

## **ANNEX B**

### **Pyraflufen-ethyl**

#### **B.6 Residue data**



### Introductory remarks

Pyraflufen-ethyl (ET-751) is a selective early post emergence herbicide. The compound exhibits good selectivity to cereal crops and a high activity on broad-leaved weeds.

Its chemical name is ethyl 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetate.

Metabolism studies were carried out with pyraflufen-ethyl labelled with  $^{14}\text{C}$  uniformly either on the phenyl ring or on the pyrazole ring.

Figure : Structure of Pyraflufen-ethyl (ET-751) showing the positions of  $^{14}\text{C}$  label.

Appendix to this section contains the different metabolic pathways with the structure of the metabolites and the chemical names of synthetic reference compounds.

### B.6.1 Metabolism, distribution and expression of residues in plants (Annex IIA 6.1)

Plant uptake study with  $^{14}\text{C}$  Pyraflufen-ethyl in immature and mature wheat plants (Goodyear A., 1995)

#### Guidelines :

EPA Pesticide Assessment Guidelines, Subdivision O, Paragraph 171-4 (October, 1982)

#### GLP :

Yes

#### Material and Methods :

*Test substances :* ( $^{14}\text{C}$  Phenyl)-pyraflufen-ethyl and ( $^{14}\text{C}$  Pyrazole)-pyraflufen-ethyl.

#### *Experimental design :*

Spring wheat plants were treated at 4 leaf growth stage at a field rate of 20 g a.s./ha.

Wheat plants were harvested 23 days after treatment at an immature growth stage (BBCH 32 to 37-Stem elongation) and at full maturity, 84 days after the treatment.

Immature wheat plants were analysed as the whole plant and mature wheat plants were sampled into grain, chaff and straw.

The total radioactive residues were analysed by combustion and LSC (liquid scintillation counting).

#### *Extraction procedures :*

Immature wheat plants were extracted with methanol/acetone and subsequently extracted with acetonitrile/HCl.

The combined extracts were partitioned against ethyl acetate which was used for metabolites' elucidation.

Mature straw was extracted with methanol/acetone and subsequently extracted with acetonitrile/HCl. However, the elucidation was conducted on the methanol/acetone extract.

Identification and characterisation of the metabolites were carried out by TLC and HPLC using reference standards.

Chaff and grain were not further analysed as a result of the very low ( $^{14}\text{C}$ ) residue levels present.

#### Findings :

Table B.6.1-1 : Investigation of the nature and amounts of residues of pyraflufen-ethyl (ET-751) in spring wheat - Immature plants and straw at maturity following a foliar spray treatment at a field rate of 20 g a.s./ha (residues expressed as µg/g equivalent of pyraflufen-ethyl).

Commodity	Immature wheat plants - PHI : 23 days				Mature wheat straw - PHI : 84 days			
Labelling group	<sup>14</sup> C Phenyl-pyraflufen-ethyl		<sup>14</sup> C Pyrazole-pyraflufen-ethyl		<sup>14</sup> C Phenyl-pyraflufen-ethyl		<sup>14</sup> C Pyrazole-pyraflufen-ethyl	
	µg/g	% TRR	µg/g	% TRR	µg/g	% TRR	µg/g	% TRR
<b>Total radioactive residues</b>								
	0.038	100	0.031	100	0.0145	100	0.0198	100
<b>Extractable radioactive residues</b>								
MeOH/acetone extraction phase	0.028	74	0.022	71	0.008	52	0.009	47
ACN/HCl extraction phase	0.006	15	0.006	19	0.002	17	0.005	25
<b>Total extracted fraction</b>	0.034	89	0.028	90	0.01	69	0.014	72
Ethyl acetate partitioned phase	0.031	82.1	0.027	86.6	-	-	-	-
<b>Elucidation of the extractable radioactive residues</b>								
Parent pyraflufen-ethyl	0.020	53.7	0.017	54.5	-	-	-	-
E1	0.003	7.6	0.004	12.1	0.002	13	0.002	10.4
E2	-	-	-	-	<0.001	-	<0.001	-
E3	-	-	-	-	<0.001	-	<0.001	-
E9	0.002	4.9	0.001	2.8	<0.001	-	<0.001	-
Unidentified metabolites	-	-	0.001	2	-	-	-	-
Polar metabolites	0.006	15.4	0.005	16.1	-	-	-	-
Others *	-	-	-	-	@0.001	6.6	@0.001	5
<b>Unextracted radioactive residues (URR)</b>								
	0.004	11	0.003	11	0.005	31	0.006	28
<b>Total recovery (Total extracted fraction+URR)</b>	0.038	100	0.031	101	0.015	100	0.02	100

- : Not radiodetected

\* : This fraction was composed of up to 7 unknown metabolites of which 4 or 5 accounted for 0.001 µg/g in each radiolabelled treatment group in straw at maturity.

The total radioactive residues were present at a very low level (0.0145 µg/g to 0.038 µg/g in all uptake trials).

72% to 90% of TRR could be extracted.

82% and 86% of TRR were partitioned into ethyl acetate respectively for the phenyl and pyrazole labelling treatment on immature wheat plants.

The organosoluble extract of immature plants contained predominantly unchanged parent compound (up to 53% of TRR for the 2 labelling positions). The metabolites E1 and E9 were observed as primary degradation products which were identified and quantified by TLC but not fully resolved by HPLC.

At maturity, the parent compound was not detected. The metabolite E1 was the major constituent of the residue (10 % to 13 % of TRR). The other metabolites E2, E3 and E9 were detected and identified but at a very low level

(<0.001 µg/g).

In total, up to 60% of TRR could be identified in the immature wheat plants whereas an important part of the radioactivity couldn't be identified at maturity (only around 10 % of TRR could be characterized ).

No further investigation was conducted on grain and chaff at maturity to identify the metabolites as a result of the very low level of radioactivity found (0.0002 µg/g and 0.0027 µg/g respectively).

#### Conclusion :

The parent compound and metabolite E1 were found to be the major constituents of the residue in immature wheat plants. E1 remained the most important metabolite of the residues in mature wheat straw.

The metabolic pathway of pyraflufen-ethyl in spring wheat plants is presented in figure 2 in appendix D to this section.

Pyraflufen-ethyl is rapidly and extensively metabolised through ester-ethyl hydrolysis giving the metabolite E1 which in turn gives rise either to E9 after de-methylation of the pyrazole ring resulting in detoxification or to the phenol E2 after hydrolysis of the ether bond.

Further methylation of E2 leads to the formation of a methoxy metabolite E3 and other polar compounds.

All these metabolites are toxicologically covered as they were also recovered in the metabolism of rat.

### **B.6.2 Metabolism, distribution and expression of residues in livestock (Annex IIA 6.2)**

Livestock metabolism studies were not required as the residue trials showed that no significant residues would have occurred at a level > 0.1 mg/kg of the total diet.

### **B.6.3 Definition of the residue**

#### *In plants :*

Based on the residue data in immature wheat plants and in straw at maturity, the sum of the parent compound and its metabolite E1 is proposed as the residue definition for monitoring in commodities of plant origin.

Moreover, these two metabolites exhibit the highest herbicidal activity . The contribution of metabolites E2 and E3 to that effect is considered as insignificant since the herbicidal reaction can be observed rapidly after the foliage application of pyraflufen-ethyl.

A method of analysis is validated for the determination of the parent compound and the metabolite E1.

### **B.6.4 Use pattern**

Table B.6.4 -1 : Intended uses of pyraflufen-ethyl - Foliar application - SC (pyraflufen-ethyl : 9 g/L, bifenox : 500 g/L)

Crop  Pests (*)	Country (Northern /Southern Europe)	Rate of application (g a.s./ha)	Maximum rate per season (g a.s./ha)	Spray concentration (g/hl)	*Maximum nb of applic. / season  *Growth stage at last application	Spray interval in days	Pre-harvest interval in days
winter & spring cereals	N	9-11.7	9-11.7	2.25-2.93	1 3 leaves to end of tillering	-	NA
winter cereals	N	13.5	13.5	3.38	1 BBCH 13-29	-	NA
Summer barley	N	9	9	2.25	1 BBCH 13-29	-	NA
winter barley & winter wheat	N	9 -12	9-12	2.25-3	1 BBCH 21->29	-	NA

(\*) : Group of pest controlled : Annual weeds.

NA : Not applicable for this GAP

Note : Conventional spray was used as the method of application in all the intended uses.

### B.6.5 Identification of critical GAPs

For cereal crops, the critical GAP covering Northern and Southern Europe is 1 application at 13.5 g a.s./ha at BBCH 13-29 (3 leaves unfolded to 9 or more tillers detectable).

### B.6.6 Residues resulting from supervised trials (Annex IIA 6.3; Annex IIIA 8.1)

Preliminary remarks :

The trials are summarized according to the usual format in the appendix F to this section.

The figures selected for MRL proposal are in bold and underlined.

In total, 28 trials covering both the North and the South of Europe were provided for winter, spring wheat and barley and for winter rye.

The trial designs are the same for both regions : one application of 14 to 18 g a.s./ha at BBCH 21, 29 and 30.

Samples of green plants at day 0 and at different PHIs up to normal harvest time for cereal grain and straw were analysed for the parent compound and its metabolite E1.

Levels of radioactive residues were determined according to the method using GC/NPD - GLP conditions.

6 residue trials were carried out on winter and spring wheat and barley and on winter rye in Germany. The levels of residues were determined according to the method using GC/MS.

The LOQ of the 2 methods was 0.010 mg/kg for grain and processed products and 0.020 mg/kg for straw.

#### B.6.6.1 Residues resulting from supervised trials - winter wheat

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1995 - Residues in soft Winter wheat (grain, straw) Study N°95-523 (Maestracci M.; 1997a).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1995 - Residues in soft Winter wheat - Decline study - N°95-524 (Maestracci M.; 1997b).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials Italy 1995 - Residues in soft Winter wheat (grain, straw) - N°95-680 (Maestracci M.; 1997f).

BIFENOX-ET-751 and E1(metabolite)-Formulation EXP31279A (SC) - Trials France 1996 - Residues in soft Winter wheat (grain, straw)-Study N° 96-503 (Maestracci M.; 1997g).

BIFENOX-ET-751 and E1(metabolite)-Formulation EXP31279A (SC) - Trials France 1996 - Residues in soft Winter wheat-Dcline study-Study N° 96-504 (Maestracci M.; 1997h).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1996 - Residues in soft Winter wheat (grain, straw) - N°96-519 (Maestracci M.; 1997k).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1996 - Residues in soft Winter wheat-Dcline study - N°96-520 (Maestracci M.; 1997l).

Ermittlung des Rückstandsverhaltens des herbiziden Wirkstoffes-ET-751 im Herbizid RPA 31279H in Getreide (Strätz J., 1997)

North :

8 residue trials were in accordance with the critical GAP of 13.5 g a.s./ha and 1 application, BBCH 13-29.

The residue values are :

- for grain :

Parent : <0.01, <0.01, <0.01, <0.01, <0.01, £0.005, £0.005, £0.005 mg/kg

Metabolite E1 : <0.01, <0.01, <0.01, <0.01, <0.01, £0.01, £0.01, £0.005 mg/kg

-for straw :

Parent : <0.020, 0.027, <0.020, <0.020, <0.020, £0.010, £0.010, £0.010, mg/kg

Metabolite E1 : 0.041, 0.023, <0.020, <0.020, <0.020, £0.010, £0.010, £0.010 mg/kg

South :

8 residue trials were in accordance with the critical GAP of 13.5 g a.s./ha and 1 application, BBCH 13-29.

The residue values are :

- for grain :

Parent : 8 x <0.010 mg/kg

Metabolite E1 : 8 x <0.010 mg/kg

-for straw :

Parent : <0.020, 0.023, <0.020, <0.020, <0.020, 0.030, 0.029, 0.029 mg/kg

Metabolite E1 : <0.020, <0.020, 0.068, <0.020, <0.020, 0.026, 0.022, 0.022 mg/kg

#### **B.6.6.2 Residues resulting from supervised trials - winter barley**

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1995 - Residues in Winter barley (grain, straw) - N°95-525 (Maestracci M.; 1997c).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1995 - Residues in Winter barley - Decline study - N°95-526 (Maestracci M.; 1997d).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials Spain 1995 - Residues in Winter barley (grain, straw) - N°95-679 (Maestracci M.; 1997e).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1996 - Residues in Winter barley (grain, straw) - N°96-505 (Maestracci M.; 1997i).

ET-751 and E1(metabolite) - Formulation EXP31217A (SC) - Trials France 1996 - Residues in Winter barley - Decline study - N°96-506 (Maestracci M.; 1997j).

Ermittlung des Rückstandsverhaltens des herbiziden Wirkstoffes-ET-751 im Herbizid RPA 31279 H (Strätz J., 1997)

North :

6 residue trials were in accordance with the critical GAP of 13.5 g a.s./ha and 1 application, BBCH 13-29.

The residue values are :

- for grain :

Parent : <0.01, <0.01, <0.01, <0.01, £0.005, £0.005 mg/kg

Metabolite E1 : <0.01, <0.01, <0.01, <0.01, £0.005, £0.005 mg/kg

-for straw :

Parent : <0.020, <0.020, <0.020, <0.020 mg/kg

Metabolite E1 : 0.023, <0.02, <0.02, <0.02 mg/kg

Note : Residue data in straw from 2 trials were not acceptable as a mix-up of corresponding control and treated sample may have occurred (see summary sheets in Appendix F).

South :

4 residue trials were in accordance with the critical GAP of 13.5 g a.s./ha and 1 application, BBCH 13-29.

The residue values are :

- for grain :

Parent : <0.01, <0.01, <0.01, <0.01 mg/kg

Metabolite E1 : <0.01, <0.01, <0.01, <0.01 mg/kg

-for straw :

Parent : <0.020, <0.020, <0.020, <0.020 mg/kg

Metabolite : <0.020, <0.020, <0.020, <0.020 mg/kg

#### **B.6.6.3 Residues resulting from supervised trials - Winter rye**

Ermittlung des Rückstandsverhaltens des herbiziden Wirkstoffes-ET-751 im Herbizid RPA 31279 H (Strätz J., 1997)

North :

One residue trial was submitted and was in accordance with the critical GAP of 13.5 g a.s./ha and 1 application, BBCH 13-29.

The residue values are :

- for grain :

Parent compound : £0.005 mg/kg

Metabolite E1 : £0.005 mg/kg

-for straw :

Residue data for the parent compound and metabolite E1 were not acceptable as the control samples showed residues of <0.020 mg/kg for pyraflufen-ethyl and 0.021 mg/kg for E1.

A mix-up of corresponding control and treated sample may have occurred.

### Conclusion :

MRL proposal for cereal grain is 0.02\*

In winter wheat straw, the residues of parent compound and the metabolite E1 were below the LOQ except for 7 trials with the highest residue level at 0.088 mg/kg for parent pyraflufen-ethyl + E1.

In winter barley straw, the highest residue level was found to be at 0.043 mg/kg.

### B.6.7 Effects of industrial processing and/or household preparation on the residue (Annex IIA 6.5; Annex IIIA 8.4)

Such studies are not required for the following reasons :

- Residues in cereal grains are  $<0.02$  mg/kg

-TMDI is <10 % ADI.

A limited information is available from one trial on winter rye conducted in Germany. Residues of parent pyraflufen-ethyl and metabolite E1 were below the limit of quantitation (0.01\* mg/kg) in meal and in bran.

### B.6.8 Livestock feeding studies (Annex IIA 6.4; Annex IIIA 8.3)

Such studies are not required as it is not expected that significant residues would occur at a level > 0.1 mg/kg of the total diet.

Metabolism studies on rat showed that pyraflufen-ethyl was rapidly metabolised in E1 and E9 which hardly translocated to tissues and organs.

Moreover, pyraflufen-ethyl and its metabolite E1 are not liposoluble.

Intake calculations for livestock (according to appendix G of the “Guidelines for the establishment of Community Maximum Residue Levels of Plant Protection Products in Food and Feedstuffs of Plant and Animal Origin”) are presented herebelow

Table B.6.8-1: Intake calculations for beef cattle (maximum intake of dry matter : 15 kg for 350 kg body weight)

Material	% of total DM/day	Intake of DM from material (kg/animal/d)	%dry matter in material	Intake of material (kg/animal/d)	Residue in material(mg/kg)	Residue intake (mg/animal/d)
Cereal grain	20	3	89	3.37	0.02*	0.0674
Cereal straw	50	7.5	86	8.7	0.088 (1)	0.765
Total						0.833

(1) : Maximum residue value found in winter wheat straw for the sum of parent pyraflufen-ethyl and of



**metabolite E1**

The potential intake of residues of pyraflufen-ethyl and its metabolite E1 by beef cattle is 0.00238 mg/kg bw.

Table B.6.8-2 : Intake calculations for dairy cattle (maximum intake of dry matter : 20 kg for 550 kg body weight)

Material	% of total DM/day	Intake of DM from material (kg/animal/d)	%dry matter in material	Intake of material (kg/animal/d)	Residue in material(mg/kg)	Residue intake (mg/animal/d)
Cereal grain	40	8	86	9.3	0.02*	0.186
Cereal straw	20	4	86	4.65	0.088 (1)	0.409
<b>Total</b>						0.595
<b>(1) : Maximum residue value found in winter wheat straw for the sum of parent pyraflufen-ethyl and of metabolite E1</b>						

The potential intake of residues of pyraflufen-ethyl and its metabolite E1 by dairy cattle is 0.00108 mg/kg bw.

Table B.6.8-3 : Intake calculations for pig (maximum intake of dry matter : 3 kg for 75 kg body weight)

Material	% of total DM/day	Intake of DM from material (kg/animal/d)	%dry matter in material	Intake of material (kg/animal/d)	Residue in material (mg/kg)	Residue intake (mg/animal/d)
Cereal grain	80	2.4	86	2.8	0.02*	0.056
<b>Total</b>						0.056

The potential intake of residues of pyraflufen-ethyl and its metabolite E1 by pig is 0.00074 mg/kg bw.

Table B.6.8-4 : Intake calculations for chicken (maximum intake of dry matter : 0.120 kg for 1.9 kg body weight)

Material	% of total DM/day	Intake of DM from material (kg/animal/d)	%dry matter in material	Intake of material (kg/animal/d)	Residue in material (mg/kg)	Residue intake (mg/animal/d)
Cereal grain	70	0.084	86	0.0976	0.02*	0.00195
<b>Total</b>						0.00195

The potential intake of residues of pyraflufen-ethyl and its metabolite E1 by chicken is 0.00102 mg/kg bw.

### B.6.9 Residues in succeeding or rotational crops (Annex IIA 6.6; Annex IIIA 8.5)

As DT<sub>90</sub> of pyraflufen-ethyl in field is 3-23 days, less than 10% of the applied a.s. would remain in soil. The presence of a.s. residues in succeeding crops is therefore unexpected.

Moreover, the notifier intends to provide a new study which will confirm that no significant residues of pyraflufen-ethyl and E1 in the succeeding crops are to be expected.

**B.6.10 Proposed pre-harvest intervals, re-entry intervals or withholding periods to minimize residues in crops, plants, plant products, treated areas or spaces (Annex IIA 6.8; Annex IIIA 8.7)**

*Pre-harvest intervals*

PHI is not applicable. Application timing is determined by the crop growth stage (BBCH 13-29).

*Re-entry period for livestock*

Not required.

*Re-entry period for man to treated crops*

Not required.

*Withholding period for animal feedingstuffs*

As there are no expected residues in animal feedingstuffs, a withholding period before milking and slaughter is not necessary.

*Waiting period between last application and handling treated products*

Not required.

*Waiting period between last application and sowing or planting succeeding crops*

A waiting period of 1 month between the application of pyraflufen-ethyl and sowing/planting of the succeeding crops should be observed (see point B 6.9).

**B.6.11 Estimates of the potential and actual exposure through diet and other means (Annex IIA 6.9; Annex IIIA 8.8)**

*Adult consumer :*

The following TMDI calculations are carried out using :

- the FAO/WHO cultural diet for the European (August 1994);
- the MRL proposals for individual commodities established in section B.6.6 (Residues resulting from supervised trials).
- the residue levels in processed commodities were not determined in section B.6.7 as no investigation on the effect of industrial processing on the level and the nature of the residue was required.

Additionally, the intake calculations rely on the following assumptions :

- for each crop, the % of ADI consumed is based on a body weight of 60 kg;
- the ADI of pyraflufen-ethyl is 0.2 mg/kg bw/day.

Commodity	Consumption (kg/day)	MRL (mg/kg)	Intake (mg/kg)
Cereals (1)	0.2014	0.02*	0.004028

(1) : including oats/barley/rye/wheat/triticale.

Taking into account a person of 60 kg body weight, the TMDI is  $6.71 \times 10^{-5}$  mg/kg bw/day. This represents **0.033 % of the ADI**.

*German 4-6 years old girl*

The following TMDI calculations are carried out using :

- the German diet for a 4-6 years old girl;
- the MRL proposal for individual commodities.
- the ADI of pyraflufen-ethyl is 0.2 mg/kg bw/day.

Commodity	Consumption (kg/day)	MRL (mg/kg)	Intake (mg/kg)
Cereals (1)	0.1017	0.02*	0.002034

(1) : including wheat/barley/rye/oat/bran/flour/white and whole meal/farinaceous pastes.

Taking into account a body weight of 13.5 kg, the TMDI of the German 4-6 years old girl is  $1.506 \times 10^{-4}$  mg/ kg bw/day. This represents **0.0753 % of the ADI**.

*Children and infants from United Kingdom*

The following TMDI calculations are carried out using :

- the Pesticides Safety Directorate Consumer Exposure Model;
- the MRL proposal for individual commodities.
- the ADI of pyraflufen-ethyl is 0.2 mg/kg bw/day.

Commodity	Child 30 kg bw		Infant 7.5 kg bw	
	“High level” intakes from single commodities			
	97.5th percentile consumption (kg/day)	TMDI for single commodity (mg/kg bw/day)	97.5th percentile consumption (kg/day)	TMDI for single commodity (mg/kg bw/day)
Wheat	0.2199	0.000147	0.0614	0.000164
Barley (assuming 1% beer consumption)	0.0036	0.000002	L/C	L/C
Oat	0.0305	0.00002	0.0182	0.000049
Bran	0.0216	0.000014	L/C	L/C
	Total dietary intakes from combinations of commodities (total TMDI) (mg/kg bw/day)			
Total	0.000167		0.000212	

The TMDIs of UK children and infants are respectively **0.083 % and 0.106 % of the ADI**.

Note : The contribution of animal products is not included in the intake calculations as the livestock feeding studies were not required.

**B.6.12 Community MRLs and MRLs in EU Member States (Document E-4)**

Pyraflufen-ethyl is a new herbicide. There is currently no community MRL.

#### **B.6.13 Proposed MRLs and justification and for the acceptability of those residues (Annex IIA 6.7; Annex IIIA 8.6)**

Based on the metabolism study in spring wheat plants, the relevant residues to be considered were the parent pyraflufen-ethyl and its metabolite E1.

Supervised residue trials indicated that there were no significant differences in the grain residue levels of the different cereal crops. The residues of parent pyraflufen-ethyl and E1 were each below the limit of quantitation (0.01\*) in all cases. Therefore, the MRL proposal for cereal grain is 0.02\*.

#### **B.6.14 Stability of residues during storage**

Stability study of ET-751 in wheat (grain, straw and shoot) after storage in a freezer at about -18°C, Intermediate Results (Anding C., 1997a)

Stability study of E1 in wheat (grain and straw) and barley (shoot) after storage in a freezer at about -18°C (Anding C., 1997b)

Guidelines :

Not specified

GLP :

The GLP statement will be included in the final report sent by the notifier.

Material and methods :

The stability of pyraflufen-ethyl residues has been determined in samples of wheat grain, wheat straw and barley green plants after frozen storage at -18°C for up to 6 months.

2 experiments were conducted, one where the samples were spiked with pyraflufen-ethyl with a subsequent analysis of pyraflufen-ethyl and its metabolite E1; the second where the samples were spiked with the metabolite E1.

Weighed aliquots of untreated samples were fortified at a rate of 0.1 mg/kg for wheat grain and 0.2 mg/kg for wheat straw and barley green plants.

These fortification levels were equivalent to 10 times the limit of quantification of the analytical method.

Untreated substrates were stored for procedural recovery determinations.

The determination of the levels of residues of pyraflufen-ethyl and its metabolite E1 was carried out by GC/NPD or ECD with analytical standards.

The results on wheat grains were not corrected for the recovery of the analytical procedures.

Findings :

Table B.6.14 -1 : Storage stability of pyraflufen-ethyl and metabolite E1 in frozen wheat grain, wheat straw and barley green plants.

Compound added	Fortification level (mg/kg)	% of recovery after frozen storage for :								
		1 month			3 months			6 months		
		a.s.	E1	S	a.s.	E1	S	a.s.	E1	S
<b>wheat grain</b>										
<b>pyraflufen-ethyl</b>	<b>0.1</b>	66	37	103	57	39	96	100	14	114
<b>E1</b>	<b>0.1</b>	-	96	-	-	82	-	-	75	-
<b>wheat straw</b>										
<b>pyraflufen-</b>	<b>0.2</b>	20	46.5	66.5	25.6	48.8	74.3	76.4	14.3	91

<b>ethyl</b>										
<b>E1</b>	<b>0.2</b>	-	76	-	-	99	-	-	65	-
<b>barley green plants</b>										
<b>pyraflufen-ethyl</b>	<b>0.2</b>	12.6	86.5	99.1	22.4	67.5	90	23	43.2	66.2
<b>E1</b>	<b>0.2</b>	-	98	-	-	93	-	-	78	-

Conclusion :

The total residue (sum of parent pyraflufen-ethyl and E1) showed acceptable stability in cereal grain samples stored at -18°C for up to at least 6 months.

The results obtained on barley green plants and on wheat straw are less conclusive.

Further analysis after 18 months storage are scheduled.

#### **B.6.15 Summary and evaluation of residue behaviour**

##### *Plants :*

The metabolism of pyraflufen-ethyl was investigated in spring wheat after post-emergence foliar application. In immature wheat plants, the parent pyraflufen-ethyl and its metabolite E1 were found to be the main compounds of the residues. Metabolite E9 was also present in high amounts; however this metabolite is a detoxification compound. In mature wheat straw, metabolite E1 was the major constituent of the residues. The metabolites E2 and E3 were observed at trace levels.

Cereal grain at harvest was characterized by very low levels of radioactive residues (0.0002 µg/g). No further investigation on residues was conducted.

Pyraflufen-ethyl is rapidly and extensively metabolised through ester-ethyl hydrolysis giving the metabolite E1 which in turn gives rise either to E9 after de-methylation of the pyrazole ring resulting in detoxification or to the phenol E2 after hydrolysis of the ether bond.

Further methylation of E2 leads to the formation of a methoxy metabolite E3 and other polar compounds.

All these metabolites are toxicologically covered as they were also recovered in the metabolism of rat.

The proposed metabolic pathway in plants is detailed in Appendix D (figure 2).

##### *Livestock :*

Neither metabolism studies nor livestock feeding studies have been performed as no significant residues occurred at a level > 0.1 mg/kg of the total diet.

##### *Supervised residue trials - MRLs :*

Residue trials under field conditions on wheat, barley and rye were provided for Northern and Southern Europe allowing a single MRL proposal of 0.02\* mg/kg for cereal grain.

A validated method of analysis of the parent pyraflufen-ethyl and metabolite E1 enabled the enforcement of the proposed MRL.

Data concerning processed commodities were not required.

The determination of residues in rotational crops is not required in the view of the DT<sub>90</sub> value in field for the parent compound (3-23 days).

A new study will confirm the absence of significant residues in the succeeding crops.

##### *Consumer safety :*

Assessment of the consumer safety indicated that the intake of pyraflufen-ethyl residues is well below the maximum acceptable level for the different consumer exposure models. (TMDI = 0.106% ADI)

**B.6.16 References relied on**

Author(s)	Year	Annex IIA Point Title Company, Report No.	GLP GEP Y/N	Published or not Y/N	Owner
Anding, C.	1997a	Annex IIA, 6.32/01 Stability study of ET-751 in Wheat (grain, straw and shoot) after storage in a freezer at about -18°C, Intermediate Results Nihon Nohyaku, Report n° A-5029, 21 April 1997	N	N	NN
Anding, C.	1997b	Annex IIA, 6.3.2/02 Stability study of E-1 in Wheat (grain, straw) and barley (shoot) after storage in a freezer at about -18°C, Intermediate Results Nihon Nohyaku, Report n° A-5030, 21 April 1997	N	N	NN
Goodyear, A.	1995	Annex IIA, 6.1 [ <sup>14</sup> C]-ET-751: Metabolism in spring wheat Nihon Nohyaku, Report No.: R-5001, April 1995	Y	N	NN
Maestracci, M.	1997a	Annex IIA, 6.3.1/01 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1995, Residues in soft winter wheat (grain, straw) Rhône-Poulenc Agro, Study n° 95-523, 25 April 1997	Y	N	NN
Maestracci, M.	1997b	Annex IIA, 6.3.1/02 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1995, Decline study, Residues in soft winter wheat Rhône-Poulenc Agro, Study n° 95-524, 25 April 1997	Y	N	NN
Maestracci, M.	1997c	Annex IIA, 6.3.1/03 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1995, Residue study in winter barley (grain, straw) Rhône-Poulenc Agro, Study n° 95-525, 25 April 1997	Y	N	NN
Maestracci, M.	1997d	Annex IIA, 6.3.1/04 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1995, Residues in winter barley, Decline study Rhône-Poulenc Agro, Study n° 95-526, 23 April 1997	Y	N	NN
Maestracci, M.	1997e	Annex IIA, 6.3.1/05 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials Spain 1995, Residues in winter barley (grain, straw) Rhône-Poulenc Agro, Study n° 95-679, 25 April 1997	Y	N	NN
Maestracci, M.	1997f	Annex IIA, 6.3.1/06 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials Italy 1995, Residues in soft winter wheat (grain, straw) Rhône-Poulenc Agro, Study n° 95-680, 25 April 1997	Y	N	NN
Maestracci, M.	1997g	Annex IIA, 6.3.1/07 BIFENOX - ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1995, Residues in soft winter wheat (grain, straw) Rhône-Poulenc Agro, Study n° 95-681, 25 April 1997	Y	N	NN

Author(s)	Year	Annex IIA Point Title Company, Report No.	GLP GEP Y/N	Published or not Y/N	Owner
		EXP31279A (SC), Trials France 1996, Residues in soft winter wheat (grain, straw) Rhône-Poulenc Agro, Study n° 96-503, 24 April 1997			
Maestracci, M.	1997h	Annex IIA, Point 6.3.1/08. BIFENOX - ET-751 and E-1 (metabolite), Formulation EXP31279A (SC), Trials France 1996, Residues in soft winter wheat, Decline study Rhône-Poulenc Agro, Study n° 965-504, 12 May 1997	Y	N	NN
Maestracci, M.	1997i	Annex IIA, Point 6.3.1/09 BIFENOX - ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1996, Residues in winter barley (grain and straw) Rhône-Poulenc Agro, Study n° 965-505, 15 May 1997	Y	N	NN
Maestracci, M.	1997j	Annex IIA, 6.3.1/10 ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1996, Residues in soft winter barley, Decline study Rhône-Poulenc Agro, Study n° 96-506, 25 April 1997	Y	N	NN
Maestracci, M.	1997k	Annex IIA, Point 6.3.1/11 BIFENOX - ET-751 and E-1 (metabolite), Formulation EXP31217A (SC), Trials France 1996, Residues in soft winter wheat (grain and straw) Rhône-Poulenc Agro, Study n° 96-519, 15 May 1997	Y	N	NN
Maestracci, M.	1997l	Annex IIA, 6.3.1/12 BIFENOX - ET-751 and E-1 (metabolite), Formulation EXP31279A (SC), Trials France 1996, Residues in soft winter wheat, Decline study Rhône-Poulenc Agro, Study n° 96-520, 24 April 1997	Y	N	NN
Strätz, J.	1997	Annex IIA, 6.3.1/13 Ermittlung des Rückstandsverhaltens des herbiziden Wirkstoffes ET-751 im Herbizid RPA31279H in Getreide Rhône-Poulenc Agro, Study n° 96-675, 7 May 1997	Y	N	NN



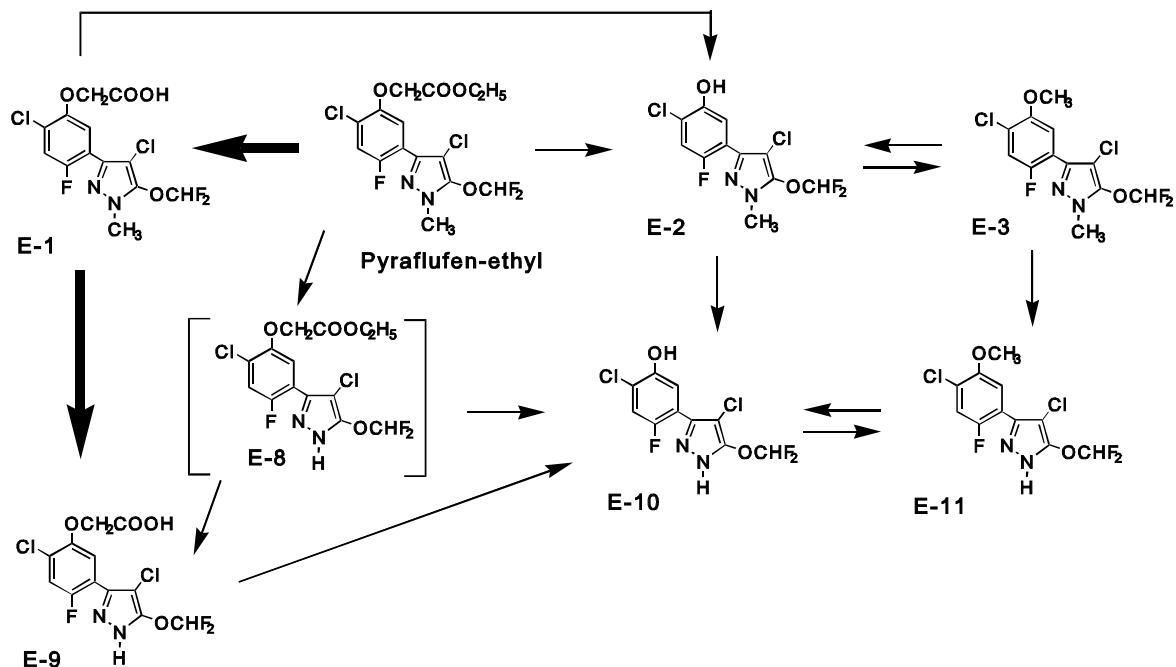
## **ANNEX B**

### **Pyraflufen-ethyl**

#### **Appendix D : Metabolic pathway in rats and in plants**



Figure 1 : Metabolic pathway of pyraflufen-ethyl in rats



Metabolic reactions of pyraflufen-ethyl in rats :

- Ester ethyl hydrolysis of ET751 --->E1
- N-dealkylation ---->E9
- N-demethylation of the pyrazole ring --->E8 ---->E9
- Hydrolysis of ether bond to phenol ---->E10
- Further methylation to form methoxy compounds.

Figure 2 : Metabolic  
pathway of  
pyraflufen-ethyl in  
spring wheat plants

## **ANNEX B**

### **Pyraflufen-ethyl**

#### **Appendix E : Chemical names of synthetic reference compounds**



Metabolite code	Chemical name
<b>Pyraflufen-ethyl (ET-751)</b>	Ethyl 2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxyacetate
<b>E-1</b>	2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazole-3yl)-4-fluorophenoxyacetic acid
<b>E-2</b>	2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazole-3yl)-4-fluorophenol
<b>E-3</b>	4-chloro-3-(4-chloro-2-fluoro-5-methoxyphenyl)-5-difluoromethoxy-1-methylpyrazole
<b>E-8</b>	ethyl 2-chloro-5-(4-chloro-5-difluoromethoxypyrazole-3yl)-4-fluorophenoxyacetate
<b>E-9</b>	2-chloro-5-(4-chloro-5-difluoromethoxypyrazole-3yl)-4-fluorophenoxyacetic acid
<b>E-10</b>	2-chloro-5-(4-chloro-5-difluoromethoxypyrazole-3yl)-4-fluorophenol
<b>E-11</b>	4-chloro-3-(4-chloro-2-fluoro-5-methoxyphenyl)-5-difluoromethoxypyrazole





## **ANNEX B**

### **Pyraflufen-ethyl**

#### **Appendix F : Residue data from supervised trials**



## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône -Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

N°	Report n° Date of delivery	Trial n° Location	Variety	Date of 1) Sowing or planting 2) Flowering	Application rate per treatment or at last treatment (average)		Dates of treatment (s) or number of treatment and	Growth stage at last treatment	Portion analysed	PHI days	Residues (average) mg/kg		Remarks
	Responsible body			3) Harvest	g a. i./ha	water l/ha	last date				ET-751	E-1	
	R&D/CRL D/ AN/vg/ 9715446  25-Apr-97  RPA France	95523BX 1 Fontaines d'Ozillac (17) France  95523RN 1 Saint- Gilles (35) France	Soissons      Sidéral	1)02-Nov- 94 3)10-Jul-95  1)25-Oct-94 3)19-Jul-95	18   18	333   330	1/ 28-Feb-95   1/ 17-Feb-95	BBCH 30  BBCH 30	grain straw  grain straw	132 132  152 152	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	foliar treatment  method of analysis : GC NPD (ILSR-R95- 024A)  <b>LOQ for each product :</b> <b>0.010 mg/kg</b> <b>(grain)</b> <b>0.020 mg/kg</b> <b>(straw)</b>

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) :EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

N°	Report n° Date of delivery	Trial n° Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and  last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRL D/ AN/vg/ 9715447  25-Apr-97  RPA France	95524OR 1 Tournois (45) France	Thésée	1)18-Oct-94 3)20-Feb-95	18	333	1/ 20-Feb-95	BBCH 29/30	shoot	hours 2	0.44	0.66	foliar treatment
				22-Feb-95						days 2			
				27-Feb-95						7			
				26-Apr-95						65			
				21-Jul-95						151			
		95524DJ1 Longvic (21) France	Soisson	1)17-Oct-94 3)27-Feb-95	18	333	1/ 27-Feb-95	BBCH 29	shoot	hours 2	0.39	0.20	method of analysis : GC NPD (ILSR-R95- 024A)  <b>LOQ : 0.010 mg/kg (grain) 0.020 mg/kg (shoot and straw)</b>
				01-Mar-95						days 2			
				07-Mar-95						8			
				27-Apr-95						59			
				13-Jul-95						136			
										136			

[illegible]

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
 Country :  
 Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
 Formulation (e.g. WP) :EXP31217A (SC)  
 Commercial product (name) :  
 Producer of commercial product : RP Agro

**Crop : soft winter wheat**

indoor/outdoor : outdoor  
 Other a. i. in formulation :  
 (Common name and content) :

N°	Report n° Date of delivery	Trial n° Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment (average)		Dates of treatment (s) or number of treatment and  last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks												
	Responsible body				g a. i./ha	water l/ha					ET-751	E-1													
	R&D/CRL D/ AN/vg/ 9715447  25-Apr-97  RPA France	95524LY 1 St. Pierre de Chandieu (69) France	Soisson	1)22-Oct-94	18	355	1/ 01-Mar-95	BBCH 30	shoot	hours	0.099 / 0.55	0.43	foliar treatment												
				3)01-Mar-95						2				days											
				03-Mar-95						2				0.31	0.095										
				08-Mar-95						7				0.20	0.077										
				12-Apr-95						42				< 0.020	< 0.020										
				12-Jul-95						grain				133	<u>&lt; 0.010</u>	<u>&lt; 0.010</u>									
										straw				133	<u>0.023</u>	<u>&lt; 0.020</u>									
				95524AV 1 Besayes (26) France						Soisson				1)18-Oct-94	18	417	1/ 28-Feb-95	BBCH 29	shoot	hours	1.5	0.34	LOQ : 0.010 mg/kg (grain) 0.020 mg/kg (shoot and straw)		
														3)28-Feb-95						2				days	
														02-Mar-95						2				0.94	0.25
														07-Mar-95						7				0.37	0.12
														11-Apr-						42				< 0.020	< 0.020
			grain		143	<u>&lt; 0.010</u>	<u>&lt; 0.010</u>																		
			straw	143	<u>&lt; 0.020</u>	<u>0.068</u>																			

				95 21-Jul-95									
--	--	--	--	-----------------	--	--	--	--	--	--	--	--	--

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : winter barley**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues (average) mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRL D/ AN/kd/ 9715562  25-Apr-97  RPA France	95525AM 1 Domart en Ponthieu (80) France	Plaisant	1)27-Sep-94 3)11-Jul-95	18	300	1/ 22-Feb-95	29	grain straw	139 139	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	<u>&lt; 0.010</u> <u>0.023</u>	foliar treatment  method of analysis: GC-NPD (ILSR-R95- 024A)  <b>LOQ for each product :</b>

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

Content of reported a. i.	(g/kg or g/l)	: 20 g ET-751 /l
Formulation	(e.g. WP)	: EXP31217A (SC)
Commercial product	(name)	:
Producer of commercial product		: RP Agro

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks
	Responsible body										g a. i./ha	water l/ha	
	R&D/CRLD / AN/kd/ 9715507  23-Apr-97  RPA France	95526AV1 Alixan (26) France	Intro	1)08-Nov-94 3)13-Mar-95  15-Mar-95 20-Mar-95 26-Apr-95 04-Jul-95	18	333	1/ 13-Mar-95	BBCH 29	shoot  " " " grain straw	hours 2 days 2 7 44 113 113	0.69  0.76 0.44 < 0.020 <u>&lt; 0.010</u> <u>&lt; 0.020</u>	0.25  0.29 0.15 < 0.020 <u>&lt; 0.010</u> <u>&lt; 0.020</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ for each product : 0.010 mg/kg</b>



														(grain) 0.020 mg/kg (shoot and straw)
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro **Crop** : winter barley  
Country :  
Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC) indoor/outdoor : outdoor  
Commercial product (name) : Other a. i. in formulation :  
Producer of commercial product : RP Agro (Common name and content) :

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues (average) mg/kg		Remarks
	Responsible body				g a. i./ha	water l/ha					ET-51	E-1	
	R&D/CRLD / AN/kd/ 9715506  25-Apr-97  RPA Spain	95679SE1 Santa Olalla (Toledo) Spain  95679SE2 Navalcarne ro (Madrid) Spain	Albacete   Beka	1)15-Nov-94 3)22-Jun-95  1)20-Dec-94 3)23-May-95	18   18	300   300	1/ 24-Mar-95   1/ 24-Mar-95	Zadocks 30  Zadocks 32	grain straw  grain straw	90 90  60 60	<u>&lt; 0.010</u> <u>&lt; 0.020</u>  < 0.010 0.038	<u>&lt; 0.010</u> <u>&lt; 0.020</u>  < 0.010 < 0.020	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ :</b> <b>0.010 mg/kg</b> <b>(grain)</b> <b>0.020 mg/kg</b> <b>(straw)</b>

--	--	--	--	--	--	--	--	--	--	--	--	--	--

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) :EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues mg/kg		Remarks
	Responsible body				g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRLD / AN/kd/ 9715569  -Apr-97  RPA Italy	95680BO1 Bologna Italy  95680BO2 Belvedere Ostrense (AN) Italy	Golia   Manital	1)15-Oct-94 3)29-Jun-95  1)20-Oct-94 3)29-Jun-95	18  18	500  500	1/ 08-Mar-95  1/ 17-Mar-95	post emergenc e  post emergenc e	grain straw  grain straw	113 113  104 104	<u>&lt; 0.010</u> <u>&lt; 0.020</u>  <u>&lt; 0.010</u> <u>&lt; 0.020</u>	<u>&lt; 0.010</u> <u>&lt; 0.020</u>  <u>&lt; 0.010</u> <u>&lt; 0.020</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ for each product : 0.010 mg/kg</b>

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

Content of reported a. i.	(g/kg or g/l)	: 500 g bifenox /l
Formulation	(e.g. WP)	: EXP31279A (SC)
Commercial product	(name)	:
Producer of commercial product		: RP Agro

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues mg/kg	Remarks
	Responsible body				g a. i./ha	water l/ha					bifenox	
	R&D/CRLD/ AN/kd/ 9715462  24-Apr-97  RPA France	96503BX1 Allas Champagne (17) France	Sidéral	1)07-Nov-95 3)15-Jul-96	750	333	1/ 29-Feb-96	BBCH 29	grain straw	137 137	< 0.010 < 0.020	foliar treatment  method of analysis : GC-EC (RP RB-30-82 modified)  <b>LOQ : 0.010 mg/kg</b>

													<b>(grain)</b> <b>0.020 mg/kg</b> <b>(straw)</b>
--	--	--	--	--	--	--	--	--	--	--	--	--	--

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 9 g ET-751 /l  
Formulation (e.g. WP) : EXP31279A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation : bifenox  
(Common name and content) : 500 g/l

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues (average) mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRLD / AN/kd/ 9715462  24-Apr-97  RPA France	96503BX1 Allas Champagne (17) France	Sidéral	1)07-Nov-95 3)15-Jul-96	14	333	1/ 29-Feb-96	BBCH 29	grain straw	137 137	<u>&lt; 0.010</u> <u>0.030</u>	<u>&lt; 0.010</u> <u>0.026</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ :</b> <b>0.010 mg/kg</b> <b>(grain)</b> <b>0.020 mg/kg</b> <b>(straw)</b>

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 500 g bifenox /l  
Formulation (e.g. WP) : EXP31279A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation : ET-751  
(Common name and content) : 9 g/l

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg	Remarks
					g a. i./ha	water l/ha					<b>bifenox</b>	
	R&D/CRLD/ AN/kd/ 9715573  12-May-97  RPA France	96504BX1 Tugeras (17) France	Etécho	1)20-Oct-95	750	277	1/ 29-Feb-96	BBCH 29	shoot	hours	24	foliar treatment
				3)29-Feb-96						2		
				08-Mar-96						days		
				15-Apr-96						8		
		96504TL1 Mauremont (31) France	Soissons	19-Jul-96						46		method of analysis : GC-EC (RP RB-30-82 modified)
				1)04-Nov-95	750	353	1/ 07-Mar-96	BBCH 29	grain	141		
				3) 07-Mar-96					straw	141		
				14-Mar-96					shoot	hours		
				16-Apr-96					grain	2	40	<b>LOQ :</b> <b>0.010 mg/kg</b> <b>(grain)</b> <b>0.020 mg/kg</b> <b>(shoot, straw)</b>
				16-Jul-96						days		
										7		
										40		
										131		
										0.50		
										< 0.010		
										< 0.020		

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 9 g ET-751 /l  
Formulation (e.g. WP) : E XP31279A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation : bifenox  
(Common name and content) : 500 g/l

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	Responsible body												
	R&D/CRLD / AN/kd/ 9715573  12-May-97  RPA France	96504BX1 Tugeras (17) France   96504TL1 Mauremont (31) France	Etécho       Soissons	1)20-Oct-95 3)29-Feb-96  08-Mar-96 15-Apr-96 19-Jul-96  1)04-Nov-95 3) 07-Mar-96  14-Mar-96 16-Apr-96 16-Jul-96	14      14	277      353	1/ 29-Feb-96      1/ 07-Mar-96	BBCH 29      BBCH 29	shoot  " " grain straw	hours 2 days 8 46 141 141	0.32  0.17 < 0.020 <u>&lt; 0.010</u> <u>0.029</u>	0.072/0.40  0.17 < 0.020 <u>&lt; 0.010</u> <u>0.022</u>	foliar treatment  method of analysis: GC-NPD (ILSR-R95- 024A)  <b>LOQ for each product : 0.010 mg/kg (grain) 0.020 mg/kg (shoot, straw)</b>

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : winter barley**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

N°	Report n° Date of delivery  Responsible body	Trial n° Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment (average)		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRLD / AN/vg/ 9715628  15-May-97  RPA France	96505AM 1 Galamez (62) France	Plaisant	1)11-Oct-95 3)18-Jul-96	18	292	1/ 01-Apr-96	29/30	grain straw	108 108	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ :</b> <b>for each</b> <b>product</b> <b>0.010 mg/kg</b> <b>(grain)</b> <b>0.020 mg/kg</b> <b>(straw)</b>



## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
 Country :  
 Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
 Formulation (e.g. WP) : EXP31217A (SC)  
 Commercial product (name) :  
 Producer of commercial product : RP Agro

**Crop : winter barley**

indoor/outdoor : outdoor  
 Other a. i. in formulation :  
 (Common name and content) :

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks	
	Responsible body				g a. i./ha	water l/ha					ET-751	E-1		
	R&D/CRLD / AN/kd/ 9715513  25-Apr-97  RPA France	96506OR1 La Chaussée St Victor (41) France	Plaisant	1)20-Oct-95	18	333	1/ 19-Mar-96	BBCH 29	shoot	hours	0.18	0.19	foliar treatment	
				3)19-Mar-96						2 days				
				26-Mar-96						7				
			Plaisant	02-May-96	18	333	1/ 12-Mar-96	BBCH 29	"	44	< 0.020	< 0.020	method of analysis : GC-NPD (ILSR-R95- 024A)	
				02-Jul-96						grain				105
										straw				105
		96506DJ1 Longvic (21) France	Plaisant	1)11-Oct-95	18	333	1/ 12-Mar-96	BBCH 29	shoot	hours	0.35/0.067	0.14	<b>LOQ for each product : 0.010 mg/kg (grain) 0.020 mg/kg (straw)</b>	
				3)12-Mar-96						2 days				
				19-Mar-96						7				
			Rebelle	30-Apr-96	18	417	1/ 13-Mar-96	BBCH 29	"	49	< 0.020	0.022		
				28-Jun-96						grain				108
										straw				108
		96506AV1 Pierrelatte (26) France	Rebelle	1)27-Oct-95	18	417	1/ 13-Mar-96	BBCH 29	shoot	hours	0.34	< 0.020/0.16		
				3)13-Mar-96						2 days				
				19-Mar-96						6				
				24-Apr-96					"	42	0.024	< 0.020		
				04-Jul-96						grain				113
										straw				113

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : winter barley**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

No.	Report no. Date of delivery  Responsible body	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRLD / AN/kd/ 9715513  25-Apr-97  RPA France	96506TL1 Le Vaux (31) France	Baraka	1)14-Nov-95 3)05-Mar-96  12-Mar-96 18-Apr-96 26-Jun-96	18	367	1/ 05-Mar-96	BBCH 29	shoot  " " grain straw	hours 2 days 7 44 113 113	0.85  0.37 0.025 <u>≤ 0.010</u> <u>≤ 0.020</u>	< 0.020  < 0.020/0.15 0.021 <u>≤ 0.010</u> <u>≤ 0.020</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95- 024A)  <b>LOQ for each product : 0.010 mg/kg (grain) 0.020 mg/kg (shoot and straw)</b>

## RESIDUES DATA SUMMARY FROM SUPERVISED TRIALS

Responsible body for reporting : Rhône-Poulenc Agro  
Country :

**Crop : soft winter wheat**

Content of reported a. i. (g/kg or g/l) : 20 g ET-751 /l  
Formulation (e.g. WP) : EXP31217A (SC)  
Commercial product (name) :  
Producer of commercial product : RP Agro

indoor/outdoor : outdoor  
Other a. i. in formulation :  
(Common name and content) :

N°	Report n° Date of delivery  Responsible body	Trial n° Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Application rate per treatment or at last treatment (average)		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI days	Residues mg/kg		Remarks
					g a. i./ha	water l/ha					ET-751	E-1	
	R&D/CRLD / AN/vg/ 9715627  15-May-97  RPA France	96519RS1 Loivre (51) France	Vivant	1)10-Oct-95 3)05-Aug-96	18	250	1/ 28-Mar-96	29	grain straw	130 130	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	<u>&lt; 0.010</u> <u>&lt; 0.020</u>	foliar treatment  method of analysis : GC-NPD (ILSR-R95-024A)  <b>LOQ for each product :</b> <b>0.010 mg/kg (grain)</b> <b>0.020 mg/kg (straw)</b>

Crop : soft winter wheat

indoor/outdoor	: outdoor
Other a. i. in formulation	:
(Common name and content)	:

No.	Report no. Date of delivery	Trial no. Location	Variety	Date of 1) Sowing or planting 2) Flowering 3) Sampling	Application rate per treatment or at last treatment (average)		Dates of treatment (s) or number of treatment and last date	Growth stage at last treatment	Portion analysed	PHI hours/ days	Residues (average) mg/kg		Remarks		
	Responsible body				g a. i./ha	water l/ha					ET-751	E-1			
	R&D/CRLD/ AN/kd/ 9715514	96520RN1 Saint- Grégoire (35) France	Sidéral	1)24-Oct-95 3)14-Feb-96	17	281	1/ 14-Feb-96	BBCH 29	shoot	hours 2 h15 days	1.02/0.021	0.38	foliar treatment		
	24-Apr-97			21-Feb-96					"	7				0.24	0.25
	RPA France			26-Mar-96					"	41				0.021	< 0.020
				22-Jul-96					grain	159				< <b>0.010</b>	< <b>0.010</b>
									straw	159				< <b>0.020</b>	< <b>0.020</b>
		96520DJ1 Longvic (21) France	Soissons	1)11-Oct-95 3)12-Mar-96	18	333	1/ 12-Mar-96	BBCH 29	shoot	hours 2 days	0.034	0.65	<b>LOQ for each product : 0.010 mg/kg (grain) 0.020 mg/kg (shoot, straw)</b>		
				19-Mar-96					"	7				0.18	0.085
				06-May-96					"	55				< 0.020	< 0.020
				17-Jul-96					grain	127				< 0.010	< 0.010
									straw	127				< 0.020	< 0.020

## RESIDUES RESULTING FROM SUPERVISED TRIALS (SUMMARY)

Rhône-Poulenc Agro GmbH

## Germany

**residue study - decline curves (DC) including processing****ET-751 (9 g/l)**

Crop

## Cereals

**EXP 31279 (SC)**

"RPA 31279

Indoor/outdoor

Outdoor

Rhône-Poulenc

Other a.i. in the

**Bifenox (500 g/l)**

N	Report No	Location incl Post	Variety	Rate of treatment			Dates of	Portion of	PHI	Residues (average) in mg/kg			Remarks
	Date of delivery Responsible body	code Country	Date of 2) Flowering 3) Harvest	a.i. (g/ha)	Water (l/ha)	Conc. (% a.i.)	treatment (s) treatments and last date	commodity	(days)	Metabolite E-1	ET-	Total as „ET-751“	
1	Study 96-675; R1/96; P 205 G PTRL Europe May 1997 Rhône-Poulenc Agro GERMANY	WTA Region 10 27234 Winkelsett- Hölingen Niedersachsen GERMANY	<b>winter</b> Ritmo 1) 14.11.95 3) 30.04.96 3) 20.06.96 3) 21.08.96	14.36	300		30.04.96 (BBCH 29)	shoot shoot grain straw	0 51 113 113	0.085 ≤ 0.005 ≤ <b>0.010</b> ≤ <b>0.010</b>	0.11 ≤ 0.005 ≤ <b>0.005</b> ≤ <b>0.010</b>	0.20 ≤ 0.010 ≤ 0.010 ≤ 0.020	<b>post emergence (foliar</b>  Method: RPA/96-017 using GC/MS/MS  <b>Limit of detection</b> <b>each for ET-751 or Metabolite</b> shoot, grain, processed 0.005 mg/kg straw: 0.010 mg/kg
		WTA Region 20 24623 Großenaspe  Schleswig-Holstein GERMANY	<b>spring</b> Nandu 1) 09.04.96 3) 17.05.96 3) 25.06.96 3) 03.09.96	14.99	300		17.05.96 (BBCH 21)	shoot shoot grain straw	0 39 109 109	0.19 ≤ 0.005 ≤ <b>0.010</b> ≤ <b>0.010</b>	0.075 ≤ 0.005 ≤ <b>0.005</b> ≤ <b>0.010</b>	0.28 ≤ 0.010 ≤ 0.010 ≤ 0.020	<b>Limit of quantification for</b> <b>material (LOQ):</b> <b>each for ET-751 or Metabolite</b> shoot, grain, processed 0.010 mg/kg straw: 0.020 mg/kg
		WTA Region 30 59457 Werl Oberbergstraße Nordrhein- GERMANY	<b>winter</b> Kanzler 1) 11.10.95 3) 04.04.96 3) 12.06.96	14.30	300		04.04.96 (BBCH 29)	shoot shoot	0 69	0.087 ≤ 0.005	0.12 ≤ 0.005	0.22 ≤ 0.010	<b>ET-751 and Metabolite E-1</b> <b>expressed as: „ET-751“</b> shoot, grain, processed

		3) 12.08.96					grain	130	≤ <b>0.005</b>	≤ <b>0.005</b>	≤ 0.010	0.020 mg/kg
							straw	130	≤ <b>0.010</b>	≤ <b>0.010</b>	≤ 0.020	straw: 0.040 mg/kg

## RESIDUES RESULTING FROM SUPERVISED TRIALS (SUMMARY)

Responsible body for reporting	Rhône-Poulenc Agro GmbH	Type of study	residue study - decline curves (DC) including processing
Country	Germany	Crop	cereals
Reported active ingredient	ET-751 (9 g/l)	Indoor/outdoor	Outdoor
Formulation	EXP 31279 (SC)	Other a.i. in the	Bifenox (500 g/l)
Commercial product	"RPA 31279		
Producer of commercial product	Rhône-Poulenc		

N	Report No Date of delivery Responsible body	Location incl Post code Country	Variety Date of 2) Flowering 3) Harvest	Rate of treatment			Dates of treatment (s) treatments and last date	Portion of commodity	PHI (days)	Residues (average) in mg/kg			Remarks
				a.i. (g/ha)	Water (l/ha)	Conc. (% a.i.)				Metabolite E-1	ET-751	Total as „ET-	
	Study 96-675; R1/96; P 205 G PTRL Europe May 1997 Rhône-Poulenc Agro GERMANY	WTA Region 50 67189 Kriegsfeld Rheinland-Pfalz GERMANY	winter rye Clou 1) 06.10.95 3) 15.04.96 3) 13.05.96 3) 09.08.96	15.41	300		15.04.96 (BBCH 29)	shoot shoot grain meal bran straw*	0 28 116 116 116 116	0.27 ≤ 0.005 ≤ <b>0.005</b> ≤ 0.005 ≤ 0.005 0.021*	0.35 ≤ 0.005 ≤ <b>0.005</b> ≤ 0.005 ≤ 0.005 < 0.020*	0.65 ≤ 0.010 ≤ 0.010 ≤ 0.010 ≤ 0.010 < 0.040*	post emergence (foliar  Method: RPA/96-017 using GC/MS/MS  <b>Limit of determination each for ET-751 or Metabolite E-</b> shoot, grain, processed 0.005 mg/kg straw: 0.010 mg/kg  <b>Limit of quantification for plant material (LOQ): each for ET-751 or Metabolite E-</b> shoot, grain, processed 0.010 mg/kg straw: 0.020 mg/kg  <b>ET-751 and Metabolite E-1</b>
		WTA Region 60 37242 Bad Sooden Allendorf Hessen GERMANY	winter Astrid 1) 24.09.95 3) 23.04.96 3) 29.05.96 3) 31.07.96	14.39	300		23.04.96 (BBCH 29/30)	shoot shoot grain straw*	0 36 99 99	0.17 ≤ 0.005 ≤ <b>0.005</b> 0.040*	0.19 ≤ 0.005 ≤ <b>0.005</b> < 0.010*	0.37 ≤ 0.010 ≤ 0.010 < 0.043*	
		WTA Region 70	spring	15.08	400		24.05.96						

