<0.01-0.04	<0.01	<0.01
13-14								
0-5 cm	<0.01	<0.01-0.11	<0.01-0.02	0.20-0.35	0.04-0.07	0.21-0.29	0.09-0.22	0.26-0.42
5-10 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.05	<0.01	<0.01
27-28								
0-5 cm	<0.01	0.13-0.20	<0.01	0.16-0.24	<0.01	0.13-0.21	<0.01	0.10-0.20
55-61								
0-5 cm	<0.01	0.04-0.14	<0.01	0.20-0.25	<0.01	0.10-0.18	<0.01	0.08-0.12
5-10 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.03	<0.01	<0.01
87-91								
0-5 cm	<0.01	0.05-0.11	<0.01	0.08-0.12	<0.01	0.08-0.17	<0.01	0.08-0.14
184-201								
0-5 cm	<0.01	<0.01-0.03	<0.01	0.02-0.10	<0.01	0.04	<0.01	<0.01-0.03
271-282								
0-5 cm	<0.01	<0.01-0.02	<0.01	0.04-0.05	<0.01	0.04-0.05	<0.01	0.02
360-367								
0-5 cm	<0.01	<0.01	<0.01	0.02-0.03	<0.01	0.03-0.04	<0.01	<0.01-0.01

Concentrations results for the metabolites E-2 and E-3 were not included in the monograph because both compounds were found at very low levels : E-2 : £ 0.01 mg/kg soil; E-3 : generally < 0.01 mg/kg soil maximum values : 0.05 mg a.s./kg soil.

Table B.7.1.3.1-3 : Field soil dissipation DT₅₀ and DT₉₀ values (days) for pyraflufen-ethyl and E-1 following spring application.

Test soil	pyraflufen-ethyl		E-1	
	DT ₅₀	DT ₉₀	DT ₅₀	DT ₉₀
clay loam, Senas (France)	1	3	11	121
silt loam, Orgon (France)	2	8	42	285
silt clay loam, Selling (UK)	6	21	44	345
sandy clay loam, Münster (Germany)	7	23	32	175

Conclusion:

Pyraflufen-ethyl is rapidly degraded in soil under field conditions following spring application with DT₅₀ values in the range 1 - 7 days. Its major metabolite E-1 is also readily degraded with DT₅₀ values of 11-44 days. No significant movement of residues down the soil profile was observed. Occasionally low levels of residues were

Sampling Interval (Days)	Senas		Orgon		Selling		Münster	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
0 0-5 cm	0.25-0.32	0.19-0.28	0.23-0.26	0.11-0.13	0.29-0.41	0.14-0.20	0.14-0.27	<0.01-0.08
1 0-5 cm	0.09	0.29-0.46	0.17-0.33	0.30-0.37	0.19-0.28	0.22-0.25	<0.01-0.19	0.07-0.46
3 0-5 cm	<0.01-0.05	<0.01-0.32	0.05-0.07	0.16-0.27	0.09-0.15	0.13-0.18	<0.01	0.03-0.11
7 0-5 cm 5-10 cm	<0.01 <0.01	0.23-0.30 <0.01-0.03	0.02-0.05 <0.01	0.16-0.23 <0.01	0.05-0.09 <0.01	0.30-0.49 <0.01	<0.01 <0.01	0.10-0.17 <0.01
14 0-5 cm 5-10 cm	<0.01 <0.01	0.12-0.30 <0.01	<0.01 <0.01	0.21-0.24 <0.01	<0.01 <0.01	0.28-0.39 <0.01	<0.01 <0.01	0.10-0.25 <0.01
28 0-5 cm 5-10 cm	<0.01 <0.01	0.19-0.33 <0.01	<0.01 <0.01	0.13-0.18 <0.01	<0.01 <0.01	0.18-0.24 <0.01	<0.01 <0.01	0.03-0.15 <0.01-0.02

Sampling Interval (Days)	Senas		Orgon		Selling		Münster	
	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1	Pyraflufen-ethyl	E-1
10-15 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.01
50-72								
0-5 cm	<0.01	0.09-0.13	<0.01	0.08-0.16	<0.01	0.15-0.36	<0.01	0.09-0.14
5-10 cm	<0.01	0.01-0.03	<0.01	<0.01-0.03	<0.01	<0.01	<0.01	<0.01-0.02
86-124								
0-5 cm	<0.01	0.03	<0.01	0.04-0.05	<0.01	0.05-0.06	<0.01	0.05-0.10
5-10 cm	<0.01	<0.01	<0.01	<0.01-0.02	<0.01	<0.01-0.04	<0.01	0.02
10-15 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.02
170-191								
0-5 cm	<0.01	<0.01-0.02	<0.01	0.02-0.03	<0.01	0.03-0.04	<0.01	0.03
5-10 cm	<0.01	<0.01	<0.01	<0.01	<0.01	0.01-0.02	<0.01	<0.01
10-15 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.01	<0.01	<0.01
262-281								
0-5 cm	<0.01	<0.01-0.02	<0.01	<0.01	<0.01	<0.01-0.01	<0.01	<0.01
362-367								
0-5 cm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Concentrations results for the metabolites E-2 and E-3 were not included in the monograph because both compounds were found at very low levels : E-2 : generally £ 0.01 mg/kg soil maximum values : 0.02 mg a.s./kg soil; E-3 : generally < 0.01 mg/kg soil maximum values : 0.07 mg a.s./kg soil.

Table B.7.1.3.1-6 : Field soil dissipation DT₅₀ and DT₉₀ values (days) for pyraflufen-ethyl and E-1 following autumn application.

Test soil	pyraflufen-ethyl		E-1	
	DT ₅₀	DT ₉₀	DT ₅₀	DT ₉₀
clay loam, Senas (France)	1	3	35	115
silt loam, Orgon (France)	2	8	51	169
silt clay loam, Selling (UK)	3	10	47	156
sandy clay loam, Münster (Germany)	<3	<10	71	236

Conclusion:

Pyraflufen-ethyl is rapidly degraded in soil under field conditions following autumn application with DT₅₀ values in the range 1 - 3 days. Its major metabolite E-1 is also readily degraded with DT₅₀ values of 35-71 days. No significant movement of residues down the soil profile was observed. Occasionally low levels of residues were detected at a depth of 15 cm. Only low levels of degradation products E-2 and E-3 were detected (E-2 : £ 0.01 - 0.02 mg/kg soil; E-3 : < 0.01- 0.07 mg/kg soil)

B.7.1.3.2 Soil residue testing - soil accumulation testing

The study is not required since the DT₉₀ field of the a.s. (as well as metabolites) is < 1 year and repeated applications are excluded.

B.7.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3; Annex IIIA 9.1.2)

B.7.2.1 Adsorption and desorption of the active substance and relevant metabolites (Annex IIA 7.1.2)

ET-751: Determination of adsorption coefficient on soil (K_{oc}) by HPLC simulation. (Bates, M. , 1996)

Guidelines :

OECD Guideline No. 106 (1994)

GLP :

Yes

Material and Methods :

Test substance : pyraflufen-ethyl, purity > 98%

Test system :

The soil adsorption/desorption coefficient ($\log K_{oc}$) was estimated by HPLC simulation. The HPLC column was calibrated for soil adsorption/desorption coefficient against retention time using 16 different reference substances of known K_{oc} values. Pyraflufen-ethyl, dissolved in methanol, was injected three times, on two occasions, onto the HPLC column and the mean retention time was used to estimate the K_{oc} value in comparison to the responses of the reference standards.

Findings :

The mean retention time on the HPLC column for pyraflufen-ethyl was found to be 6.88 minutes. By comparison with the range of reference standards used, the adsorption/desorption coefficient ($\log K_{oc}$) was estimated to be 3.29 with 95% confidence limits of 3.17 - 3.43.

Conclusions :

Pyraflufen-ethyl has low mobility according to its adsorption/desorption coefficient with a K_{oc} value of greater than 1000.

(14 C)-E-1 (ET-751 metabolite): Adsorption/Desorption in three soils. (Yeomans, P. ,1996d).

Guidelines:

OECD 106 (May 1981).

GLP:

Yes

Material and methods :

Test substance :

[14 C-pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetic acid (E-1), specific activity : 130.86 μ Ci/mg, radiochemical purity = 98.7%

Soils :

Table B.7.2.1-1 : Characteristics of the soils - Adsorption /desorption of metabolite E-1

Soil Type (UK Classification)	Sandy loam-A	Sandy loam-B	Clay loam
Organic carbon (%)	1.2	2.2	3.7
Organic matter (%)	2.1	3.8	6.4
Cation exchange capacity (meq/100g)	11.5	17.4	31.8
Particle size distribution (%)			
clay	15	11	29
silt	15	35	38
sand	70	54	33
pH in KCl	4.3	6.4	6.9
pH in water	5.2	6.7	7.6
Maximum water holding capacity (%)			
pF 2.5	13.7	21.9	36.4
pF 0	49.3	60.0	86.7

Experimental design :

The adsorption and desorption of [^{14}C] E-1 in three field soils was determined by the equilibrium method. Soil samples (5 g soil/25 ml CaCl_2 solution) were shaken in calcium chloride solutions (four dilutions: 0.04, 0.2, 1.0, 5.0 $\mu\text{g/ml}$) continuously for one hour at 20°C to measure adsorption and then twice for a further one hour, after centrifuging and the addition of calcium chloride, to measure desorption in two steps. The Freundlich adsorption constants K_f and $1/n$, and the K_{oc} and K_{om} values, were calculated for each soil.

The recovery of the radioactivity was 89-91% for the 3 soils at the highest concentration (5.0 $\mu\text{g/ml}$)

Table 7.1.2-2: Adsorption/desorption of E-1

Soil type	Adsorption				First desorption		Second desorption	
	K_f	$1/n$	K_{oc}	K_{om}	K_f	K_{oc}	K_f	K_{oc}
Sandy loam-A	2.36	0.95	197	112	4.87	406	12.99	1083
Sandy loam-B	2.21	0.93	100	58	4.02	183	8.11	369
Clay loam	3.02	0.93	81	47	5.19	140	9.04	244

Conclusion:

The metabolite E-1 has 'high' to 'medium mobility' according to Mc Call classification.

(^{14}C)-E-2 (ET-751 metabolite): Adsorption/Desorption in three soils (Yeomans, P., 1996e)

Guidelines:

OECD 106 (May 1981).

GLP:

Yes

Material and methods :*Test substance :*

[^{14}C -pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenol (E-2), specific activity : 158.37 $\mu\text{Ci/mg}$, radiochemical purity = 98%

Soils :

See Table B.7.1.2-1

Experimental design :

The adsorption and desorption of [^{14}C] E-1 in three field soils was determined by the equilibrium method. Soil samples (5 g soil/25 ml CaCl_2 solution) were shaken in calcium chloride solutions (four dilutions: 0.04, 0.2, 1.0, 5.0 $\mu\text{g/ml}$) continuously for 4 hours at 20°C to measure adsorption and then twice for a further 4 hours, after centrifuging and the addition of calcium chloride, to measure desorption in two steps. The Freundlich adsorption constants K_f and $1/n$, and the K_{oc} and K_{om} values, were calculated for each soil.

The recovery of the radioactivity was 84-88% for the 3 soils.

Table 7.1.2-3 : Adsorption/desorption of E-2

Soil type	Adsorption				First desorption		Second desorption	
	K_f	$1/n$	K_{oc}	K_{om}	K_f	K_{oc}	K_f	K_{oc}
Sandy loam-A	26.15	0.94	2179	1245	35.01	2917	41.15	3429
Sandy loam-B	47.19	0.98	2145	1242	62.18	2826	67.12	3051
Clay loam	52.68	0.97	1424	823	63.61	1719	65.75	1777

Conclusion:

The metabolite E-2 has 'low' to 'slight mobility' according to Mc Call classification.

(¹⁴C)-E-3 (ET-751 metabolite): Adsorption/Desorption in three soils. (Yeomans, P. ,1996f)

Guidelines:

OECD 106 (May 1981).

GLP:

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] 4-chloro-3-(4-chloro-2-fluoro-5-methoxyphenyl)-5-difluoromethoxy-1-methylpyrazole (E-3), specific activity : 146.58 µCi/mg, radiochemical purity = 98.4%

Soils :

See Table B.7.1.2-1

Experimental design :

The adsorption and desorption of [¹⁴C] E-1 in three field soils was determined by the equilibrium method. Soil samples (2.5 g soil/25 ml CaCl₂ solution) were shaken in calcium chloride solutions (four dilutions: 0.04, 0.15, 0.5, 1.0 µg/ml) continuously for 24 hours at 20°C° to measure adsorption and then twice for a further 24 hours, after centrifuging and the addition of calcium chloride, to measure desorption in two steps. The Freundlich adsorption constants K_f and $1/n$, and the K_{oc} and K_{om} values, were calculated for each soil.

The recovery of the radioactivity was 74-94% for the 3 soils.

Findings :

Table 7.1.2-4 : Adsorption/desorption of E-3

Soil type	Adsorption				First desorption		Second desorption	
	K_f	$1/n$	K_{oc}	K_{om}	K_f	K_{oc}	K_f	K_{oc}
Sandy loam-A	52.24	0.91	4354	2488	77.49	6457	60.65	5054
Sandy loam-B	91.80	0.96	4173	2416	114.91	5223	105.66	4803
Clay loam	114.62	0.93	3098	1791	176.32	4765	160.73	4344

Conclusion:

The metabolite E-3 has 'slight mobility' according to Mc Call classification.

B.7.2.2 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)

Soil column leaching of [pyrazole-5-¹⁴C] ET-751 (normal study). (Kimura, Y. ,1996a).

Guidelines :

FAO, Environmental Testing Guidelines, Revision 3, pp 17 - 18, 1993.

GLP:

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 60.2 mCi/mmol, radiochemical purity >98%

Soils :

Table B.7.2.2-1 : Characteristics of the soils - Column leaching

Soil Type (UK Classification)	Sandy loam-A	Sandy loam-B	Sandy silt loam	Clay loam
Organic carbon (%)	2.2	1.3	1.7	3.1
Organic matter (%)	3.8	2.2	2.9	5.3
Cation exchange capacity (meq/100g)	18.5	11.9	18.2	32.2
Particle size distribution (%)				
clay (< 2 µm)	10	13	12	26
silt (2 µm to 63 µm)	35	15	54	37
sand (63 µm to 2 mm)	55	72	34	37
pH in KCl	6.5	4.7	6.0	6.9
pH in water	6.8	5.2	6.5	7.5
Maximum water holding capacity at pF 0 (%)	57.9	44.9	58.7	76.4

The mobility of [^{14}C -pyrazole] pyraflufen-ethyl was investigated in four soils using glass columns (30 cm length, 5 cm internal diameter). The test substance was applied to the top of two pre-conditioned soil columns for each soil type at a rate equivalent to 20 g a.s./ha (3.93 µg/ column) and leached with 393 cm³ 0.01 M calcium chloride solution (200 mm rainfall) over a period of two days at room temperature (18 - 27°C). At the end of the leaching period the radioactivity in the leachate was determined by liquid scintillation counting (LSC). The soil columns were divided into six 5 cm segments which were extracted with solvent and analysed by LSC. Samples containing greater than 5% of the applied radioactivity were analysed by thin layer chromatography (TLC). Radioactivity remaining in the soil after extraction was determined by combustion and LSC.

Findings :

Table B.7.2.2-2 : Mean distribution of radioactivity (% of applied) in soil columns and leachates from columns treated with pyraflufen-ethyl

	Sandy loam-A	Sandy loam-B	Sandy silt loam	Clay loam
Soil				
0 - 5 cm	81.5	88.4	93.3	83.3
5 - 10 cm	18.6	6.6	4.2	18.7
10 - 15 cm	0.2	0.1	0.1	0.1
15 - 20 cm	0.1	0.1	N.D.	0.1
20 - 25 cm	0.1	0.1	0.1	0.1
25 - 30 cm	0.1	0.2	0.1	0.1
Leachate	0.2	0.2	0.2	0.2
Total	100.8	95.7	98.0	102.6

Table B.7.2.2-3 : Mean distribution of radioactivity (% of applied) in the top 0 - 10 cm of soil columns treated with pyraflufen-ethyl

	Sandy loam-A	Sandy loam-B	Sandy silt loam	Clay loam
Pyraflufen-ethyl	7.8	9.7	9.1	5.4
E-1	83.3	46.0	78.3	81.2
E-2	3.6	27.9	6.5	2.2
E-3	1.8	2.7	0.9	0.6
E-9	N.D.	1.5	N.D.	N.D.
Unknown A	N.D.	0.4	N.D.	N.D.
Unknown B	N.D.	0.4	N.D.	N.D.

Conclusions :

The column leaching study with fresh residue showed that pyraflufen-ethyl and its metabolites are retained in the top

10 cm of soil (5.4-9.7% a.s., 46.0-83.3% E-1, 2.2-27.9% E-2, very limited amounts of E-3, E-9). The amount of radioactivity recovered in the leachate is very limited (0.2%).

B.7.2.3 Aged residue column leaching (Annex IIA 7.1.3.2; Annex IIIA 9.1.2.1)

Soil column leaching of [pyrazole-5-¹⁴C] ET-751 (Aged study). (Kimura, Y. ,1996b).

Guidelines :

FAO, Environmental Testing Guidelines, Revision 3, pp 17 - 18, 1993.

GLP:

Yes

Material and methods :

Test substance :

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 60.2 mCi/mmol, radiochemical purity >98%

Soils :

Table B.7.2.3-1 : Characteristics of the soils - Aged residue column leaching

Soil Type (UK Classification)	Sandy loam
Organic carbon (%)	1.3
Organic matter (%)	2.2
Cation exchange capacity (meq/100g)	11.9
Particle size distribution (%)	
clay (< 2 µm)	13
silt (2 µm to 63 µm)	15
sand (63 µm to 2 mm)	72
pH in KCl	4.7
pH in water	5.2
Maximum water holding capacity at pF 0 (%)	44.9

The mobility of 'aged' residues of [¹⁴C-pyrazole] pyraflufen-ethyl was investigated in a sandy loam soil using glass columns (30 cm length, 5 cm internal diameter). The test substance was 'aged' in the soil under aerobic conditions at 20 ± 2°C for a period of 30 days (2µg/100 g soil) and applied to the top of two pre-conditioned soil columns at a rate equivalent to 20 g a.s./ha. The distribution of radioactivity in the 'aged' soil was determined at the end of the aging period by extraction, TLC, combustion and LSC. (Extractable : 97.2% ; 3.8% a.s.; 50.5% E-1; 12.8% E-3; 1.6% E-9; 16.8% several unknown / Unextractable : 5.4%) , The columns were leached with 393 cm³ 0.01 M calcium chloride solution (200 mm rainfall) over a period of two days at room temperature (21 - 26°C). At the end of the leaching period the radioactivity in the leachate was determined by liquid scintillation counting (LSC). The soil columns were divided into six 5 cm segments which were extracted with solvent and analysed by LSC. Samples containing greater than 5% of the applied radioactivity were analysed by thin layer chromatography (TLC). Radioactivity remaining in the soil after extraction was determined by combustion and LSC.

Findings :

Table B.7.2.3-2 : Mean distribution of radioactivity (% of applied) in soil columns and leachates from columns treated with pyraflufen-ethyl

	Sandy loam
Soil	
0 - 5 cm	67.9
5 - 10 cm	29.5
10 - 15 cm	3.9
15 - 20 cm	0.3
20 - 25 cm	0.1
25 - 30 cm	0.2
Leachate	0.5
Container washings	0.1

Total	102.5
--------------	-------

Table B.7.2.3-3 : Mean distribution of radioactivity (% of applied) in the top 0 - 10 cm of soil columns treated with pyraflufen-ethyl

Component	Sandy loam
Pyraflufen-ethyl	2.6
E-1	30.3
E-2	33.4
E-3	13.5
E-8	N.D.
E-9	1.4
Unknown B	0.2
Unknown C	1.4
Unknown F	0.1

Conclusions :

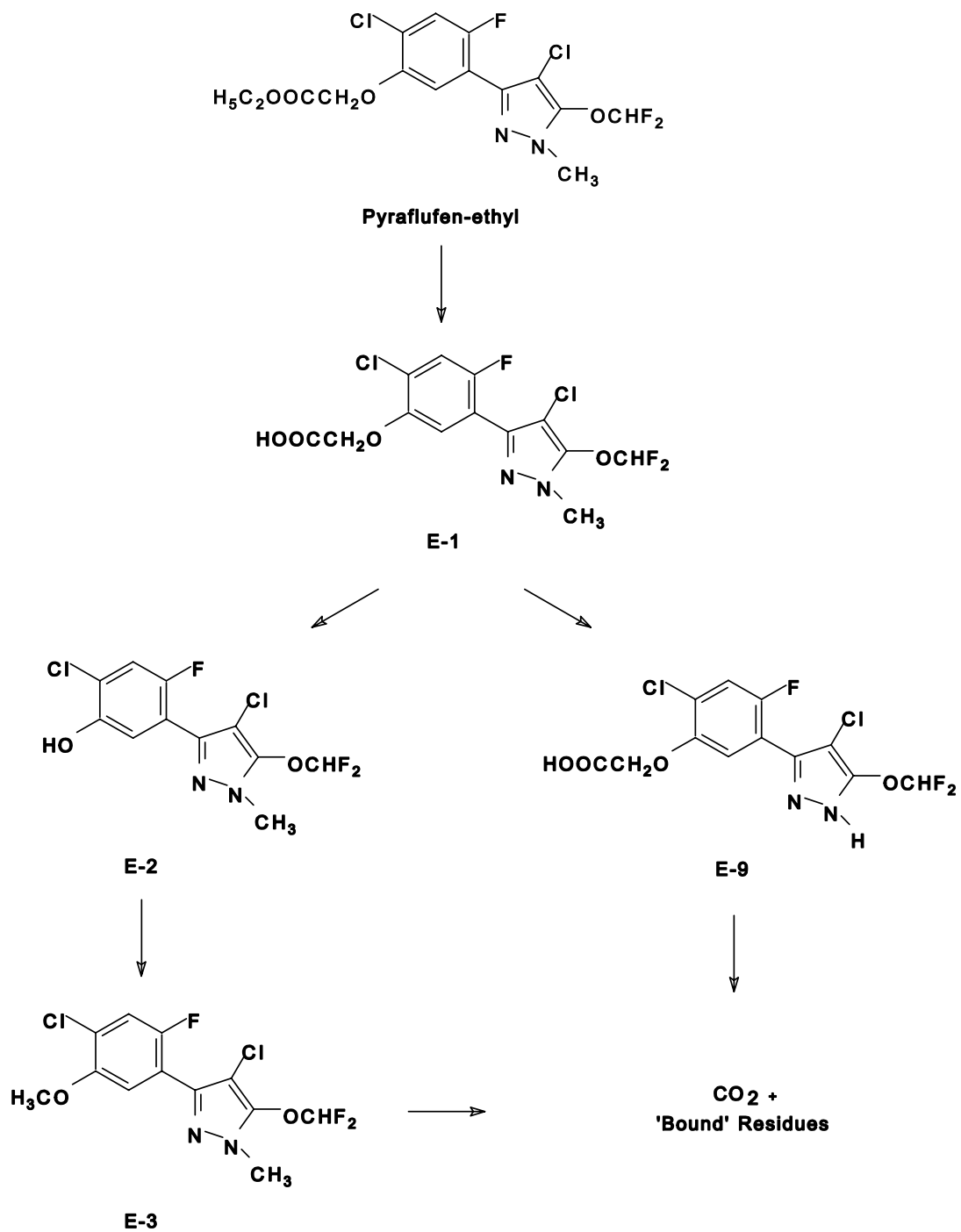
The column leaching study with aged residue showed that pyraflufen-ethyl and its metabolites are mainly retained in the top 15 cm of soil (67.9, 29.5 % and 3.9% in the 0-5, 5-10 and 10-15 cm soil layers, respectively). The amount of radioactivity recovered in the leachate is very limited (0.5%).

B.7.2.4 Lysimeter and field leaching studies (Annex IIA 7.1.3.3; Annex IIIA 9.1.2.2)

The PEC groundwater model calculation reveals that neither the active substance nor its 3 major metabolites (E-1, E-2, E-3) are expected to be recovered at level > 0.1 µg/l. Therefore no lysimeter study is required.

B.7.3 Summary of behaviour in soil and predicted environmental concentration in soil (PECs) and ground water (PECgw) (Annex IIIA 9.1.3)

Figure B.7.3-1 : Proposed metabolic pathway of pyraflufen-ethyl in soil



B.7.3-1 : Summary of behaviour in soil - Rate of degradation of pyraflufen-ethyl and its metabolites E-1, E-2 and E-3 in laboratory studies

Test soil				Test system	Results		References
Soil type	Soil pH _(KCl)	CEC	OC content (%)		DT50	DT90	
Active substance							
sandy loam	5.8	14.7	2.0	aerobic, 20°C	<0.5 d	0.83-2.1 d	Purser, 1996a
sandy silt loam	5.3	13.1	1.4	aerobic, 20°C	<0.5 d	4.0 d	Purser, 1995a
sandy loam	4.0	9.6	1.1		<0.5 d	1.9 d	
clay loam	6.9	30.6	3.4		<0.5 d	0.8 d	
sandy silt loam	5.8	17.4	2.1	Soil photolysis	299 d irradiated samples	993 d irradiated samples	Lewis, 1996a
sandy loam	5.8	14.7	2.0	anaerobic, 20°C	<1 d	<1 - <3 d	Purser, 1996b
sandy silt loam	5.3	13.1	1.4	aerobic, 10°C	1 d	22 d	Purser, 1995b
E-1							
sandy loam	5.8	14.7	2.0	aerobic, 20°C	16-20 d	52-67 d	Purser, 1996a
sandy silt loam	5.3	13.1	1.4	aerobic, 20°C	53d	175 d	Purser, 1995a
sandy loam	4.0	9.6	1.1		22 d	73 d	
clay loam	6.9	30.6	3.4		25 d	84 d	
sandy loam	5.8	14.7	2.0	anaerobic, 20°C	125-191 d	414-634 d	Purser, 1996b
sandy silt loam	5.3	13.1	1.4	aerobic, 10°C	328 d	1089 d	Purser, 1995b
E-2							
sandy silt loam	5.8	17.4	2.1	aerobic, 20°C	9-9 d	30-29 d	Yeomans, 1996a
sandy loam	4.3	11.5	1.2		10-11 d	34-36 d	
clay loam	6.9	31.8	3.7		6-6 d	20-22 d	
sandy loam	6.4	17.4	2.2	anaerobic, 20°C	392 d	1304 d	Yeomans, 1996c
E-3							
sandy silt loam	5.8	17.4	2.1	aerobic, 20°C	321-318 d	1067-1056 d	Yeomans, 1996b
sandy loam	4.3	11.5	1.2		496-388 d	1648-1291 d	
clay loam	6.9	31.8	3.7		153 -162 d	509-540 d	

Table B.7.3-2 : Summary of behaviour in soil - Rate of degradation of pyraflufen-ethyl and its metabolite E-1; Field dissipation studies

Test soil				Test system	Results (days)				References
Soil type	pH	CEC meq/100g	O.M. (%)		pyraflufen-ethyl		E-1		
					DT ₅₀	DT ₉₀	DT ₅₀	DT ₉₀	
clay loam Senas (France)	7.5	13.9	3.1	200 g a.s./ha spring application	1	3	11	121	Benwell, 1997
silt loam Orgon (France)	7.7	5.9	1.2		2	8	42	285	
silt clay loam Selling (UK)	6.9	14.6	1.4		6	21	44	345	
sandy clay loam Münster (Germany)	7.2	14.6	1.7		7	23	32	175	
clay loam Senas (France)	7.5	13.9	3.1	200 g a.s./ha autumn application	1	3	35	115	Burden, 1997
silt loam Orgon (France)	7.7	5.9	1.2		2	8	51	169	
silt clay loam Selling (UK)	6.9	14.6	1.4		3	10	47	156	
sandy clay loam Münster (Germany)	7.2	14.6	1.7		<3	<10	71	236	

Table B.7.3-3 : Summary of behaviour in soil - Adsorption constants Kf, Koc, adsorption exponent 1/n of pyraflufen-ethyl and its metabolites

Test soil				Test system	Results			References
Soil type	pH (KCl)	CEC meq/ 100g	O.C. (%)		Kf	1/n	Koc	
pyraflufen-ethyl								
-				Koc determination by HPLC	log Koc = 3.29 (3.17-3.43)			Bates, 1996
metabolite E-1								
sandy loam	4.3	11.5	1.2	Laboratory adsorption - desorption	2.36	0.95	197	Yeomans, 1996d
sandy loam	6.4	17.4	2.2		2.21	0.93	100	
clay loam	6.9	31.8	3.7		3.02	0.93	81	
metabolite E-2								
sandy loam	4.3	11.5	1.2	Laboratory adsorption - desorption	26.15	0.94	2179	Yeomans, 1996e
sandy loam	6.4	17.4	2.2		47.19	0.98	2145	
clay loam	6.9	31.8	3.7		52.68	0.97	1424	
metabolite E-3								
sandy loam	4.3	11.5	1.2	Laboratory adsorption - desorption	52.24	0.91	4354	Yeomans, 1996f
sandy loam	6.4	17.4	2.2		91.80	0.96	4173	
clay loam	6.9	31.8	3.7		114.62	0.93	3098	

Table B.7.3-4 : Summary of behaviour in soil - leaching of pyraflufen-ethyl and its main metabolites

Test soils	Test system	Residues (% of the applied amount)	References
Active substance - Fresh and aged residue			
4 soils	Fresh residue	soil 0-5 cm : 81.5-93.3% (mainly E-1) soil 5-10cm : 4.2-18.7% leachate : 0.2%	Kimura, 1996a
1 soil	Aged residue (30 days)	soil 0-5 cm : 67.9% (mainly E-2 and E-1) soil 5-10cm : 29.5% soil 10-15 cm : 3.9% leachate : 0.5%	Kimura, 1996b

Predicted Environmental Concentrations in soil

The formulation EXP31279A is a post-emergence herbicide in cereals (SC containing 9 g/l pyraflufen-ethyl and 500 g/l bifenox) which will be applied at an application rate of 1-1.5 l/ha at stage BBCH 13-29 (9-**13.5** g pyraflufen-ethyl/ha).

The estimations of the PECs were calculated assuming that :

- DT₅₀ pyraflufen-ethyl = 7 days (maximum field DT₅₀)
- DT₅₀ E-1 = 71 days (maximum field DT₅₀). The a.s. is rapidly degraded to the metabolite E-1 (DT₅₀ <1-7 days under field conditions). It was assumed that degradation of the a.s. to E-1 was complete and instantaneous.
- Equal distribution in the top 5 cm of the soil with a bulk density of 1.5 g/cm³
- The substance is applied at the maximum application rate of 13.5 g a.s./ha at stage BBCH 13-29 (no interception of the spray by the crop)

Table B.7.3-9 : PEC soil of the active substance and metabolite E-1

Time after applications (days)	Cereals 13.5 g a.s./ha 1 application 100% of applied dose reaching the soil			
	pyraflufen-ethyl		metabolite E-1	
	Actual concentration (mg/kg soil)	TWA concentration (mg/kg soil)	Actual concentration (mg/kg soil)	TWA concentration (mg/kg soil)
0	0.018	0.018	0.018	0.018
1	0.016	0.017	0.018	0.018
2	0.015	0.016	0.018	0.018
4	0.012	0.015	0.017	0.018
7	0.009	0.013	0.017	0.017
14	0.004	0.010	0.016	0.017
21	0.002	0.008	0.015	0.016
28	0.001	0.006	0.014	0.016
50	0	0.003	0.011	0.014
100	0	0.002	0.007	0.011

Metabolites E-2 and E-3 were found at low concentrations in the field dissipation studies. Maximum concentrations expected in the soil after an application at rate of 13.5 g a.s. could be estimated to be 0.001 and 0.005 mg/kg respectively for metabolites E-2 and E-3.

Predicted Environmental Concentrations in groundwater

To assess potential concentrations in ground water, simulations were performed with the computer model PELMO 2.01 using standard German scenarios (Wicks, 1997). Parameters used in these calculations were consistent with those used to calculate predicted environmental concentrations in soil. Annual applications of pyraflufen-ethyl to winter wheat at the maximum rate of 13.5 g a.i./ha were assumed on November 25 for autumn applications and April 25 for spring applications. Data describing the properties of pyraflufen-ethyl, E-1, E-2, and E-3 are given below:

	Pyraflufen-ethyl	E-1	E-2	E-3
Formula	$C_{15}H_{13}O_4N_2Cl_2F_3$	$C_{13}H_9O_4N_2Cl_2F_3$	$C_{11}H_7O_2N_2Cl_2F_3$	$C_{12}H_9O_2N_2Cl_2F_3$
Molecular weight (g mol ⁻¹)	413	385	327	341
Water solubility (mg/l at 20 °C)	0.082	83.1	7.6	0.53
Vapour pressure (Pa)	1.6×10^{-8}	$< 4.2 \times 10^{-4}$	Not available	Not available
Koc value (cm ³ /g)	1995	81 - 197 Average 126	1424 - 2179	3098 - 4354
Dissipation (DT ₉₀ , days)	3 - 10 (autumn) 3 - 22 (spring)	115 - 236 (autumn) Average 169 121 - 345 (spring) Average 232	21 - 35 *	525 - 1470*

Bold numbers indicate the parameters used for the simulation. The worst case values (and average for E-1 only) were used.

* Indicates DT₉₀ values were laboratory data.

Simulations for metabolites assumed an application equivalent to the amount of parent (corrected for molecular rate on the application days already described for pyraflufen-ethyl. This is a very conservative assumption, especially for E-2 and E-3. The simulations were performed using a Borstel soil and standard weather scenarios (low: Hamburg 1971; average: Hamburg 1961; high: Hamburg 1978; with total annual rainfall of 542, 778, and 872 mm, respectively).

For all three sets of weather data, the model predicts that no pyraflufen-ethyl, E-1, E-2, or E-3 will enter the ground water at a yearly average concentration greater than 0.1 µg l⁻¹. Steady state annual values from PELMO simulations:

Compound	Weather scenario	K _{oc} (cm ³ g ⁻¹)	DT ₉₀ (days)	Groundwater recharge (l m ⁻²)	Amount moved below core (g ha ⁻¹)	Concentration in recharge (µg l ⁻¹)
Pyraflufen-ethyl (autumn)	Hamburg 1971	1195	10	112.1	< 0.0001	< 0.001
	Hamburg 1978	1195	10	413.4	< 0.0001	< 0.001
	Hamburg 1961	1195	10	497.7	< 0.0001	< 0.001
Pyraflufen-ethyl (spring)	Hamburg 1971	1195	22	112.1	< 0.0001	< 0.001
	Hamburg 1978	1195	22	413.4	< 0.0001	< 0.001
	Hamburg 1961	1195	22	497.7	< 0.0001	< 0.001
E-1 (autumn)	Hamburg 1971	81	236	112.1	0.0002	< 0.001
	Hamburg 1978	81	236	413.4	0.0472	0.011
	Hamburg 1961	81	236	497.7	0.1145	0.023
E-1 (autumn)	Hamburg 1971	126	169	112.1	< 0.0001	< 0.001
	Hamburg 1978	126	169	413.4	0.0003	< 0.001
	Hamburg 1961	126	169	497.7	0.0011	< 0.001
E-1 (spring)	Hamburg 1971	81	345	112.1	0.0120	0.011
	Hamburg 1978	81	345	413.4	0.3069	0.074
	Hamburg 1961	81	345	497.7	0.4798	0.096
E-1 (spring)	Hamburg 1971	126	232	112.1	< 0.0001	< 0.001
	Hamburg 1978	126	232	413.4	0.0037	0.001
	Hamburg 1961	126	232	497.7	0.0093	0.002
E-2 (autumn)	Hamburg 1971	1424	35	112.1	< 0.0001	< 0.001
	Hamburg 1978	1424	35	413.4	< 0.0001	< 0.001
	Hamburg 1961	1424	35	497.7	< 0.0001	< 0.001
E-2 (spring)	Hamburg 1971	1424	35	112.1	< 0.0001	< 0.001
	Hamburg 1978	1424	35	413.4	< 0.0001	< 0.001
	Hamburg 1961	1424	35	497.7	< 0.0001	< 0.001
E-3 (autumn)	Hamburg 1971	3098	1470	112.1	< 0.0001	< 0.001
	Hamburg 1978	3098	1470	413.4	< 0.0001	< 0.001
	Hamburg 1961	3098	1470	497.7	< 0.0001	< 0.001
E-3 (spring)	Hamburg 1971	3098	1470	112.1	< 0.0001	< 0.001
	Hamburg 1978	3098	1470	413.4	< 0.0001	< 0.001
	Hamburg 1961	3098	1470	497.7	< 0.0001	< 0.001

Conclusions :

Since all simulations were run with conservative input parameters, residues in ground water resulting from classical leaching through the soil profile under normal agricultural conditions are unlikely to exceed the drinking water limit of 0.1 µg/l

B.7.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2)

B.7.4.1 Hydrolysis rate of relevant metabolites, degradation and reaction products (Annex IIA 7.2.1.1)

See table B.2.1-1 : Physical and chemical properties of pyraflufen-ethyl
and table B.2.1-2 : Physical and chemical properties of metabolites of pyraflufen-ethyl

Main results of the hydrolysis study (Ikemoto, 1996a)

pH	temperature	
4	50	the a.s. is hydrolytically stable
9	50	the a.s. is rapidly hydrolyzed ($t_{1/2} < 2.4\text{h}$)
7	50	$t_{1/2} = 0.697\text{ d}$
7	25	$t_{1/2} = 13.1\text{ d}$, only hydrolysis product is E-1

The metabolite E-1 is hydrolytically stable at 50°C pH 4, 7, 9 ($t_{1/2} > 1\text{ year}$).

B.7.4.2 Direct phototransformation of relevant metabolites, degradation and reactions products in water (Annex IIA 7.2.1.2)

The main photodegradation product of pyraflufen-ethyl is PD-1 (ethyl 2-hydroxy-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetate). PD-1 was easily photodegraded to many minor polar products (estimated half-life : $\approx 15.3\text{ h}$)

The photodegradation of the metabolite E-1 which is the major water metabolite was investigated.

Aqueous photolysis study of metabolites of ET-751 using distilled water and river water (Ikemoto, 1996)

Guidelines :

Japanese MAFF guideline

GLP :

No

Material and Methods :

Test substance:

[^{14}C -pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetic acid (E-1), specific activity : 1.86 GBq/nmol, radiochemical purity = 99.3%

[^{14}C -pyrazole] 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenol (E-2), specific activity : 1.92 GBq/nmol, radiochemical purity = 96.2%

[^{14}C -pyrazole] 4-chloro-3-(4-chloro-2-fluoro-5-methoxyphenyl)-5-difluoromethoxy-1-methylpyrazole (E-3), specific activity : 1.85 GBq/nmol, radiochemical purity = 99.5%

Test conditions:

- The 3 metabolites were continuously irradiated in natural (pH : 7.5-7.6) and distilled water (pH : 4.7-5.3) in a Heraeus Xenon-arc lamp at $25\text{ }^{\circ}\text{C} \pm 3$ for up to 38 h. The Xenon lamp was equipped with a UV cut-off filter at 270 nm and provided a constant irradiation intensity of $8582.5\text{ }\mu\text{W}/\text{cm}^2$.

- no photosensitizer

- Application rate was 0.06 mg equivalent of ET-751/l water

- sampling at 0, 12, 18, 24, 38 h

Analytical methods :

HPLC with RI detection at 248 nm.

Findings and conclusions :

Table B.7.2.1.2-1 : Photodegradation of the water metabolites E-1, E-2, E-3

Compound	Half-lives in distilled water (h)	half-lives in river water (h)
E-1	22.1	17.2
E-2	8.7	1.3
E-3	29.1	30.1

In the degradation with E-1, the degradation products (PD-2, PD-3, PD-4 and PD-5) were determined but not identified. These degradates would be more polar than E-1.

B.7.4.3 Ready biodegradability of the active substance (Annex IIA 7.2.1.3.1)

The active substance is not readily biodegradable. A study for confirmation is ongoing.

B.7.4.4 Water/sediment study (Annex IIA 7.2.1.3.2)

(¹⁴C)-ET-751: Degradation and retention in water/sediment systems. (Lewis, C. J. ,1996b).

Guidelines :

BBA Part IV, Section 5-1 (December 1990). SETAC Procedures for assessing the environmental fate and ecotoxicity of pesticides, Section 8.2 (March 1995).

GLP :

Yes

Material and Methods :

Test substance :

[¹⁴C-pyrazole] pyraflufen-ethyl, specific activity : 60.2 mCi/mmol, radiochemical purity >99%

Water and sediment :

Samples were collected in 2 streams (15-25 cm depth) in UK. ‘No pesticides have been applied to either site in the last 3 years.’

Table B.7.4.4-1 : Characteristics of the sediments

	Mill Stream	Iron Hatch
Redox potential at collection (mv)	-71.3	-44.3
pH at collection	7.89	8.28
Soil Type (UK Classification)	clay loam	sand
Organic carbon (%)	8.1	0.2
Cation exchange capacity (meq/100g)	44.7	0.8
Particle size distribution (%)		
clay (< 2 µm)	26.85	1.24
silt (2 µm to 63 µm)	51.73	1.19
sand (63 µm to 2 mm)	21.42	97.56
pH in KCl	7.4	8.2
pH in water	7.6	8.2
Total nitrogen (mg/kg)	5963.6	161.0
Total phosphorus (mg/kg)	2400.5	2462.2

Table B.7.4.4-2 : Characteristics of the waters

	Mill Stream		Iron Hatch	
Temperature at collection	5.8		5.9	
pH at collection	8.03		7.99	
Oxygen concentration (%)				
- surface	91.0		86.7	
- above the sediment	83.3		86.0	
Redox potential	+83.7		+70.3	
	Initial	Termination	Initial	Termination
Total nitrogen (mg/l)	1.4	19.6	5.6	4.2
Total phosphorus (mg/l)	0.8	6.9	0.6	0.9
Dissolved organic carbon (mg/l)	<0.05	18.6	2.4	9.9
Water hardness (mg/l as CaCO ₃)	136	263	148	246
Suspended solids (mg/l)	28.0	1210	24.0	104

Oxygen concentration, pH and redox potential of water and sediment were monitored during the experiment.

Experimental design :

[¹⁴C] Pyraflufen-ethyl was applied at 20 g a.s./ha to glass cylinders containing two equilibrated water/sediment systems at a depth of 2.5 cm of sediment and 6 cm of water and maintained at 20°C. The radioactivity in the water was determined by liquid scintillation counting and high performance liquid chromatography (HPLC) after extraction with ethyl acetate or elution through a C₁₈ solid phase extraction (SPE) cartridge. Radioactivity in the sediment was analysed by HPLC after elution through a C₁₈ SPE cartridge. Analysis was confirmed by two-dimensional TLC.

Findings :

Table B.7.4.4-3 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole] pyraflufen-ethyl to Mill stream pond water/sediment system under aerobic conditions (HPLC)

	Sampling Interval								
	0 h	6 h	1d	2 d	7 d	14 d	30 d	59 d	100 d
<u>Volatile traps</u>	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.07	N.D.
<u>Water extract</u>	81.26	83.76	83.66	79.11	N.A.	N.A.	N.A.	N.A.	N.A.
Pyraflufen-ethyl	73.42	3.11	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-1	5.58	74.56	83.09	77.92	62.31	47.18	35.50	21.33	11.01
E-2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.50
E-3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SUnknown 1, 3, 4, 5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Unresolved Background	1.23	1.35	0.57	1.19	0.27	0.91	0.31	0.23	0.24
<u>Sediment extract</u>	18.75	12.96	16.42	21.80	34.99	47.42	56.10	60.36	71.68
Pyraflufen-ethyl	8.24	2.72	0.14	0.46	N.D.	N.D.	N.D.	N.D.	N.D.
E-1	10.14	9.98	15.32	20.74	23.15	39.07	39.02	23.37	7.14
E-2	N.D.	N.D.	0.71	N.D.	11.33	7.67	15.56	31.23	54.09
E-3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.31	2.19	7.24
SUnknown 1, 3, 4, 5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.21	2.74
Unresolved Background	0.37	0.25	0.24	0.60	0.51	0.67	1.21	0.36	0.46

<u>Sediment residue</u>	0.22	0.17	0.26	0.54	0.83	2.06	4.30	15.92	12.82
<u>Probe and unit washes</u>	0.25	0.56	0.12	0.35	N.D.	0.23	N.D.	N.D.	0.15
<u>Mass balance</u>	100.48	97.44	100.45	101.79	98.40	97.79	96.21	97.91	96.39

Table B.7.4.4-4 : Distribution of applied radioactivity (mean %) after application of [¹⁴C-pyrazole] pyraflufen-ethyl to Iron Hatch water/sediment system under aerobic conditions (HPLC)

	Sampling Interval								
	0	6 h	1d	2 d	7 d	14 d	30 d	59 d	100 d
<u>Volatile traps</u>	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
<u>Water extract</u>	81.40	97.83	95.69	93.25	N.A.	N.A.	N.A.	N.A.	N.A.
Pyraflufen-ethyl	75.26	11.63	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-1	5.15	84.73	94.01	92.97	84.32	78.88	71.03	66.40	41.95
E-2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.07
SUnknown 2, 3, 4, 6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.87
Unresolved Background	0.99	1.49	1.67	0.28	0.35	1.37	0.96	0.22	0.58
<u>Sediment extract</u>	17.04	3.93	5.17	7.53	13.17	17.62	23.35	29.68	42.16
Pyraflufen-ethyl	10.90	0.44	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
E-1	5.70	3.43	5.07	6.97	10.28	10.99	11.17	13.41	12.50
E-2	N.D.	N.D.	N.D.	N.D.	2.54	6.54	11.64	12.07	20.65
E-3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.52	3.80	6.39
E-9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.15
SUnknown 2, 3, 4, 6	N.D.	N.D.	N.D.	0.40	N.D.	N.D.	N.D.	N.D.	1.68
Unresolved Background	0.45	0.06	0.10	0.16	0.35	0.09	0.02	0.39	0.79
<u>Sediment residue</u>	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.93	2.22	4.57
<u>Probe and unit washes</u>	0.79	N.D.	0.11	0.28	N.D.	0.25	N.D.	N.D.	0.50
<u>Mass balance</u>	99.23	101.76	100.96	101.05	97.83	98.12	96.27	98.52	97.69

Table B.7.4.4-5 : Degradation rates of pyraflufen-ethyl in water/sediment systems

Soil Type	Total system		Surface water	
	DT ₅₀ (h)	DT ₉₀ (h)	DT ₅₀ (h)	DT ₉₀ (h)
Mill Stream	2	6	1	4
Iron Hatch	2	7	2	7

Conclusions :

The a.s. is rapidly degraded with a DT₅₀ value of < 2 hours.

The main degradation product is E-1, mainly found in water phase, reached maximum concentrations 24 h after a.s. application. It degraded then slowly and attained 11% and 42% of applied radioactivity at day 100. (DT₅₀ E-1 whole system» 50-100 days).

The metabolite E-2 was produced after E-1 and was found almost exclusively in sediment. (21- 54 % RR after 100 days)

The metabolite E-3 was found in sediment. Its concentrations increased steadily from 30 to 100 days (6-7 % after 100 days)

B.7.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products (Annex IIA 7.2.1.4)

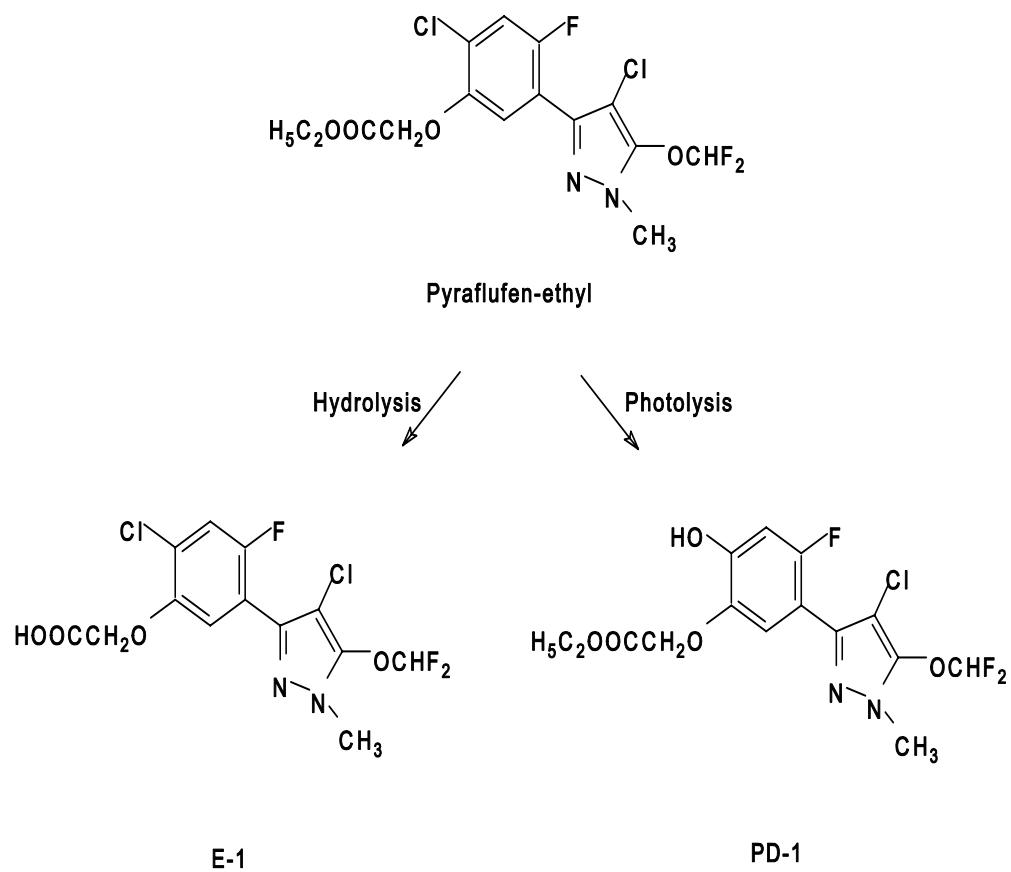
Studies to investigate the behaviour of the a.s. and metabolites in the saturated zone are not required.

B.7.5 Impact on water treatment procedures (Annex IIIA 9.2.2)

Due to its use pattern (herbicide in cereals), it is not expected that the a.s. would contaminate water treatment plants.

B.7.6 Summary of behaviour in water and predicted environmental concentrations in surface water (PEC_{sw}) (Annex IIIA 9.2.3)

Figure B.7.6-1 : Proposed degradation pathway of pyraflufen-ethyl in water



Hydrolysis

Hydrolysis rate ($t_{1/2}$) of pyraflufen ethyl is = 13.1 d at pH 7, 25°C. The only hydrolysis product is E-1.

The active substance is hydrolytically stable at pH 4.

Metabolite E-1 is hydrolytically stable at pH 4-7-9.

Photodegradation

The main photodegradation product of pyraflufen-ethyl is PD-1 (ethyl 2-hydroxy-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetate).

The major water metabolite E-1 has a photodegradation half-life of 17.2-22.1 hours. Its degradation products (PD-2, PD-3, PD-4 and PD-5) were determined but not identified. These degradates would be more polar than E-1.

Ready biodegradability

Pyraflufen-ethyl is not ready biodegradable.

Water sediment study

The a.s. and the metabolites E-1, E-2 E-3 were observed in the water/sediment study.

- Pyraflufen-ethyl is rapidly degraded with a DT_{50} water of 1-2 hours .
- The metabolite E-1 reaches rapidly a maximum after a few days. It is mainly present in the water phase. Its DT_{50} can be estimated at 50-100 days. Its log Pow is 2.90.
- The metabolite E-2 is present at high level in sediment. The degradation rate of this compound cannot be estimated. Its log Pow is 2.88.
- The metabolite E-3 is mainly found in sediment at relatively low level (6-7% after 100 days). Its log Pow is 3.66.

PEC surface water

The estimations of the PEC_{sw} were calculated assuming that :

- Drift scenarios according to Ganzelmeier (1992) is applied.
- The waterbody is 30 cm deep
- The application rate is 13.5 g a.s./ha
- Calculations according to a first order kinetics
- For the a.s. only initial PEC was calculated. Due to its very short DT₅₀, short and long term PEC are not relevant.
- For E-1, it is assumed that the a.s. is completely and almost instantaneously degraded to E-1. The DT₅₀ of E-1 is 100 days
- For E-2 and E-3 no accurate PEC can be calculated. However, as both compounds degraded slowly, it can be assumed that the concentrations will remain at the level of the calculated initial PEC. TER are calculated with comparison against the initial PEC (assuming complete degradation of the a.s. into its metabolites)

Table B.7.6-1 : PEC surface water of the active substance and metabolite E-1

Time after applications (days)	Cereals 13.5 g a.s./ha 1 application, 1m drift 4% of applied dose reaching the water body		
	pyraflufen-ethyl	metabolite E-1	
	Actual concentration (mg/l)	Actual concentration (mg/l)	TWA concentration (mg/l)
0	0.00018	0.00018	0.00018
1	-	0.00018	0.00018
2	-	0.00018	0.00018
4	-	0.00018	0.00018
7	-	0.00017	0.00018
14	-	0.00017	0.00017
21	-	0.00016	0.00017
28	-	0.00015	0.00016
50	-	0.00013	0.00015
100	-	0.00009	0.00013

B.7.7 Fate and behaviour in air (Annex IIA, 7.2.2; Annex IIIA 9.3)

B.7.8 Summary of behaviour in air and predicted environmental concentrations in air (PECa) (Annex IIIA 9.3)

vapour pressure = $1.6 \cdot 10^{-8}$ Pa
water solubility = 0.082 mg/L

$P_H = 8.1 \cdot 10^{-5}$ Pa.m³/mol (Russell, 1996a)

Pyraflufen-ethyl is very slightly volatile. It is therefore not relevant to calculate PECa

B.7.9 Definition of the residue (Annex IIA 7.3)

Residue in soil : pyraflufen-ethyl and the major metabolites E-1, E-2, E-3 recovered in the soil metabolism studies.

Residue in water : pyraflufen-ethyl and the metabolite E-1

B.7.10 References relied on**Environmental fate and behaviour of the active substance (Annex IIA 7)**

Author(s)	Year	Annex IIA Point Title Company, Report No.	GLP GEP	Published or not	Owner
			Y/N	Y/N	
Bates, M.	1996	IIA, 7.1.2/01 ET-751: Determination of adsorption coefficient on soil (K _{oc}) by HPLC simulation. Nihon Nohyaku, Report No: E-5005	Y	N	NN
Benwell, L. and Burden, A. N.	1997	IIA, 7.1.1.2.2/01 ET-751 SC (containing 20 g ET-751/l): Dissipation from four field soils following spring application. Nihon Nohyaku, Report No: R-5028	Y	N	NN
Burden, A. N. and Dunn, L	1997	IIA, 7.1.1.2.2/02 ET-751 SC (containing 20 g ET-751/l): Dissipation from four field soils following autumn application. Nihon Nohyaku, Report No: R-5031	Y	N	NN
Ikemoto, Y.	1996	IIA, 7.2.1.1/01 Aqueous hydrolysis study of ET-751. Nihon Nohyaku Co. Ltd., Report No: E-5008	Y	N	NN
Ikemoto, Y.	1996	IIA, 7.2.1.2 Aqueous photolysis study of metabolites of ET-751 using distilled water and river water . Nihon Nohyaku Co. Ltd., Report No: LSRC-E96-059A	N	N	NN
Ikemoto, Y.	1997	IIA, 7.2.1.2 Aqueous photolysis study of ET-751. Nihon Nohyaku Co. Ltd., Report No: E-5025	Y	N	NN
Kimura, Y.	1996a	IIA, 7.1.3.1 Soil column leaching of [pyrazole-5- ¹⁴ C] ET-751 (Normal study) Nihon Nohyaku, Report No: E-5009	Y	N	NN
Kimura, Y.	1996b	IIA, 7.1.3.2 Soil column leaching of [pyrazole-5- ¹⁴ C] ET-751 (Aged study) Nihon Nohyaku, Report No: E-5010	Y	N	NN
Lewis, C. J.	1996a	IIA, 7.1.1.1.2/02, 7.1.1.2.1/08 (¹⁴ C)-ET-751: Photodegradation on a soil surface. Nihon Nohyaku, Report No: E-5006	Y	N	NN
Lewis, C. J.	1996b	IIA, 7.2.1.3.2 (¹⁴ C)-ET-751: Degradation and retention in water/sediment systems. Nihon Nohyaku, Report No: E-5011	Y	N	NN
Lewis, C. J.	1997	IIA, 7.2.1.1/02 (¹⁴ C)-E-1: Hydrolytic stability. Nihon Nohyaku, Report No.: E-5024	Y	N	NN
Purser, D.	1995a	IIA, 7.1.1.2.1/02 (¹⁴ C)-ET-751: Soil degradation at 20°C.	Y	N	NN

Author(s)	Year	Annex IIA Point Title Company, Report No.	GLP GEP Y/N	Published or not Y/N	Owner
		Nihon Nohyaku, Report No: E- 5001			
Purser, D.	1995b	IIA, 7.1.1.2.1/03 (¹⁴ C)-ET-751: Soil degradation at 10°C Nihon Nohyaku, Report No: E- 5003	Y	N	NN
Purser, D.	1996a	IIA, 7.1.1.1.1/01, 7.1.1.2.1/01 (¹⁴ C)-ET-751: Aerobic soil metabolism Nihon Nohyaku, Report No: E-5018	Y	N	NN
Purser, D.	1996b	IIA, 7.1.1.1.2/01, 7.1.1.2.1/05 (¹⁴ C)-ET-751: Anaerobic soil metabolism. Nihon Nohyaku, Report No: E-5004	Y	N	NN
Purser, D.	1997	IIA, 7.1.1.1.1/02 (¹⁴ C)-ET-751: Aerobic soil metabolism - Addendum Nihon Nohyaku, Report No: E-5027	Y	N	NN
Yeomans, P.	1996a	IIA, 7.1.1.2.1/04 (¹⁴ C)-E-2 (ET-751 metabolite): Soil degradation at 20°C. Nihon Nohyaku, Report No: E-5013	Y	N	NN
Yeomans, P.	1996b	IIA, 7.1.1.2.1/05 (¹⁴ C)-E-3 (ET-751 metabolite): Soil degradation at 20°C. Nihon Nohyaku, Report No: E-5014	Y	N	NN
Yeomans, P.	1996c	IIA, 7.1.1.2.1/07 (¹⁴ C)-E-2 (ET-751 metabolite): Anaerobic soil degradation at 20°C. Nihon Nohyaku, Report No: E-5012	Y	N	NN
Yeomans, P.	1996d	IIA, 7.1.2/02 (¹⁴ C)-E-1 (ET-751 metabolite): Adsorption/desorption in three soils. Nihon Nohyaku, Report No: E-5016	Y	N	NN
Yeomans, P.	1996e	IIA, 7.1.2/03 (¹⁴ C)-E-2 (ET-751 metabolite): Adsorption/desorption in three soils. Nihon Nohyaku, Report No: E-5017	Y	N	NN
Yeomans, P.	1996f	IIA, 7.1.2/04 (¹⁴ C)-E-3 (ET-751 metabolite): Adsorption/desorption in three soils Nihon Nohyaku, Report No: E-5020	Y	N	NN

Environmental fate and behaviour of the formulation MILAN (Annex IIIA 9)

Author(s)	Year	Annex IIA Point Title Company, Report No.	GLP GEP Y/N	Published or not Y/N	Owner
Wicks, R.J.	1997	Annex IIIA, 9.2.1 ET-751 and Its Soil Metabolites E-1, E-2 and E-3: Computer Simulation of the Behaviour in Soil After Autumn and Spring Applications Using the PELMO 2.01 Model) Report n°: 2014236, April 1997 Rhône-Poulenc Agro, Essex, UK	No, but good modelling practices followed	N	RPA