AMINOPYRALID (220)

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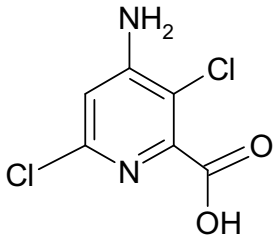
EXPLANATION

Aminopyralid is a new herbicide that is used for the control of broadleaf weeds in pastures and cereal crops. It was advanced to the 2006 JMPR schedule of new compounds by the 37th session of the CCPR. The manufacturer has submitted studies on metabolism in plants and animals, analytical methods, storage stability, environmental fate and degradation, supervised field trials, processing and farm animal (livestock) feeding.

IDENTITY

ISO common name	Aminopyralid
Synonyms	DE-750; XDE-750; XR-750; X660750
IUPAC name	4-amino-3,6-dichloropyridine-2-carboxylic acid
Chemical Abstracts name	2-pyridinecarboxylic acid, 4-amino-3,6-dichloro
CAS Number	150114-71-9
Molecular formula	$C_6H_4Cl_2N_2O_2$
Molecular weight	207.026

Structural formula



PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Purity: 99.5% wt/wt ± 0.1%

Physico-chemical properties		Ref.
Appearance	off-white powder (at 22.7 °C)	FAPC 013087
Odour	odourless	FAPC 013087
Melting Point	163.5 °C	FAPC 023263
Density	1.72 ± 0.065 at 20 °C	FAPC 013087
pH	2.31 (1% w/w aq solution at 23.4 °C)	FAPC 013087
Vapour pressure	9.52×10^{-9} at 20 °C	DECO GL-AL MD-2001-000921
	2.59×10^{-8} Pa at 25 °C	DECO GL-AL MD-2001-000921
Henry's Law constant	5.18×10^{-10} Pa m^3/mol unbuffered at 18 °C	NAFST540
	9.30×10^{-12} Pa m^3/mol at pH 5 and 20 °C	
	9.61×10^{-12} Pa m^3/mol at pH 7 and 20 °C	
	9.71×10^{-12} Pa m^3/mol at pH 9 and 20 °C	
Solubility in water	2.48 g/L unbuffered at 18 °C (pH 2.35)	FOR01015

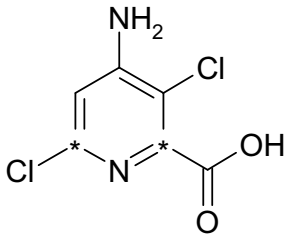
Physico-chemical properties		Ref.
	212 g/L in pH 5 buffer at 20 °C	
	205 g/L in pH 7 buffer at 20 °C	
	203 g/L in pH 9 buffer at 20 °C	
Dissociation constant in water	average pKa 2.56 ± 0.03 (pH range 2 to 3.4; n=9)	01-822-AG; GHF-P-2332
Solubility in organic solvents	acetone 29,195 µg/mL	GHE-P-9228
	1,2-dichloroethane 189 µg/mL	
	ethyl acetate 3,939 µg/mL	
	Heptane insoluble (< 10 µg/mL)	
	methanol 52,191 µg/mL	
	n-octanol 4,548 µg/mL	
	xylene 43 µg/mL	
Octanol/water partition coefficient	log K_{ow} = 0.201 ± 0.049 in unbuffered water (mean K_{ow} = 1.59 ± 0.18 (n=6))	FOR01009
Hydrolysis in sterile buffer at 20 °C and 50 °C	Hydrolytically stable at pH 5, 7 and 9 at 20 °C (31 days) and at 50 °C (5 days).	020067
Photolysis in water at 20 °C	Half-life of 0.6 days at pH 5; DT_{90} 2 days at pH 5*	020066

*The half-life of photolysis of ^{14}C-aminopyralid in sterile pH 5 buffer solution is 0.6 days, with a DT_{90} of 2 days. Samples were continuously irradiated at 20°C for the equivalent of 38 days summer sunlight at 40° N latitude. Photolysis products identified were oxamic acid, malonamic acid and CO_2 (≈ 28% of applied radiocarbon).

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The meeting received metabolism studies for aminopyralid administered to lactating goats and laying hens. In both studies, aminopyralid (or XDE-750) was labelled in the 2- and 6-positions of the pyridine ring, as shown below.



Lactating goat

A single lactating goat was orally dosed for 6 days with ^{14}C aminopyralid at 13.96 ppm in the feed (0.26 mg/kg bw/day) (MacPherson and Gedik 2003). Mean food consumption over 6 days was 1.38 kg dry matter; the mean dose was 19.23 mg/goat. The dose was administered immediately after the morning milking and prior to the morning feeding.

Urine and faeces were collected prior to dose administration and at 24 hour intervals thereafter for the duration of the dosing period. The animal cage was washed at the end of the excreta collection period.

Milk was collected immediately prior to dosing (am) and in the afternoon (pm) each day; the final milk sample was collected immediately prior to sacrifice. Less than 24 hours after the final dose, the goats were slaughtered and samples of liver, kidney, omental fat, perirenal fat, triceps muscle, semi-membranous muscle and longissimus dorsi muscle were collected for analysis. The two fats (omental and perirenal) were composited in equal amounts to form one fat sample; similarly the

muscle samples were composited into one muscle sample. Liver and kidney samples were processed on the day of collection and placed in freezer storage (–20° C); muscle and fat samples were placed in the freezer pending analysis. All samples were analysed within 245 days of collection.

Total radioactivity was measured in all samples of milk, urine, faeces, cage wash and tissues using scintillation counting and combustion analysis. Total radioactive residues (TRR) as a percentage of the administered dose is shown below.

Urine	Faeces	Cage wash	Milk	Liver	Kidneys	**Total**
46.03%	46.46%	2.88%	0.05%	0.01%	0.01%	**95.6%**

Elimination of the radioactivity via urine and faeces was similar, with each accounting for approximately 46% of the total administered dose; total eliminated 92%. Approximately 9% and 8% of the administered dose was excreted daily via faeces and urine, respectively, during 48 to 144 hours of the study.

The radioactivity in milk was found to plateau within 24 to 48 hours after dosing had commenced, i.e., by dose 2 to 3. The total radioactivity in milk was about 0.05% of the total administered dose, with concentrations ranging from 0.003 to 0.008 mg/kg parent equivalents[1].

TRR in tissues were 0.008 mg/kg equivalents in liver, 0.071 mg/kg equivalents in kidneys, 0.001 mg/kg equivalents in composite fat and non-detectable in composite muscle.

Extraction of milk samples with MeOH recovered 72.6% (0.004 mg/kg equivalents) and 72.4% TRR (0.006 mg/kg equivalents) from the 32 and 128 hour samples, respectively.

The MeOH extracts were partitioned with ether:hexane (1:1 v/v) followed by hexane to remove lipids which led to 70.7% and 70.9% TRR in the MeOH, respectively (processed extracts) for the 32 hour and 128 hour samples. Pepsin hydrolysis of the remaining non-extracted radioactivity in the post-extraction solids (PES) released another 8.5 and 4.4% TRR, respectively (see Table 1). The milk extracts were not analysed further by HPLC due to very low levels of radioactivity being present.

Extraction of liver and kidney samples with MeOH recovered 75.6% and 95.5% TRR, respectively. Partitioning of the MeOH extracts from liver with hexane gave an overall recovery of 57.8% TRR (0.004 mg/kg equivalents). Approximately 24% TRR remained in the PES. The liver extracts were not analysed with HPLC due to the low levels of radioactivity present.

The hexane extracts from kidney (initial extracts) were further processed by drying and reconstitution in 0.1% formic acid in H_2O:CH_3CN giving an overall recovery of 79.9% TRR. One radiolabelled component was identified by HPLC analysis of the processed kidney extracts; this was parent aminopyralid present at 0.057 mg/kg.

The distribution of radioactivity following various extraction steps outlined above is shown in Table 1.

Table 1. Distribution of radioactivity in extracts of milk and tissues from a lactating goat.

TRR and extracts	% TRR (mg/kg equivalents) in extracted milk and tissues			
	Milk (32 hrs)	Milk (128 hrs)	Liver	Kidney
TRR (mg/kg equiv)①	0.006	0.008	0.008	0.071
Initial extracts②	72.6 (0.004)	72.4 (0.006)	75.6 (0.006)	95.5 (0.067)
Processed extracts③	70.7 (0.004)	70.9 (0.006)	57.8 (0.004)	79.9 (0.057)
Pepsin hydrolysates④	8.5 (0.001)	4.4 (< 0.001)	–	–
PES⑤	10 (0.001)	12.9 (0.001)	24.4 (0.002)	4.5 (0.003)

① From radioanalysis data. ② Extracted with MeOH (3×), (1× for milk). ③Combined initial extracts were partitioned with hexane (milk partitioned with ether:hexane 1:1), then concentrated and centrifuged. Kidney initial extracts were dried and reconstituted in 0.1% formic acid in H_2O:CH_3CN (95:5 v/v). ④The milk pepsin hydrolysates were not processed further due to low levels of radioactivity. ⑤Post extracted solids after extraction and/or enzyme hydrolysis.

[1] LOD for milk was reported as 0.00007 mg/kg parent equivalents.

Although urine is not normally considered important compared to edible tissues and milk, TRR in urine was investigated further. Centrifugation and concentration of urine samples collected at 24 and 120 hours resulted in 100% and 94.8% of the TRR being recovered without further clean-up; this represented 3.10% and 13.72% of the total administered dose, respectively. HPLC analysis of the concentrated urine samples at 24 and 120 hours revealed that the major component of the radioactivity was aminopyralid (96.8% and 90.9% of the 24 and 120 hr samples, respectively). An unknown component was present at 3.2%TRR in the 24 hour urine sample and two unknown components were present at 1.4% and 2.5% of the TRR in the 120 hour sample. Similarly, in faeces collected at 24 and 120 hours, parent aminopyralid comprised 94.4% and 95.6% of the TRR, respectively. Therefore > 94% the total amount of recovered radioactivity that was eliminated via urine and faeces was composed of unchanged aminopyralid.

In summary aminopyralid was readily excreted from the goat, with residues of 0.06 mg/kg aminopyralid present in kidneys only.

Laying hens

Ten laying hens of 45 weeks age were orally dosed for 7 days with ^{14}C aminopyralid at the equivalent of 10.5 ppm in the feed (daily dose of 1.7 mg/bird; mean bodyweight 1.7 kg and mean feed consumption 161 g/day) (Magnussen 2004). Another 10 birds were used as control animals.

The hens received capsules containing the dose each morning following collection of eggs and excreta. Eggs were collected twice a day (morning and evening) and prepared for analysis; eggs from the evening collection were refrigerated overnight (4°C) and pooled with those collected the following morning, to give a composite sample for each day. Both control and test groups were sampled in an identical fashion. Eggs were cracked open, the shells discarded and the composite samples weighed, homogenised (hand-whisk) and stored frozen prior to analysis.

Prior to each dose, excreta were collected from the previous 24-hour period from each pen with the excreta pooled for the treatment group. All samples were stored frozen prior to analysis for TRR.

Approximately 24 hours after administration of the final dose, hens were slaughtered and samples of liver, abdominal fat, muscle (light and dark meat) and skin with subcutaneous fat were collected from each bird. Each sample type was pooled and stored frozen prior to analysis. Samples of eggs, excreta and tissues were assayed for radioactivity using LSC and/or combustion. Assays of total radioactivity were completed within two weeks of sample collection.

TRR in excreta collected daily ranged from 55% to 87% of the nominal daily dose over 1 to 6 days; approximately 55% on days 1 and 2 and > 80% day 3 onwards. This indicates that a large percentage of the dose was excreted daily. TRR in eggs over 7 days and in tissues on day 7 is shown in Table 2.

Table 2. TRR in eggs and hen tissues dosed for 7 days at 10 ppm in the diet.

Sample	Sampling Interval (days)	mg/kg aminopyralid equivalents①
Eggs	1	<LOD (< 0.0012)
	2	0.0023
	3	0.0029
	4	0.003
	5	0.0036
	6	0.0036
	7	0.004
Skin/fat	7	0.0029
Muscle	7	ND (0.0018)
Fat	7	ND (0.0017)
Liver	7	0.0024

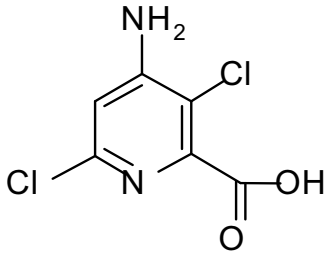
① based on sample mean dpm/g/666000 µg/mg activity of test material

With the exception of egg samples at day 1, all eggs contained low levels of radioactivity that gradually increased to a plateau level within 5 to 7 days of the study. Levels on day 2 were 0.0023 mg/kg equivalents, which had not quite doubled to 0.004 mg/kg equivalents by day 7. TRR in all eggs collected over the study period accounted for < 0.01% of the total administered dose.

TRR in tissues were << 0.01% of the total administered dose. TRR in muscle and fat were comparable, corresponding to 0.0018 and 0.0017 mg/kg aminopyralid equivalents, respectively and were reported as non-detectable. TRR in skin (with fat) and liver were detectable and were 0.0029 and 0.0024 mg/kg aminopyralid equivalents, respectively. The levels of radioactivity in eggs and tissues were low and were not further characterised.

Residues in day 7 excreta were however further characterised and identified. Extraction and analysis occurred approximately 49 days after slaughter. Residues were readily extracted into $CH_3CN:H_2O$ with < 96% TRR being recovered. HPLC analysis of the extracts indicated that 93% of the extracted radioactivity was due to aminopyralid, while another 3% was attributed to a component that was more polar than the parent compound.

In summary, aminopyralid is readily excreted by hens following oral dosing for 7 days at 10 ppm in the feed. TRR in eggs on days 6 and 7 of the study were 0.004 mg/kg aminopyralid equivalents. TRR in muscle and fat were non-detectable (< 0.002 mg/kg aminopyralid equivalents), while TRR in liver and skin/fat were 0.002 – 0.003 mg/kg aminopyralid equivalents.



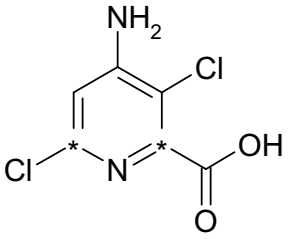
aminopyralid

Goats: Less than 3 – 4% converted to unknown components.
Hens: Less than 10% converted to aqueous soluble residues that in part can be converted back to aminopyralid using base or acid hydrolysis.

Figure 1. Proposed metabolic pathway for goats and hens.

Plant metabolism

The meeting received metabolism studies for aminopyralid applied to wheat and grass/pastures. In both studies, aminopyralid (or XDE-750) was labelled in the 2- and 6-positions of the pyridine ring, as shown below.



Wheat

^{14}C aminopyralid was applied to spring wheat at rates of 40 and 80 g ai/ha (2× and 4× nominal application rate) (Graper *et al.* 2003). The wheat was at stages BBCH 26–28 (6 to 8 tillers detectable) when treated and grown outdoors. Samples of plant material (forage) were taken at 0 and 14 days after treatment (DAT); hay was sampled at 35 DAT and grain and straw at 86 DAT.

Harvested samples were analysed by combustion; TRR in the various samples are shown below:

Table 3. TRR in various wheat samples.

Sample	TRR aminopyralid XDE-750 equivalents (mg/kg)	
	40 g ai/ha	80 g ai/ha
Forage 0 DAT	2.022	4.121
Forage 14 DAT	0.418	0.874
Hay 35 DAT	0.284	0.691
Straw 86 DAT	0.281	0.623
Grain 86 DAT	0.039	0.084

LOD and LOQ from combustion data are 0.001 and 0.003 mg/kg equivalents, respectively.

Homogenised samples were initially extracted with 70:30 $CH_3CN:H_2O$. Extraction occurred within 15 to 42 days after sample collection. All samples, except for the 0 DAT forage, were subjected to a cold extraction followed by reflux in the same 70:30 $CH_3CN:H_2O$ mixture. The initial CH_3CN/H_2O extraction and reflux of grain and straw samples was followed by partitioning of extractable radioactivity (CH_3CN/CH_2Cl_2) prior to HPLC analysis. Extraction and recovery of ^{14}C in CH_3CN/H_2O is shown in Table 4.

All extractable radioactivity was analysed using HPLC and the results are shown in Tables 5 and 6. HPLC analyses occurred within 38 to 93 days after sample collection. Non-extracted radioactivity (extracted tissue) increased from < 2% TRR in 0 DAT forage to 25% TRR in 86 DAT grain. For all samples, the initial extractions recovered 75% to 98% TRR.

Table 4. Distribution of ^{14}C in CH_3CN/H_2O extracted wheat samples as %TRR and mg/kg equivalents.

Sample TRR (mg/kg equivalents)	%TRR and (mg/kg aminopyralid equivalents)					
	CH_3CN/H_2O extract	Reflux filtrate	Total ^{14}C extracted	Organic phase	Aqueous phase	Extracted tissue
Forage 0 DAT 2× (2.022)	98.3% (1.988)	– –	98.3% (1.988)	– –	– –	1.7% (0.034)
Forage 0 DAT 4× 4.121	98.7% 4.069	– –	98.7% 4.069	– –	– –	1.3% 0.052

Sample TRR (mg/kg equivalents)	%TRR and (mg/kg aminopyralid equivalents)					
	CH_3CN/H_2O extract	Reflux filtrate	Total ^{14}C extracted	Organic phase	Aqueous phase	Extracted tissue
Forage 14 DAT 2×	91%	2.3%	93.3%	–	–	6.7%
0.418	0.38	0.01	0.390	–	–	0.028
Forage 14 DAT 4×	90.7%	1.8%	92.5%	–	–	7.5%
0.874	0.793	0.016	0.809	–	–	0.066
Hay 35 DAT 2×	88.8%	2.1%	90.9	–	–	9.1%
0.284	0.252	0.006	0.258	–	–	0.026
Hay 35 DAT 4×	88.4%	2.3%	90.6%	–	–	9.4%
0.691	0.610	0.016	0.626	–	–	0.065
Straw 86 DAT 2×	64.2%	16.6%	80.8%	1.8%	79.1%	19.2%
0.281	0.18	0.047	0.227	0.005	0.222	0.054
Straw 86 DAT 4×	78.6%	4.4%	83%	1.7%	81.3%	17%
0.623	0.490	0.027	0.517	0.011	0.506	0.106
Grain 86 DAT 2×	63.7%	16%	79.8%	11.4%	68.4%	20.2%
0.039	0.025	0.006	0.031	0.004	0.026	0.008
Grain 86 DAT 4×	60.1%	14.9%	75%	13.4%	61.6%	25%
0.084	0.051	0.013	0.063	0.011	0.052	0.021

The wheat forage and hay samples were analysed with HPLC after initial extraction. The levels of aminopyralid and other metabolites at various HPLC retention times (regions) are shown in Table 5.

Table 5: HPLC Characterisation of radioactivity in CH_3CN/H_2O extracts of wheat forage and hay samples.

Sample (mg/kg parent equivalents extracted)	%TRR and (mg/kg aminopyralid equivalents)				
	aminopyralid (Region 3)	Region 1	Region 5	Region 6	Total of XDE-750 + regions 1 & 5
Forage 0 DAT 2×	87.2%	5.3%	3.5%	1.8%	96%
(1.988)	1.762	0.108	0.071	0.037	1.941
Forage 0 DAT 4×	89.9%	4.6%	2.1%	2.2%	96.6%
(4.069)	3.703	0.19	0.087	0.089	3.980
Forage 14 DAT 2×	40.6%	34.7%	17.9%	–	93.2%
(0.390)	0.170	0.145	0.075	–	0.39
Forage 14 DAT 4×	37.9%	36%	18.6%	–	92.5%
(0.809)	0.332	0.314	0.163	–	0.809
Hay 35 DAT 2×	11.6%	55.1%	23.7%	–	90.4%
(0.258)	0.033	0.156	0.067	–	0.256
Hay 35 DAT 4×	12.7%	50%	25.7%	–	88.4%
(0.626)	0.088	0.345	0.178	–	0.611

The radioactivity that was attributed to parent aminopyralid (based on co-chromatography with reference standard) was present in Region 3. The levels of parent compound ranged from almost 90% extracted TRR in day 0 forage samples to 11% extracted TRR in day 35 hay samples. As parent aminopyralid decreases, the levels of radioactivity present in Regions 1 and 5 increase and form the majority of the extracted TRR. The radioactivity in Regions 1 and 5 comprised a glucose conjugate of aminopyralid and a glucose conjugate of hydroxylated aminopyralid, which were identified in hay samples following base and acid hydrolysis.

The levels of aminopyralid and other metabolites in straw and grain at various HPLC retention times (regions) are shown in Table 6.

Table 6. HPLC Characterisation of radioactivity in aqueous phase and organic partitioned extracts of wheat straw and grain samples.

Sample	%TRR and (mg/kg aminopyralid XDE-750 equivalents)				
	aminopyralid (Region 3)	Region 1	Region 2	Region 5	Total of aminopyralid + regions 1 & 5
Straw 86 DAT 2×					
Aqueous phase	7.9%	42%	6.1%	23.1%	73%
(0.227)	(0.022)	(0.118)	(0.017)	(0.065)	(0.205)
Straw 86 DAT 4×					
Aqueous phase	11.3%	32.9%	–	37%	
	(0.071)	(0.205)	–	(0.230)	
Organic phase	0.1%	< 0.1%	–	0.3%	
	(< 0.001)	(< 0.001)	–	(0.002)	
Total	11.4%	33%	–	37.3%	81.7%
(0.517)	(0.071)	(0.205)	–	(0.232)	(0.508)
Grain 86 DAT 2×					
Aqueous phase	17.7%	11.6%	–	39%	68.3%
(0.031)	(0.007)	(0.004)	–	(0.015)	(0.026)
Grain 86 DAT 4×					
Aqueous phase	15.9%	12.3%	–	33.3%	
	(0.013)	(0.01)	–	(0.028)	
Organic phase	0.3%	<LOQ	<LOQ	6.9%	
	(< 0.001)	<LOQ	<LOQ	(0.006)	
Total	16.2%	12.3%	<LOQ	40.2%	68.7%
(0.063)	(0.014)	(0.01)	<LOQ	(0.034)	(0.058)

Following partitioning of the initial extracts with CH_2Cl_2:CH_3CN, the radioactivity is predominantly soluble in the aqueous phase. Acid/base treatment of the aqueous phase and the extracted tissues resulted in further release of radioactivity that was identified as aminopyralid. The analysis of straw and grain (86 DAT 4×) is shown in Table 7.

Table 7. HPLC Characterisation of radioactivity in wheat straw and grain samples following acid/base treatment of aqueous phase and extracted tissues.

Sample	%TRR and (mg/kg aminopyralid equivalents)				
	XDE-750	Region 1	Region 2	Region 5	Region 6
Straw 86 DAT 4×					
Aqueous phase	71.9%	6.1%	–	–	3.3%
	(0.448)	(0.038)	–	–	(0.02)
Extracted tissue	6.6%	1.5%		0.7%	0.9%
	(0.041)	(0.009)		(0.004)	(0.005)
Total	78.5%	7.6%		0.7%	4.2%
	(0.489)	(0.047)		(0.004)	(0.025)
Grain 86 DAT 4×					
Aqueous phase	48.6%	1.8%	1.1%	0.5%	5.4%
	(0.041)	(0.002)	(0.001)	(< 0.001)	(0.005)
Extracted tissue	11%	<LOQ		<LOQ	1.6%
	(0.009)	(<LOQ)		(<LOQ)	(0.001)
Total	59.6%	1.8%	1.1%	0.5%	7%
	(0.05)	(0.002)	(0.001)	(< 0.001)	(0.006)

LOQ = 0.1%TRR.

Of the total extractable ^{14}C as reported in Table 4, aminopyralid comprised 78.5% of the TRR in wheat straw either as free, conjugated or bound forms. Approximately 12 – 13 % remained in other HPLC regions, and up to 3.5% TRR remained in unextracted tissue following acid/base treatment.

In grain, aminopyralid comprised 60% of the TRR (86 DAT 4×) again as free, conjugated or bound forms. Approximately 10% remained in other HPLC regions, and 0.7% TRR remained in unextracted tissue following acid/base treatment.

The data for the straw and grain demonstrate that acid/base treatment led to another HPLC region (region 6) that formed < 10% of the total extractable radioactivity for both sample types. This region is thought to be due to a minor component of region 5.

Acid/base stability of aminopyralid was demonstrated by subjecting ^{14}C aminopyralid to acid/base treatments used in the metabolism studies. Approximately 97% of the radioactivity from the parent compound was recovered in HPLC region 3 as aminopyralid.

In relation to storage stability, repeated analyses were conducted for samples that had been stored frozen for up to 277 days (– 20 °C). The results of repeated analyses were similar to the initial analyses, indicating that the extracts were stable under conditions of frozen storage.

In summary, aminopyralid when applied to wheat is predominantly present as parent compound either in free, conjugated or bound forms. Acid/base treatment leads to good recovery of the applied material as parent compound.

Grass/Pastures

Three types of grasses that comprise pastures (perennial ryegrass, big bluestem and *Panicum maximum*) were treated with a single spray application of ^{14}C aminopyralid at a rate of 360 g ai/ha (Magnussen and Balcher 2004). ^{14}C aminopyralid was labelled in the 2- and 6-positions of the pyridine ring. The grasses were germinated and established in large tubs in a greenhouse. The containers were then moved outdoors and the grasses were cut to give a uniform stand (height 12 to 14 cm) in each container, prior to treatment.

Samples of grass were collected for analysis at 0 time (2 to 4 hours after application) and at 7, 14, 21 and 42 days after treatment (DAT). All samples were rinsed and then kept in frozen storage (– 20 °C) until further analysis. For the 42 DAT samples, half of the sample was weighed and then allowed to air dry over 1 to 2 days to produce a hay sample. After drying, the sample was reweighed and kept in frozen storage pending analysis. All samples were analysed within 2 months of collection, with the exception of the storage stability samples which were analysed within 660 days after collection.

TRR in all samples was determined using combustion analysis and LSC of liquid samples or extracts. Extracted material was analysed using HPLC and LC/MS. TRR in the unrinsed samples of the three grass species is shown in Table 8.

Table 8. TRR in unrinsed grass samples at varying times after application.

Sampling Interval	TRR (mg/kg aminopyralid equivalents)		
	Ryegrass	Big Bluestem	*Panicum maximum*
0 time	48.84	25.84	17.96
7 DAT	36.91	21.03	18.87
14 DAT	22.90	8.29	10.08
21 DAT	20.85	9.03	10.03
42 DAT grass	6.57	5.61	4.81
42 DAT hay	23.34	12.64	19.13

The results indicate that there is a decline in TRR with time, with 0 day values being highest in ryegrass compared to the other two grass species. The differences reported for the 42 DAT grass and hay samples are due to loss of moisture and the dry matter content.

Extraction of radioactive residues from each of the grasses involved rinsing of the samples sequentially with water then MeOH, and HPLC analysis of the water and MeOH extracts. The rinsed grass was homogenised with CH_3CN:H_2O (70:30), filtered and the resulting extract analysed by HPLC. Acid and base hydrolysis of the spent grass extracts resulted in aqueous and organic extracts that were further characterised using HPLC and LC/MS. Data from the extracts of each pasture type are shown in Table 9.

Table 9. Characterisation of TRR in various extracts of grasses by HPLC analysis.

Sampling Interval	% TRR (mg/kg parent equivalents) and % recovered residue	aminopyralid (% recovered)	C-1[a]	C-2[b]	C-3[c]
Ryegrass					
0 time	*48.84*				
H_2O/MeOH	40.1 (82.1)	80.3	1.4	0.3	–
CH_3CN/H_2O	8.30 (17)	16.7	< 0.18%	0.2	–
spent grass	0.44 (0.9)	–	–	–	–
Totals		97	1.4	0.5	–
7 DAT	*36.91*				
CH_3CN/H_2O	30.23 (81.9)	42	4.7	2.3	32.9
CH_3CN/acid	6.27 (17)	5.8	3.8	1	6.4
spent grass	0.41 (1.1)	–	–	–	–
Totals		47.8	8.5	3.3	39.3
14 DAT	*22.90*				
CH_3CN/H_2O	13.26 (57.9)	23.8	3.6	0.9	29.5
CH_3CN/acid	8.89 (38.8)	10.9	4.6	4	19.3
spent grass	0.76 (3.3)	–	–	–	–
Totals		34.7	8.2	4.9	48.8
21 DAT	*20.85*				
CH_3CN/H_2O	11.57 (55.5)	17.1	3	0.6	34.7
CH_3CN/acid	8.32 (39.9)	8.2	3.8	4	23.3
spent grass	0.76 (4.6)	–	–	–	–
Totals		25.3	6.8	4.6	58
42 DAT grass	*6.57*				
CH_3CN/H_2O	3.52 (53.6)	13.8	3.4	1.2	35.2
CH_3CN/acid	2.76 (42)	8.1	4.1	5.5	24.3
spent grass	0.29 (4.4)	–	–	–	–
Totals		21.9	7.5	6.7	59.5
42 DAT hay	*23.34*				
CH_3CN/H_2O	9.67 (41.5)	12.6	2	ND	26.9
CH_3CN/acid	11.27 (48.3)	11.2	4.2	3.9	29.1
spent grass	2.38 (10.2)	–	–	–	–
Totals		23.8	6.2	3.9	56
Big Bluestem					
0 time	*25.84*				
H_2O/MeOH	22.58 (87.4)	85.4	1.8	0.1	–
CH_3CN/H_2O	3.10 (12)	11.7	ND	0.3	–
spent grass	0.16 (0.6)	–	–	–	–
Totals		97.1	1.8	0.4	–
7 DAT	*21.03*				
CH_3CN/H_2O	18.02 (85.7)	61.3	6.2	3.5	14.6
CH_3CN/acid	2.71 (12.9)	5.3	3.2	< 0.39	4.2
spent grass	0.27 (1.3)	–	–	–	–
Totals		66.6	9.4	3.5	18.8
14 DAT	*8.29*				
CH_3CN/H_2O	6.83 (82.4)	38.1	7.4	5.2	31.5
CH_3CN/acid	1.3 (15.7)	6.8	2.8	ND	6.1
spent grass	0.16 (1.9)	–	–	–	–
Totals		44.9	10.2	5.2	37.6
21 DAT	*9.03*				
CH_3CN/H_2O	6.75 (74.7)	28.2	8.5	3.3	34.8
CH_3CN/acid	2.06 (22.8)	9.8	2.5	1.7	8.8
spent grass	0.23 (2.5)	–	–	–	–
Totals		38	11	5	43.6
42 DAT grass	*5.61*				
CH_3CN/H_2O	3.8 (67.7)	18.3	8.9	2.3	37.9
CH_3CN/acid	1.65 (29.5)	10.3	2.3	3.7	12.2
spent grass	0.16 (2.8)	–	–	–	–
Totals		28.6	11.2	6	50.1

Sampling Interval	% TRR (mg/kg parent equivalents) and % recovered residue	aminopyralid (% recovered)	C-1[a]	C-2[b]	C-3[c]
42 DAT hay	*12.64*				
CH_3CN/H_2O	7.46 (59)	18.8	6.3	1.2	32.8
CH_3CN/acid	4.61 (36.5)	13	2.6	2.1	18.8
spent grass	0.57 (4.5)	–	–	–	–
Totals		31.8	8.9	3.3	51.6
Panicum maximum					
0 time	*17.96*				
H_2O/MeOH	16.07 (89.5)	86.2	0.1	< 0.14	2.4
CH_3CN/H_2O	1.86 (10.3)	9.9	ND	< 0.14	0.2
spent grass	0.04 (0.2)	–	–	–	–
Totals		96.1	0.1	< 0.14	2.6
7 DAT	*18.87*				
CH_3CN/H_2O	17.08 (90.5)	64.3	5.5	1.6	19
CH_3CN/acid	1.59 (8.4)	3.4	1.9	< 0.35	2.7
spent grass	0.21 (1.1)	–	–	–	–
Totals		67.7	7.4	1.6	21.7
14 DAT	*10.08*				
CH_3CN/H_2O	8.10 (80.4)	27	3.6	2.2	47.6
CH_3CN/acid	1.72 (17.1)	5.9	1.8	1.8	7.6
spent grass	0.24 (2.4)	–	–	–	–
Totals		32.9	5.4	4	55.2
21 DAT	*10.03*				
CH_3CN/H_2O	7.29 (72.9)	25.9	4	1.4	41.4
CH_3CN/acid	2.37(23.6)	8	2	2.8	10.8
spent grass	0.37 (3.7)	–	–	–	–
Totals		33.9	6	4.2	52.2
42 DAT grass	*4.81*				
CH_3CN/H_2O	2.69 (56)	19.9	3.9	2.1	30
CH_3CN/acid	1.92 (39.9)	10.7	2.5	5.6	21.1
spent grass	0.2 (4.1)	–	–	–	–
Totals		30.6	6.4	7.7	51.1
42 DAT hay	*19.13*				
CH_3CN/H_2O	10.43 (54.5)	24	3.7	0.8	26
CH_3CN/acid	7.86 (41.1)	10.9	2.6	5.2	22.4
spent grass	0.84 (4.4)	–	–	–	–
Totals		34.9	6.3	6	48.4

[a] The C-1 Region represented those residues eluting just after the column void volume (4-7 minutes);

[b] The C-2 Region represented those residues eluting just after XDE-750 (12-15 minutes);

[c] The C-3 Region represented those residues that were even less polar than the C-2 residues (17-21 minutes). The retention time for XDE-750 in this system was approximately 9 minutes.

The data show that during the first 2 weeks after application, aminopyralid forms a large proportion of the radioactivity, however it is slowly metabolised and transformed to other components denoted C-1, C-2 and C-3. Metabolite C-3 forms a large proportion of the isolated radioactivity (> 50% TRR) from day 7 onwards. It is easily extracted into the solvent mixtures that also extract aminopyralid and radiochromatograms showed that the extracts elute as single peaks.

To further characterise components C-1 to C-3, the CH_3CN/H_2O and CH_3CN/acid extracts from the 21 DAT grass samples were subjected to acid (1 or 3 N HCl) and/or base (1 N NaOH) hydrolysis, followed by organic solvent partitioning. Base hydrolysis was found to be more efficient than acid hydrolysis and 75% to 90% of the TRR in the C-1 and C-3 components from the CH_3CN/H_2O and CH_3CN/acid fractions was released following base hydrolysis. HPLC and LC/MS analysis of the organosoluble residues following base hydrolysis showed that 87–96% of the released radioactivity in the three grasses was eluted as aminopyralid.

The stability of selected samples of ryegrass and *Panicum maximum* after 650 days of frozen storage was investigated and details are given in Table 10.

Table 10. Stability of extracts from grass samples following frozen storage.

Sample	Storage Interval	Extracts	%TRR (mg/kg parent equivalents) and % recovered residue	%TRR			
				aminopyralid	C-1	C-2	C-3
Rye grass 14 DAT	0 days	CH_3CN/H_2O	57.9	23.8	3.6	0.9	29.5
		CH_3CN/acid	38.8	10.9	4.6	4.0	19.3
		Spent grass	3.3	–	–	–	–
	665 days	CH_3CN/H_2O	54.2	23.1	2.8	–	26.7
		CH_3CN/acid	40.1	10.2	4.5	2.4	22.9
		Extracted grass	5.7	–	–	–	–
Pan. max 14 DAT	0 days	CH_3CN/H_2O	80.4	27	3.6	2.2	47.6
		CH_3CN/acid	17.1	5.9	1.8	1.8	7.6
		Spent grass	2.4	–	–	–	–
	671 days	CH_3CN/H_2O	71.8	25.5	3.5	2	40.8
		CH_3CN/acid	22.9	NA	NA	NA	NA
		Extracted grass	5.4	–	–	–	–
Pan. max 21 DAT	0 days	CH_3CN/H_2O	72.7	25.9	4	1.4	41.4
		CH_3CN/acid	23.6	8	2	2.8	10.8
		Spent grass	3.7	–	–	–	–
	698 days	CH_3CN/H_2O	62.1	25.7	3.2	–	33.2
		CH_3CN/acid	33	NA	NA	NA	NA
		Extracted grass	4.8	–	–	–	–

NA = not analysed.

The data show that although there are small differences in the extractability of the TRR in the CH_3CN/H_2O and CH_3CN/acid fractions, the overall amount of aminopyralid and other components recovered was the same. There were no significant issues in relation to storage stability of aminopyralid residues.

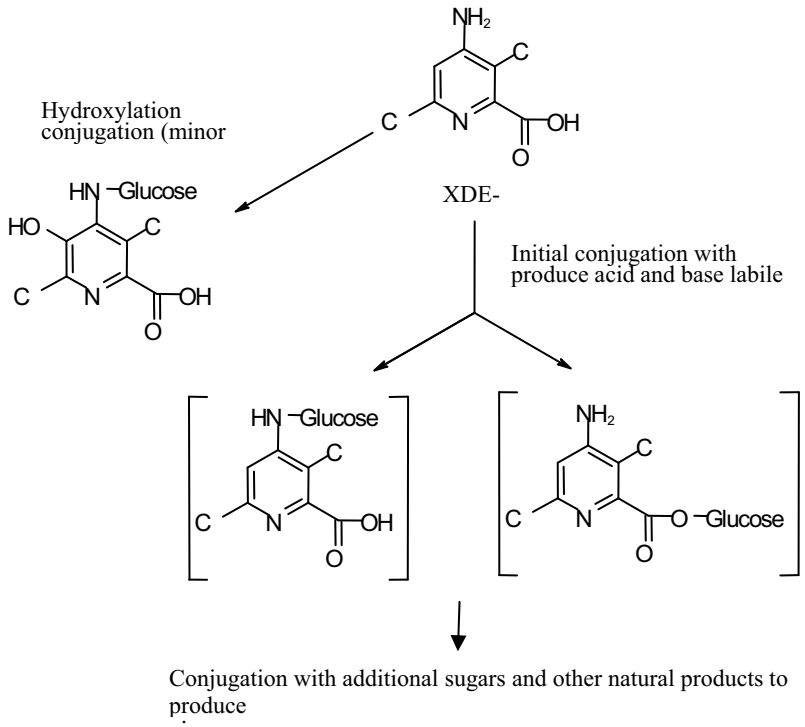


Figure 2: Proposed metabolic pathway for wheat and pasture grasses.

Environmental fate in soil

The meeting received information on the environmental fate of aminopyralid in soil, including studies on photodegradation on soil, aerobic soil degradation and crop rotation studies (confined and field). The studies are reported in the following sections. ^{14}C aminopyralid was labelled in the 2- and 6-positions of the pyridine ring in all soil studies.

Photodegradation on soil

The photodegradation of aminopyralid was investigated in a German silt loam soil (Parabraun Erde) at 25 °C and 75% of ⅓ bar moisture using a Xe lamp as a light source (Rutherford 2004). Samples were irradiated at the equivalent of 28 days summer at 40 °N latitude.

The ^{14}C aminopyralid was applied to samples of soil in flasks at a concentration of 5.2 mg ai/kg; samples were intermittently irradiated in a 12-hour irradiation/12-hour dark cycle to simulate regular sunlight. Treated samples were connected to traps for collection of CO_2 and other volatiles. Control samples were stored in the dark in an incubator at 25 °C. Samples were taken at 0, 2, 7, 14, 26, 35 and 44 days after treatment for the determination of parent compound and possible transformation products. A chemical actinometer was used to measure the amount of light that the samples had been subjected to; 44 DAT was equivalent to 28 days of irradiation in summer sun at 40 °N latitude.

Samples were extracted with acetone: 1 N HCl (90:10) and ^{14}C residues were analysed using HPLC. Parent aminopyralid accounted for < 90% of the radioactivity present in any HPLC determination of organic extracts. The mass balance in the dark and irradiated samples was 100 ± 4% and 94 ± 7%, respectively. After 44 days, 92% of the applied ^{14}C remained as aminopyralid in the dark samples; no transformation had occurred in the dark samples.

In the irradiated samples, the concentration of aminopyralid decreased from 104% at day 0 to 69% at day 44; up to 3% of the applied ^{14}C was present in the traps as CO_2 and acid gases. Extracted ^{14}C residues decreased from 105% of the applied amount at day 0 to 74% and 93% of the applied amount in the irradiated and dark samples, respectively. In irradiated samples, non-extracted ^{14}C (as determined by combustion analysis) increased from 0.6% at day 0 to 8% at day 44. In the dark samples, the corresponding values were 0.6% at day 0 and 3.8% at day 44.

Aminopyralid had degraded into non-extracted ^{14}C and volatile components. The half-life (DT_{50}) for photodegradation of aminopyralid was 61 days and DT_{90} was 203 days.

Aerobic soil degradation

The rate of aerobic soil degradation of ^{14}C aminopyralid in four European soils was investigated (Yoder and Smith 2003). The characteristics of the four soils are shown in Table 11.

Table 11. Characteristics of European soils used in a soil degradation study.

Parameter	Soils and characteristics			
Location, Country	Thessaloniki, Greece	Cuckney, UK	Charentilly, France	Parabraun Erde, Germany
Texture	Clay loam	Sand	Light clay	Loam
Sand (%)	41	91	42	60
Silt (%)	36	6	32	26
Clay(%)	23	3	26	14
pH	7.7	5.6	5.8	7.7
Organic matter (%)	2.5	2.4	1.9	2
Soil biomass (μg/g) Initial	216.1	111.4	54.7	40.6
Final	94.1	39.5	50.8	72
CEC① (meq/100 g)	14.4	6.8	15.1	10
MHC② (%)	86.9	43.7	68.4	56
Bulk density (g/cm^3)	0.88	1.28	1.08	1.18

①CEC is cation exchange capacity. ②MHC is moisture holding capacity.

Samples of each soil type were prepared 7 days before treatment to achieve 40% moisture holding capacity (MHC) and were incubated in the dark at 20 °C. Additional samples of the Parabraun Erde loam were used to investigate the effect of temperature on aerobic soil degradation by incubating in the dark at 10° and 30 °C for 8 days. Additional samples of Parabraun Erde soil were also sterilised before treatment to differentiate between microbial and aerobic degradation of aminopyralid. The samples (as prepared above at 20 °C) were irradiated with γ rays for 350 minutes prior to treatment with aminopyralid.

The ^{14}C aminopyralid was applied at concentrations of 0.14–0.17 mg ai/kg soil to simulate actual application rates of 110–120 g ai/ha. The treated samples were connected to NaOH traps (0.2 M) to collect CO_2 and to maintain constant relative humidity. All samples were incubated in the dark for up to 4 months after treatment. Duplicate samples of each soil type were taken at 0, 4, 7, 14, 28, 61, 92 and 123 days after treatment. At each sampling time, aliquots of the trapping solution were also taken and analysed by LSC. All soil samples were extracted several times using acetone: 1 N HCl 90:10; all extracts were combined and assayed for ^{14}C using LSC and HPLC. The extracted soil was also combusted to determine the amount of non-extracted ^{14}C. The data is presented in Table 15, calculated DT_{50} and DT_{90} values are shown in Table 12.

Table 12. DT_{50} and DT_{90} values determined for European soils from an aerobic degradation study.

Soil	DT_{50} (days)	DT_{90} (days)
Thessaloniki (clay loam)	18	58
Cuckney (sand)	143	476
Charentilly (light clay)	22	72
Parabraun Erde (loam)	84	280
Parabraun Erde (10° C)	409	1359
Parabraun Erde (30° C)	115	382
Parabraun Erde (sterile)	NA	NA

NA = degradation was not observed.

The degradation half-life of aminopyralid ranged from 18 days in a clay loam to 143 days in a sandy soil.

In the Parabraun Erde soils, degradation at 10 °C was significantly slower than at 20 °C, however at 30 °C there was no increase in degradation or temperature-based dependence observed. No degradation was found in the sterile soil, indicating that abiotic degradation had not occurred.

The relative percentage of ^{14}C detected as CO_2 at the end of the study ranged from 30 to 70% of the applied radioactivity for samples incubated at 20 °C. Non-extracted radioactivity (NER) accounted for up to 23% of the applied ^{14}C. $^{14}CO_2$ was higher in both clay-based soils, with 65% and 70% in the Thessaloniki clay and Charentilly light clay, respectively.

In the HPLC analysis of the soil extracts, only aminopyralid was present; no other component was present in the chromatograms.

In summary, aminopyralid degrades to CO_2 and non-extracted radioactivity or residues under ambient aerobic conditions.

In another study conducted in the US, the degradation of ^{14}C aminopyralid was investigated on five soils (Yoder and Smith 2002). Soils were selected from sites that were representative of typical pasture growing regions in the US and Canada. The characteristics of the 5 soils are shown in Table 13.

Table 13. Characteristics of US soils used in a soil degradation study.

Parameter	Soils and characteristics				
Location, Country	Kansas, USA	Manitoba, Canada	N Dakota, USA #1	N. Dakota, USA # 2	Texas, USA
Texture	Silt loam	Loam	Sandy loam	Clay loam	Clay
Soil series	Holdrege	Regent	Manning	Barnes	Houston Black
Sand (%)	21	45	74	34	17
Silt (%)	60	40	16	34	32
Clay(%)	19	15	10	32	51
pH	4.6	7.5	7.3	4.8	7.5
Organic matter (%)	NA	NA	2.4	7.1	5.9
Soil biomass (µg/g)					
Initial	81.5	313.5	NA	NA	672.8
Final	61.3	220.4	105.3	93.6	759.9
CEC (meq/100 g)	14.5	25.6	15.5	23.5	45
MHC (%)*	25.9	30.3	14.3	33.1	40.8
Bulk density (g/cm^3)	1.06	1.03	1.24	0.96	0.99

* at ⅓ bar moisture

Samples of each soil were prepared 7 days before treatment to achieve 75% of ⅓ bar moisture content and incubated at 25 °C in the dark. The ^{14}C aminopyralid was applied at soil concentrations equivalent to 5, 20, 60 and 120 g ai/ha. The Houston Black clay soil was treated at 60 and 120 g ai/ha rates only; the remaining four soils were treated at all rates. Treated samples were connected to NaOH traps (0.2 M) to collect CO_2 and to maintain constant relative humidity. All samples were incubated in the dark up to 12 months after treatment and samples were taken at intervals of 0, 1, 4, 8, 14, 22 days and 1, 2, 3, 4, 6, 9 and 12 months after treatment. At each sampling time, the trapping solution was assayed by LSC. As in the European study described above, all soil samples were extracted several times using acetone: 1 N HCl 90:10; all extracts were combined and assayed for ^{14}C using LSC and HPLC. The extracted soil was also combusted to determine the amount of non-extracted ^{14}C.

Calculated half-lives (DT_{50}) and DT_{90} values are shown below.

Table 14. DT_{50} and DT_{90} values determined for US soils from an aerobic degradation study.

Soil series	Application Rate (g ai/ha)	DT_{50} (days)	DT_{90} (days)
Holdrege (Kansas USA)	5	60	199
	20	48	161
	60	59	195
	120	46	153
Regent (Manitoba, Canada)	5	25	83
	60	49	163
	120	34	113
Manning (Nth Dakota, USA)	5	14	48
	60	21	70
	120	14	45
Barnes (Nth Dakota, USA)	5	ND	ND
	20	266	885
	60	341	1134
	120	343	1141
Houston Black (Texas, USA)	60	5	16
	120	5	16

ND = degradation was not observed.

The half-lives ranged from 5 days in the Houston Black soil to 343 days in the Barnes soil; little difference was observed in the rate of degradation in the range of concentrations tested for each soil. Again, as observed in the European soil study, the clay based soil resulted in the shortest degradation half-life (DT_{50}).

The relative percentage of ^{14}C detected as CO_2 at the end of the study ranged from 30 to 70% of the applied radioactivity for all samples. Non-extracted radioactivity (NER) accounted for 2 % to

25% of the applied ^{14}C at the end of the incubation period, with the highest levels present in the Houston Black clay. In the HPLC analysis of the soil extracts, only aminopyralid was present, no other component was present in the chromatograms.

In summary, aminopyralid degrades to CO_2 and non-extracted radioactivity or residues under aerobic conditions.

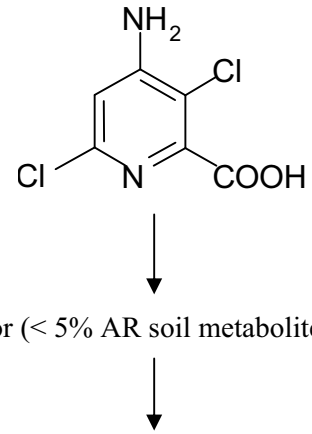


Figure 3: Proposed degradation of aminopyralid in soil.

Table 15. Material balance of radioactivity for each of four European soil types.

DAT	%^{14}C of applied aminopyralid															
	Thessaloniki clay loam (20 °C)				Cuckney sand (20 °C)				Charentilly light clay (20 °C)				Parabraun Erde loam (20 °C)			
	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total
0	NA	94.1	0.9	95	NA	92.9	1.1	94	NA	92	1.9	93.9	NA	94.3	2.5	96.8
0	NA	97	0.9	97.8	NA	91.3	0.9	92.1	NA	91.7	2.5	94.2	NA	91.3	2.3	93.7
4	2.1	91.8	3	96.9	1.2	94	1.2	96.4	3.3	91.5	2	97.1	1.3	94.1	2.3	97.7
4	2.2	92.9	3.1	98.2	1.2	94	1	96.3	3.3	92.5	2	97.9	1.3	95	1.9	98.2
7	3.9	88.1	4.3	96.4	1.8	92.3	1.6	95.6	5.6	85.	2.3	93.5	2.2	90.2	2.6	95
7	3.7	88.9	4.1	96.7	1.2	90.8	1	93	5.1	87	2.3	94.3	2.3	90.7	2.2	95.2
14	6.2	81.5	5.5	93.3	3.2	88.4	1.4	93	10.4	79.3	2.8	92.5	2.2	86.1	2.	90.8
14	9.1	78.4	6.9	94.3	3.3	87.6	1.2	92	10.9	77.5	3.4	91.8	4.3	83.5	2.9	90.7
28	22.4	55.6	13.1	91.1	5.9	84.1	1.8	91.8	23.6	57.6	13.2	94.4	9.5	78	3.2	90.7
28	18.2	62.6	11.5	92.2	6	84.4	1.5	91.9	23.5	56	14	93.5	9.7	78.1	3.7	91.5
61	56.7	8.4	22.4	87.5	14.4	72.6	3.5	90.5	55.2	14.6	20.8	90.6	22.7	58.8	5.6	87.1
61	55.7	9.1	22.7	87.6	13.3	73.3	2.5	89.1	53	17.4	20.6	91.1	23	59.1	5.4	87.6
92	68.6	1.5	21.5	91.6	24.1	60.2	11.2	95.5	69.4	4.2	17.7	91.3	35.4	44.8	13.3	93.5
92	67.9	1.5	21.7	91.1					69.2	4.2	15.4	88.8	33.7	46.9	14.2	94.8
123	64.8	2.4	19.6	86.8	28.4	52.7	8	89.1					41.7	33.7	14.3	89.7
123					28.8	50.4	9.2	88.3					40.9	34.4	15.2	90.5

DAT	%^{14}C of applied aminopyralid											
	Parabraun Erde loam (10 °C)				Parabraun Erde loam (30 °C)				Parabraun Erde loam (sterile)			
	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total
0	NA	98.4	1.4	99.8	NA	96.7	1	97.7	NA	98.2	0.4	98.6
0	NA	96.2	1.1	97.3	NA	98	1.4	99.4	NA	98.3	0.5	98.9
7	0.7	98.2	1.5	100.4	4	88.5	2.3	94.8	0.1	97.1	0.7	97.9
7	0.7	94.7	1.3	96.7	4	88.7	2.4	95	0.1	93.9	0.8	94.8
14	1.4	91.3	1.7	94.4	8.1	81.6	3.3	92.9	0.7	95.1	1	96.8
14	1.4	91.8	1.7	95	6.1	83.7	3.3	93.1	0.7	94.3	1.1	96.1
28	2.1	91.2	2	95.3	13.3	73	4.6	91	0.8	99.4	2	102.3
28	2.7	90.4	2	95.1	13.1	73.5	4.4	90.9	0.8	97	1.3	99.1

DAT	%^{14}C of applied aminopyralid															
	Thessaloniki clay loam (20 °C)				Cuckney sand (20 °C)				Charentilly light clay (20 °C)				Parabraun Erde loam (20 °C)			
	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total	CO_2	Extract	NER	Total
61	7.1	84.5	5.5	97	27.7	59.5	9.9	97.1	1.6	98.5	1.6	101.6				
61	6.4	86.4	6.3	99	26.5	58.9	11.4	96.8	1.3	96.1	1.5	98.9				
92	8.7	82.3	6.5	97.6	32.8	51.4	9.5	93.6	2.1	100.5	2.1	104.7				
92	8.3	82.4	5.3	95.9	32.2	51.5	9.3	93	2.5	95.3	2	99.8				
123	10.2	78.2	7.1	95.5	37	44.8	12.7	94.6	3.3	100.2	2.3	105.8				
123	10.6	78.3	7	96	35.4	46.3	11.3	93	3	100.7	2.2	106				

Field Dissipation

The Meeting received data from field dissipation studies conducted in Europe, US and Canada.

The dissipation of aminopyralid in soil under field conditions in Europe was investigated (Unsworth *et al.* 2003). Sites in the U.K., Germany, Northern and Southern France that represented typical pasture growing areas were selected for the study. Three soil types were included in the study; clay loam in the U.K., sandy loam in Germany and Northern France and clay in Southern France. A commercial formulation containing both aminopyralid and triclopyr was used in the study, however only aminopyralid residues were determined.

Aminopyralid was applied at a rate of 60 g acid equivalents/ha (g ae/ha) using a boom sprayer. Each trial plot was divided into 4 sub-plots. A single application was made to bare soil and samples of soil were collected from 0 days to 12 months after application. At each sampling point, five core samples (30 cm depth) were taken from each of the four sub-plots and bulked to give a single sample of 20 cores. All samples were stored frozen (< –18°C) prior to analysis. Each core was cut into 10 cm "horizons" and replicate horizons from each sample were bulked for extraction. Although samples were taken up to 12 months after application, only samples up to 5 months were analysed, as DT_{90} had been reached within this time. Additional samples were taken for biomass determination immediately prior to application and 6 and 12 months after application.

Residues of aminopyralid were determined using method GRM 02.34 which has a reported LOQ of 1.5 µg/kg. The method itself, including extractions, is described in the analytical methods section of this report. Fortified recoveries were conducted over the concentration range of 1.5–150 µg/kg and ranged 70 to 95% with a mean of 84% (n = 11) for extraction using 1 N HCl and 68 to 101% with a mean of 82% (n = 18) for extraction using 9 N HCl.

Soil characteristics and residues in the different soils are given in Tables 16 and 17.

Table 16. Characteristics of European soils used in a field dissipation study.

Parameter	Soils and characteristics			
Location, Country	Derbyshire, U.K.	Dollern, Germany	Challons le Verger, Nth France	Sourges, Sth France
Texture	Clay loam	Sandy loam	Sandy loam	Clay
Sand (%)	44	71	76	18
Silt (%)	32	19	15	35
Clay(%)	24	10	9	47
pH	6.6	6.2	7.5	8
Organic carbon (%)	1.5	3.6	0.9	3
Soil biomass① (mg/100 g soil)				
Initial	43.94 (2.3)	33.82 (0.99)	28.87 (2.62)	34.38 (0.9)
6 months	29.04 (1.56)	28.42 (0.84)	24.44 (2.22)	56.29 (1.54)
12 months	38.06 (2.05)	23.68 (0.76)	28.69 (2.47)	21.30 (0.68)

Parameter	Soils and characteristics			
Location, Country	Derbyshire, U.K.	Dollern, Germany	Challons le Verger, Nth France	Sourges, Sth France
Texture	Clay loam	Sandy loam	Sandy loam	Clay
CEC (meq/100 g)	10.8	11.2	10.5	38.7
MHC (%)②*	13.7	5	6.6	20.3
Bulk density (g/cm^3)	1.2	1.3	1.1	0.9

① Also expressed as % organic matter carbon in (). ② at 15 bar.

Table 17. Aminopyralid residues at varying soil depths and days after application.

Trial Location	DAA	Aminopyralid (µg/kg dry wgt)		
		0 – 10 cm	10 – 20 cm	0 – 20 cm
UK	Pre-application	ND	ND	ND
	0	43.98	ND	22.06
	3	52.49	ND	26.32
	7	53.64	ND	26.89
	14	40.23	ND	20.19
	28	30.57	(0.43)	15.50
	61	13.41	(0.44)	6.92
	119	1.95	ND	(1.05)
Germany	Pre-application	ND	ND	ND
	0	50.43	(1.28)	25.86
	3	45.83	ND	22.99
	7	29.72	2.84	16.28
	14	18.50	14.18	16,34
	28	12.53	12.94	12.74
	55	8.77	8.68	8.72
	158	(0.88)	(0.73)	(0.80)
Nth France	Pre-application	ND	ND	ND
	0	34.58	(0.71)	17.65
	3	21.15	(1.22)	11.19
	7	15.37	ND	7.76
	14	19.88	ND	10.02
	28	15.74	(0.58)	8.16
	59	4.54	(0.36)	2.45
	127	2.17	2.56	2.37
Sth France	Pre-application	ND	ND	ND
	0	43.94	3.67	23.80
	3	23.29	2.79	13.04
	7	14.88	6.46	10.67
	14	11.83	4.86	8.34
	28	4.60	(1.02)	2.81
	61	(0.77)	ND	(0.46)
	125	(0.35)	ND	(0.25)

ND = not detected (< 0.3 µg/kg). For the values at 0 – 20 cm, ND was < 0.15 µg/kg. Residues values in brackets are > 0.3 µg/kg but < 0.15 µg/kg.

The calculated DT_{50} and DT_{90} values were as follows:

	UK	Germany	Nth France	Sth France
DT_{50} (days)	35	31	26	8
DT_{90} (days)	116	105	87	26

The data indicate that $t_{½}$ or DT_{50} values are highly soil dependant and ranged from 8 days in a clay soil to 31 days in a sandy loam to 35 days in a clay loam.

In the field dissipation studies conducted in the US and Canada in 2002, aminopyralid was applied to test sites at a rate of 150 g ae/ha (Roberts and Schelle, 2004). Three test sites were selected in the US and five in Canada. The soil characteristics were determined for core samples taken down to 90cm depth, however only measurements for the 0–15 cm and 15–30 cm soil samples are shown in Table 19, for ease of comparison with the European study. Where values for specific parameters differ for the two core samples, the values for the 15–30 cm samples are given in parentheses.

Aminopyralid was applied using a tractor mounted spray rig and broadcast boom. At each site there were three replicated test plots, each consisting of five sub-plots. At each sampling interval (0 – 180 days in the US and 0–450 days in Canada), the five sub-plots were sampled from each replicate to produce a total of 15 core samples for analysis. The 15 core samples were cut and/or combined to produce three composite samples of 15 cm depth segments. Composite samples stored at – 20°C prior to analysis in accordance with method GRM 02.34. The data are shown in Tables 20 and 21 and DT_{50} and DT_{90} values are reported in Table 18.

The DT_{50} or $t_{½}$ values from the field studies range from 8 to 54 days, with the majority of values approximating 30 to 35 days (Table 18). The DT_{90} values are not as consistent, ranging from 26 days to 430 days. These values may be compared to the values derived from the radiolabelled aerobic soil degradation study where the DT_{50} values ranged from 18 to 143 days in the European study and 5 to 343 days in the US study. The temperatures at the sites in the US and Canada ranged 18–26 C and 10–18 °C, respectively. Temperatures were not given for the European sites.

Table 18. DT_{50} ($t_{½}$) and DT_{90} values from all field dissipation studies.

Trial Site	DT_{50} (days)	DT_{90} (days)	Study Reference
UK	35	116	GHE-P-10573; Unsworth et al. 2003
Germany	31	105	
Nth France	26	87	
Sth France	8	26	
CA, USA	26	85	020032; Roberts & Schelle 2004
MS, USA	34	114	
MT, US	35	220	
NB, Canada	21	60	020031, Roberts & Schelle, 2004
ON, Canada	31	260	
MB, Canada	30	110	
SK, Canada	9	40	
AB, Canada	54	430	

Table 19. Soils characteristics of test sites for dissipation studies conducted in US and Canada.

Parameter	US and Canada Soils and Characteristics							
Location, Country	Fresno County, CA, USA	Washington County, MS, USA	Chouteau County, MT, USA	Kings County, NB, Canada	Brant County, ON, Canada	Whitewater County, MB, Canada	Corman Park County, SK, Canada	Lacombe County AB, Canada
Texture	Sandy loam	Silt loam	Sandy loam	Sandy loam	Loam	Loam/Clay loam	Loam	Clay loam
Sand (%)	52 (54)	29	77 (81)	60 (66)	35	35 (33)	41	31 (27)
Silt (%)	30	60 (56)	14 (10)	28 (26)	46 (40)	42 (38)	38 (36)	38 (40)
Clay(%)	18 (16)	11 (15)	9	12 (8)	19 (25)	23 (29)	21 (23)	31 (33)
pH	7.2	6 (6.5)	8.2	5.4 (5.7)	7.2 (7.7)	7.5 (8.1)	5.9 (6.9)	5.3 (6)
Organic matter (%)	1.3 (0.5)	1.1 (0.8)	1.3 (0.9)	7.1 (6)	3 (2.1)	5.3 (2)	4.6 (2.5)	13.2 (8.1)
Soil biomass (µg/g)	121.2 (14.1)	52.1 (7.1)	156 (81)	292 (229)	158 (70)	236 (117)	114 (119)	459 (142)
CEC① (meq/100 g)	16.4 (17.4)	10.3 (13.7)	14.1 (12.2)	17.5 (15.4)	14.1 (14.6)	28.1 (26.7)	20	25.5 (29.1)
MHC② (%) ⅓ bar 15 bar	19.2 (16) 9.6 (8.7)	19.3 (23.7) 7.2 (9.8)	12.8 (9.8) 7.6 (6)	39.2 (30.3) 21.3 (18.8)	24.4 12 (11)	29.2 (26.7) 21.6 (18.4)	25.3 (21.9) 18 (15.6)	40 (38) 30.2 (27.8)
Bulk density (g/cm^3)	1.15 (1.17)	1.18	1.24 (1.29)	1.03 (0.96)	1.17	1.07	1.12 (1.07)	0.91 (0.98)

① CEC is cation exchange capacity. ② MHC is moisture holding capacity.

Table 20. Aminopyralid residues in soils in US and Canada.

Fresno County, CA, USA			Washington County, MS, USA			Chouteau County, MT, USA			Kings County, NB, Canada		
DAT	Residues µg/kg soil	% AR	DAT	Residues µg/kg soil	% AR	DAT	Residues µg/kg soil	%AR	DAT	Residues µg/kg soil	%AR
0①	940, 65	100, 91	0②	1232, 152	100, 99	0③	1353, 68	100, 83	0④	976, 56.7	100, 81
9	86.20	97	8	47.4	59	7	31.5	59.2	6	60.8	81
15	55.1	64	15	92.6	105	14	38.2	64	15	42.1	58
22	53.3	59	29	35.8	46	28	24.8	51	29	30.4	43
65	10.7	11	57	20.1	27	56	12.6	26	62	7.9	8.4
91	0.78	1	93	8	11	98	7.9	14	90	4.6	5.9
126	0.83	1.7	122	12.9	17	129	8.4	15	121	2.1	2.7
182	0.52	0.6	183	1.2	1.6	372	ND	0			

① 15 and 45 minutes after treatment, soil pans and 15 cm cores, respectively.

② 5 and 35 minutes after treatment, soil pans and 15 cm cores, respectively.

③ 6 and 50 minutes after treatment, soil pans and 15 cm cores, respectively.

④ 10 and 35 minutes after application, soil pans and 15 cm cores, respectively.

Table 21. Aminopyralid residues in soils in US and Canada.

Brant County, ON, Canada			Whitewater County, MB, Canada			Corman Park County, SK, Canada			Lacombe County, AB, Canada		
DAT	Residues µg/kg soil	% AR	DAT	Residues µg/kg soil	% AR	DAT	Residues µg/kg soil	%AR	DAT	Residues µg/kg soil	%AR
0⑤	1914, 58	100, 67	0⑥	2629, 98	100, 84	0⑦	9706, 95	100, 85	0⑦	2084, 101	100, 54
9	61.8	98	7	80.8	86	7	27.3	30	7	106	60
16	45.5	66	14	94.5	103	14	22.8	25	14	83.7	54
32	30.7	36	28	75.7	78	30	10.9	12	28	96.3	60
62	17.8	30	63	36.9	37	63	2.1	2.4	61	80	48
97	8.9	14	92	15.6	16	88	4.7	3.7	91	62.6	37
130	14.8	18	121	5.2	6	123	1.6	1.9	123	39.3	24
368	2.5	2.7							370	39.6	22
									455	10.8	6

⑤ 11 and 60 minutes after treatment for soil pans and 15 cm cores, respectively.

⑥ 10 and 60 minutes after treatment for soil pans and 15 cm cores, respectively.

⑦ 1 hour after treatment for soil pans and 15 cm cores.

Environmental fate in water-sediment systems

The meeting received studies on the anaerobic aquatic metabolism of aminopyralid and degradation in a sediment-water system. Due to the nature of the use of the compound, these studies are not considered necessary for the meeting, as indicated in the *Revised Data Requirements for Studies of Environmental Fate* (JMPR 2003, section 2.11, p. 12).

Crop Rotation Studies

A confined crop rotation study was conducted in the US in a sandy loam soil (Magnussen 2004). ^{14}C aminopyralid was applied to the soil at a rate of 10 g ai/ha, equivalent to the application rate for wheat. The characteristics of the soil were as follows: 71% sand; 20% silt; 9% clay; pH 6.1; CEC 9.5 meq/100 g; 2.3% OM; 10% MHC at ⅓ bar; 1.2 g cm^{-3} density. The ^{14}C aminopyralid was applied to each test plot (1.38 mg/plot) and allowed to remain fallow for 90 or 120 days outdoors. Plots were tilled to a depth of 7–8 cm immediately prior to sowing with lettuce, turnips or sorghum.

Samples of immature lettuce were collected from each of the plots at 46–50 days after planting and mature samples were collected at harvest at 59–61 days after planting. Immature turnip plants were collected at 39–42 days after planting, while mature turnips were sampled at 73–82 days after planting. For sorghum, “early forage” samples were taken at 29–34 days after planting and “late

forage" samples were taken at 80–97 days after planting. At harvest (110–127 days after planting) samples of grain and stover (fodder) were collected for analysis. Soil samples were collected at the time of application, at the time of planting and at the time that each sample was collected. At all other sampling times, core samples were collected at random from each plot. All samples (except turnip roots) were homogenised and stored frozen (-20 °C) prior to combustion analysis. The turnip roots were washed in water prior to frozen storage; the water rinsates were retained for LSC analysis.

TRR in representative crop and soil samples were determined by combustion before extraction of the remainder of the samples. Early sorghum forage, sorghum stover and mature turnip tops were the only ones that required extraction and HPLC analysis of radioactivity. Homogenised samples were extracted using CH3CN:H2O (70:30) and partitioned against hexane. Following acidification (pH 2), the samples were partitioned using CH3CN:CH2Cl2. All fractions were assayed using LSC and the CH3CN:CH2Cl2 and aqueous fractions were analysed using HPLC. Values of TRR in each of the samples are shown in Table 22.

Table 22. TRR in various follow crops at 90 and 120 DAT in a crop rotation study.

Sample	90 day plots		120 day plots	
	Days after planting	TRR (mg/kg parent equivalents)①	Days after planting	TRR (mg/kg parent equivalents)①
Lettuce				
immature	50	0.002	45	0.001
mature	61	< 0.002	58	< 0.001
Turnip				
immature	39	0.007	42	0.007
mature tops	79	0.004	72	0.01
mature roots	79	< 0.001	72	< 0.001
Sorghum				
early forage②	29	0.027	33	0.017
late forage③	97	0.003	80	0.003
stover	127	0.027	110	0.003
grain	127	0.006	110	0.003

① mg/kg aminopyralid equivalents. ②18″ high crop. ③ Equivalent to soft to hard dough stage. LOD = 0.0005 mg/kg aminopyralid equivalents; LOQ = 0.002 – 0.003 mg/kg aminopyralid equivalents.

The data show that TRR above the reported LOQs are present in immature turnips, turnip tops, sorghum forage and sorghum stover harvested from both the 90 day and 120 day plots. Very little radioactivity is present in mature crop parts, such as lettuce, turnips or grain. The distribution of the radioactivity in extracted samples is shown in Table 23.

Table 23. Distribution and characterisation of radioactivity in extracts of follow crops.

Sample Extracts	Total % TRR	% TRR			
		aminopyralid	C-1	C-2	NER
Sorghum forage (90 days (early))					
CH_3CN/CH_2Cl_2	49	39.6	–	9.4	–
Extracted tissue	39.9	4.6	20.5	13.7	
Spent tissue①	11.1	–	–	–	11.1
Total % TRR		44.2	20.5	23.1	11.1
(mg/kg)		(0.012)	(0.006)	(0.006)	(0.003)
Sorghum forage (120 days (early))					
CH_3CN/CH_2Cl_2	38.4	23.7	–	14.2	–
Extracted tissue	45.8	3.2	17	24	–
Spent tissue①	15.8	–	–	–	15.8
Total % TRR		26.9	17	38.2	15.8
(mg/kg)		(0.005)	(0.003)	(0.006)	(0.003)
Sorghum stover (90 days)					
CH_3CN/CH_2Cl_2 of CH_3CN/H_2O	15.3	5.4	1.4	8.5	–
Extracted CH_3CN/H_2O	50.2	7.2	15.9	27.2	–
CH_3CN/CH_2Cl_2 of reflux	7.7	5.5	–	2.2	–
Reflux spent aqueous	16.7	NA	NA	NA	–

Sample Extracts	Total % TRR	% TRR			
		aminopyralid	C-1	C-2	NER
Spent tissue①	11.1	–	–	–	11.1
Total % TRR (mg/kg)		18.1 (0.005)	17.3 (0.005)	37.9 (0.01)	11.1 (0.003)
Turnip tops (120 days)					
CH_3CN/CH_2Cl_2 (1st CH_3CN/H_2O)	15.5	4.4	–	11.1	–
Extracted aqueous	75	12.6	5.4	56.8	–
2nd CH_3CN/H_2O	7.2	NA	NA	NA	–
Spent tissue①	2.3	–	–	–	2.3
Total % TRR (mg/kg)		17.2 (0.002)	5.4 (0.001)	67.9 (0.007)	2.3 (0.001)

① Spent tissue = PES or post extraction solids. C-1 and C-2 are metabolite components, NER: non-extractable residue

A large proportion of the radioactivity was extracted, with TRR in spent tissues (or post extraction solids) ranging from 2% to 16% of the TRR in the selected samples. The data in Table 23 indicate that the residue profile in the extracted fractions is similar to that found in the wheat metabolism study. The majority of the extracted radioactivity is composed of aminopyralid and two metabolite components C-1 and C-2. C-1 is more polar than aminopyralid, while C-2 is less polar than aminopyralid. As the crop matures, less aminopyralid is present, with a large proportion of the radioactivity being associated with another component, C-2. Results from base hydrolysis of the spent aqueous fractions show that there is significant conversion of both C-1 and C-2 metabolites to aminopyralid. The results are very similar to those seen in the wheat and grass metabolism studies, where base hydrolysis of aqueous and organosoluble fractions followed by purification resulted in the identification of free and bound forms of aminopyralid.

In relation to soil, the amounts of radioactivity remaining at the time of planting and at various times up until harvest are shown in Table 24. At the time of planting, approximately 35 to 60% of the applied radioactivity was present in the plots. Of the remaining TRR in the soil of both plots at planting, approximately 16% to 32% was extracted as aminopyralid and another 15 to 25% comprised non-extracted residues. Additional components in the HPLC profile, being either more or less polar than aminopyralid, were present at levels of 1–3% of the TRR.

Table 24. TRR in soil at various times after application.

Sample	DAT	%TRR in Soil	% of Applied Radioactivity in Soil (90 days)			
			parent	Spent AQ	NER①	Other②
Lettuce						
0 DAT	0	88	80.3	3.6	0.7	3.2
Planting	90	51.6	24.5	2	22.7	1.6
Harvest	151	31.4	13.5	0.9	15.9	1
Turnips						
0 DAT	0	87.5	79.9	3.6	0.7	3.2
Planting	90	40.5	19.6	2.5	16.7	< MQL③
Immature	129	37.3	16.4	2.1	17.1	1.2
Harvest	179	16.1	5.4	0.1	9.8	0.7
Sorghum						
0 DAT	0	106	91.3	4.1	0.8	3.6
Planting	90	61.6	32.2	1.6	22.9	4.4
Early forage	119	21.1	NA	NA	NA	NA
Late forage	187	22.7	2.8	0.6	17.1	2.2
Harvest	217	20.9	3.7	2.2	13.2	1.5
Sample	DAT	%TRR in Soil	% of Applied Radioactivity in Soil (120 days)			
			parent	Spent AQ	NER①	Other②
Lettuce						
0 DAT	0	87.5	79.1	0.3	5.7	2.2
Planting	120	57.2	31.8	1.6	20.2	3.5
Harvest	179	38.5	14.5	3.6	17.8	2.2
Turnips						
0 DAT	0	87.9	79.5	0.3	5.8	2.2
Planting	120	37	18.2	1	15.8	2
Harvest	193	32.9	9.4	4.5	18	0.9

Sample	DAT	%TRR in Soil	% of Applied Radioactivity in Soil (90 days)			
			parent	Spent AQ	NER①	Other②
Sorghum						
0 DAT	0	93.3	85.2	3.8	0.8	3.4
Planting	120	36.4	16.3	1.8	17.3	< MQL③
Early forage	154	38	9	1.5	25.7	1.3
Late forage	200	34.4	5.5	2.7	23.4	2.8
Harvest	230	23.9	3.6	1.9	17.2	1

① NER = Non-extractable residues ② Other = HPLC regions other than parent aminopyralid composed of 1 to 2 other components. ③ MQL = minimum quantifiable limit equivalent to 1% of the total applied radioactivity.

At harvest, aminopyralid had decreased to levels ranging 3.6–14.5% of the applied radioactivity for both plots.

Further extraction and workup of the non-extracted residues in soil using strong acid resulted in the release of another 15% of the TRR. In all cases, the additional ^{14}C released was not aminopyralid *per se*, but an aqueous soluble component.

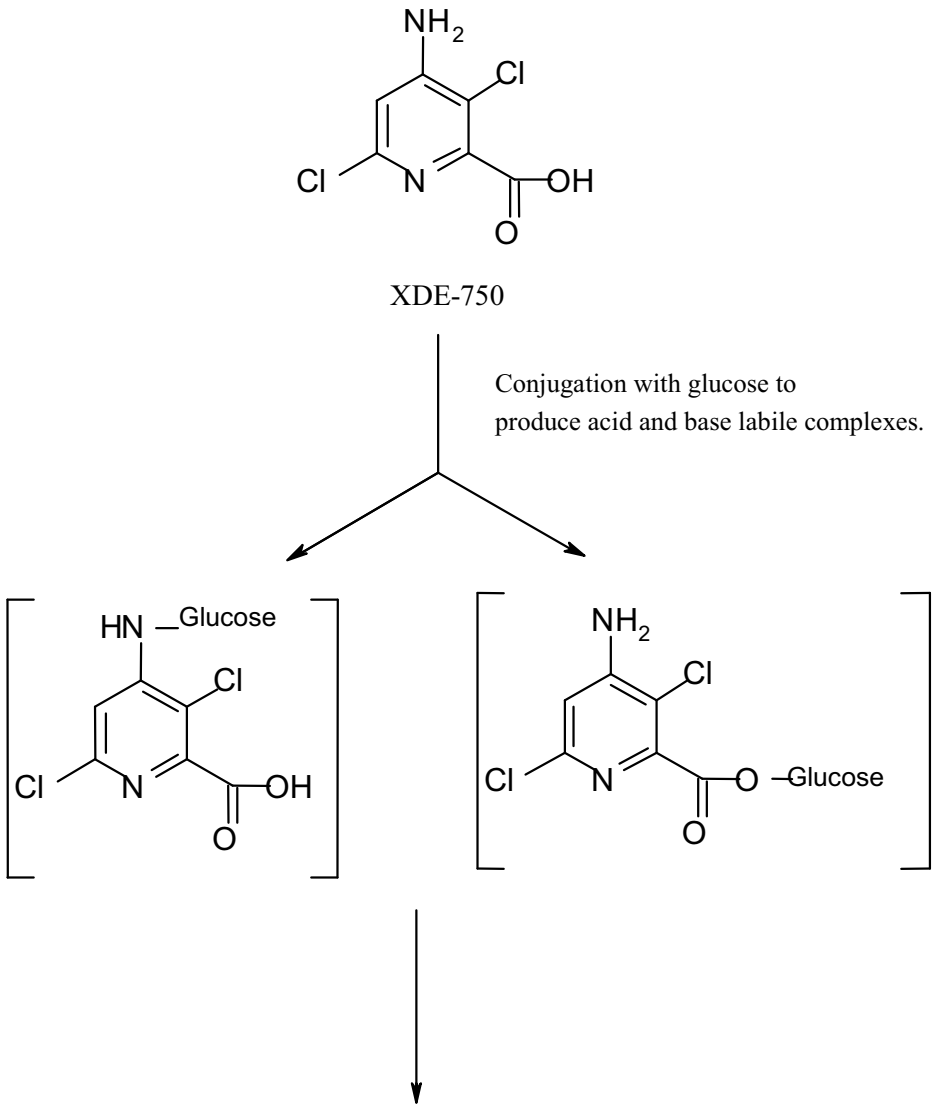


Figure 4: Proposed metabolic pathway of aminopyralid in rotational crops.

RESIDUE ANALYSIS

The Meeting received details of analytical methods for the determination of residues of aminopyralid in agricultural commodities (namely pasture, cereal grains, cereal forage and straw), bovine tissues and milk, soil, water, air and human blood and urine. Only relevant studies are summarised in this evaluation.

Analytical methods

Crop Matrices

Method GRM 02.31 (Olberding, Arnold and Hastings, 2004) was developed for the quantitative determination of aminopyralid residues in barley, sorghum, wheat and grass pasture. Residues are determined using LC/MS/MS. The validated LOQ for all matrices is reported as 0.01 mg/kg.

Residues of aminopyralid are extracted from the sample matrices by homogenisation with 0.1 N NaOH. An aliquot of the NaOH solution is acidified using HCl and the solution is heated at 80 °C for approximately 90 minutes. Following hydrolysis, the sample is purified using a mixed-mode polymeric anion exchange solid-phase extraction (SPE) column. After elution from the SPE column with ethyl acetate/trifluoroacetic acid (99:1), an internal standard is added ($^{13}C_2{}^{15}N$-aminopyralid) and the eluate is evaporated to dryness. The remaining residue is dissolved in CH_3CN/pyridine/1-BuOH solution (22:2:1) and then derivatized with butyl chloroformate to form the 1-butyl esters (1-BE) of both the analyte and the internal standard. Following derivatization, the mixture is diluted to volume with MeOH/H_2O/CH_3COOH (50:49.9:0.1) and analysed using liquid chromatography with positive-ion electrospray tandem mass spectrometry (LC/MS/MS). The MS/MS ion transitions are $(M + H)^+$ at *m/z* 263 and fragment ions (daughter ions) at *m/z* 134 and *m/z* 161 for aminopyralid-BE. For the internal standard, $^{13}C_2{}^{15}N$-aminopyralid 1-BE, the ion transitions are $(M + H)^+ +2$ at *m/z* 268 and fragment ions at *m/z* 139 and *m/z* 166. HPLC operating conditions include use of a Diazem 3000 C_{18} column (4.6 mm × 100mm, 3 µm particle size) operating at 35 °C; mobile phase A: MeOH/CH_3COOH (99.9:0.1) and mobile phase B: H_2O/CH_3COOH (99.9: 0.1).

Isotopic overlap between the analyte and the internal standard was determined by analysing standard solutions of each compound individually, i.e. determining peak areas for each derivatised compound. The analyte → ISTD crossover factor was determined as 0.00532 and the ISTD → analyte crossover factor was 0.00266.

Calculated LOQs ranged from 0.004 to 0.006 mg/kg, which support the method LOQ of 0.01 mg/kg. The calculated LOD was < 0.002 mg/kg. In actual samples, results are reported as ND for residues that were > LOD and < validated LOQ if ≥ LOD.

In the method validation component of the study, untreated control samples of barley, sorghum and wheat grain; barley, sorghum and wheat forage; barley straw, sorghum stover and wheat straw; grass forage and hay were fortified with aminopyralid at concentrations ranging 0.01 – 0.5 mg/kg for grain, 0.01–5 mg/kg for forage and straw and 0.01–20 mg/kg for grass forage and hay. Recoveries are summarised in Table 26.

Table 25. Recovery of aminopyralid from barley, sorghum, wheat matrices and grass forage and hay.

Sample matrix	Fortification level (mg/kg)	Number of samples (n)	Recovery Range (%)	Mean Recovery (%)
Cereal grains (barley, sorghum, wheat)	0.01	10	92 – 112	102
	0.025	2	107, 109	108
	0.05	5	96 – 111	104
	0.1	2	109, 110	109
	0.25	3	95, 101, 103	100
	0.5	5	97 – 107	103

Sample matrix	Fortification level (mg/kg)	Number of samples (n)	Recovery Range (%)	Mean Recovery (%)
Cereal forages (barley, sorghum, wheat)	0.01	12	88 – 105	97
	0.05	6	86 – 104	97
	0.25	3	93, 97, 98	96
	1	3	101, 106, 106	104
	5	6	90 – 106	99
Cereal straw/stover (barley, sorghum, wheat)	0.01	12	89 – 108	97
	0.05	6	95 – 104	100
	0.25	3	93, 94, 94	94
	1	3	94, 97, 97	96
	5	6	92 – 97	95
Grass forage	0.01	8	87 – 101	92
	0.05	4	94 – 98	96
	0.25	4	99 – 103	101
	1	4	95 – 101	98
	5	3	95, 95, 97	96
	20	6	93 – 103	100
Grass hay	0.01	8	89 – 105	98
	0.05	4	95 – 105	100
	0.25	4	92 – 101	97
	1	4	93 – 100	98
	5	4	92 – 108	99
	20	6	98 – 102	100

Independent laboratory validation (Reed, 2005) confirmed the LOQ of 0.01 mg/kg in fortified wheat grain and grass forage samples, using LC/MS/MS. Recoveries in wheat grain at concentrations of 0.01 and 0.1 mg/kg ranged 100–116% and 93–118%, respectively. The mean recovery in wheat grain was 110 ± 8.2% (n = 9). Recoveries in grass forage at concentrations of 0.01 and 60 mg/kg ranged 94–105% and 111–120%, respectively. The mean recovery in grass forage was 108 ± 9.5% (n = 10).

A GC/MS method for the determination of aminopyralid, fluroxypyr and 2,4-D residues in pastures was provided (Pinheiro and De Vito, 2003). The method is a modified version of GRM 02.31 and has a validated LOQ of 1 mg/kg. Modifications of method GRM 02.31 include acidification with H_2SO_4 in place of HCl and ethyl acetate partitioning prior to derivatisation to form the 1-butyl ester. Recoveries were validated over a range of concentrations (1 – 100 mg/kg) and ranged 78 – 115% with a mean recovery of 95 ± 7%. The reported LOD was 0.2 mg/kg in pasture samples.

An assessment of European multi-residue methods for the determination of aminopyralid was provided to the meeting (Class, 2003). It was concluded that the German DFG S19 or the Netherlands multi-residue methods are not appropriate for the determination of aminopyralid in plant materials, foodstuffs of animal origin or soil without major adaptations. The lack of basic and/or acidic extraction procedures in the multi-residue methods preclude their use for aminopyralid. It was recommended that for enforcement purposes, methods GRM 02.31, GRM 02.34 and GRM 03.18 be used until a LC/MS/MS based multi-residue method with extraction and clean-up steps targeting carboxylic acid analytes was made available.

Animal matrices

Method GRM 03.18 was developed for the determination of aminopyralid residues in bovine tissues (muscle, fat, liver and kidney) and milk (Rutherford and Hastings, 2003). The validated limit of quantitation is 0.01 mg/kg.

Aminopyralid residues are extracted from tissue samples by homogenising and shaking with MeOH/$NaHCO_3$ solution (20:1, v:w). An aliquot is diluted with H_2O and purified using a SPE plate (Waters Oasis MAX solid-phase extraction plate). The SPE plate is washed with CH_3CN and a MeOH/CH_3COOH solution (97:3) and eluted with an ethyl acetate/trifluoroacetic acid solution (99:1).

The internal standard ($^{13}C_2{}^{15}N$-aminopyralid) is added to the eluate, which is evaporated to dryness and the remaining residues are re-dissolved in CH_3CN/pyridine/BuOH (22:2:1) coupling reagent. The samples and standards are derivatized at room temperature with butyl chloroformate to form the 1-butyl esters of the analyte and internal standard. Following derivatization, the samples are diluted with MeOH/H_2O/CH_3COOH (50:50:0.1) mobile phase. The final solution is analysed by liquid chromatography with positive-ion electrospray ionisation (ESI) tandem mass spectrometry (LC/MS/MS). All instrumental conditions are identical to those reported for method GRM 02.31.

The method was validated over the concentration range of 0.01–2.5 mg/kg in kidney and 0.01–1 mg/kg for all other tissues and milk. The recoveries in various tissues and milk are shown in Table 27.

Table 26. Recovery of aminopyralid from animal matrices.

Sample	Fortification level (mg/kg)	Number of samples (n)	Recovery Range (%)	Mean Recovery (%)
Bovine fat	0.01	5	85 – 99	92
	0.1	2	94, 97	96
	1	5	88 – 97	93
Bovine muscle	0.01	5	81 – 96	86
	0.1	2	91, 92	92
	1	5	75 – 85	79
Bovine kidney	0.01	5	67 – 86	79
	0.5	2	83, 89	86
	2.5	5	72 – 95	82
Bovine liver	0.01	5	77 – 88	83
	0.1	2	89, 93	91
	1	5	77 – 82	79
Whole milk	0.01	5	78 – 87	81
	0.1	2	86, 91	89
	1	5	76 – 83	79
Milk cream	0.01	2	71, 91	81
	0.1	1	88	
	1	2	64, 71	68
Skim milk	0.01	2	77, 82	79
	0.1	1	99	
	1	2	71, 75	73

Recoveries were conducted in whole milk, milk cream and skim milk. The mean recovery in all milk fractions was 80 ± 10% (n = 22) over the concentration range 0.01 – 1 mg/kg (whole milk 82%, cream 77% and skim milk 81%).

In an independent laboratory validation of method GRM 03.18 (Reed 2004), the LOQ of 0.01 mg/kg was confirmed for aminopyralid in bovine milk and kidneys using LC/MS/MS. Recoveries in bovine milk at concentrations of 0.01 and 0.1 mg/kg ranged 72 – 97% and 84 – 90%, respectively. The mean recovery in bovine milk was 83 ± 8% (n = 10). Recoveries in bovine kidney at concentrations of 0.01 and 0.5 mg/kg ranged 72 – 97% and 93 – 97%, respectively. The mean recovery in bovine kidney was 87 ± 11% (n = 10).

Soil

Residues of aminopyralid in soil are determined using method GRM 02.34 (Lindsey and Hastings, 2004). Aminopyralid is extracted from soil by shaking with a CH_3CN/1 N HCl solution (90:10). The sample is then centrifuged and the extract is decanted. A second extraction is performed by adding the CH_3CN/HCl solution to the soil and mechanically shaking for 30 minutes. The sample is centrifuged and the second extract is combined with the first extract. The extract is evaporated to dryness and re-dissolved in 1N HCl. An aliquot of the extract is purified on an SPE plate which is then washed with H_2O/MeOH (95:5) and eluted with CH_3CN. Internal standard ($^{13}C_2{}^{15}N$-aminopyralid) is added to the

eluate and evaporated to dryness and taken up in CH_3CN/pyridine/BuOH solution (22:2:1) prior to derivatisation. The remaining residue is derivatised using butyl chloroformate and diluted with $MeOH/H_2O/CH_3COOH$ mobile phase (50:50:0.1). The purified extract is analysed using HPLC with ESI LC/MS/MS. Residue identity is confirmed by matching retention time in conjunction with monitoring the MS/MS ion transitions of aminopyralid butyl ester at *m/z* 263/134 and $^{13}C_2{}^{15}N$-aminopyralid butyl ester at *m/z* 268/139.

The method was validated with recoveries being conducted in four soil types at concentrations ranging 0.0015–0.1 mg/kg; the validated LOQ was 0.0015 mg/kg. A summary of the soil recoveries is given in Table 28. The overall mean recovery at fortifications ranging 0.0015 – 0.1 mg/kg was 88 ± 6%.

Table 27. Recoveries of aminopyralid in soils samples.

Matrix	Number of samples	Fortification Level (mg/kg)	Recovery Range (%)	Mean Recovery (%)
Sandy soil	10	0.0015 – 0.1	80 – 102	92 ±
Silt	10	0.0015 – 0.1	86 – 94	90 ±
Loam	10	0.0015 – 0.1	81 – 91	87 ±
Clay	10	0.0015 – 0.1	81 – 91	85 ±
All soils	40	0.0015 – 0.1	80 – 102	88 ± 6

Extraction efficiency

To determine the extraction efficiency of the procedures in method GRM 02.31, samples taken in the ^{14}C plant metabolism studies were extracted and hydrolysed in the manner described above ('cold' method). The 42 DAT samples of ryegrass, big bluestem and *Panicum maximum* from the grass metabolism study (Magnussen and Balcher 2004) and samples of the wheat forage (14 DAT), wheat hay (35 DAT) and wheat grain and straw (86 DAT) from the spring wheat metabolism study (Graper *et al* 2003) were extracted, hydrolysed and prepared for quantitation according to Method GRM 02.31. Following extraction and preparation, the remaining residues were analysed using capillary gas chromatography with negative-ion chemical ionisation mass spectrometry (GC/NCI-MS). The results are shown in Table 30. For grass samples the extraction efficiency ranged from 88 – 114%; for 14 DAT wheat forage and 35 wheat DAT hay the extraction efficiency was 101% and 72%, respectively. For 86 DAT straw, the extraction efficiency was 87%. For the 86 DAT grain, the extraction efficiency was 101% when calculated based on total radioactivity but 170% when calculated on the basis of extractable ^{14}C labelled aminopyralid.

Table 28. Summary of extraction efficiency of aminopyralid from grass and wheat matrices.

Sample Matrix	Radioactivity (mg/kg) Total	Extractable	Aminopyralid (mg/kg) ^{14}C	'Cold'①	Extraction Efficiency②
42 DAT grass					
Ryegrass	6.57③	6.28④	5.84⑤	6.65	114%
Big bluestem	5.61③	5.45④	5.04⑤	4.45	88%
Panicum maximum	4.81③	4.61④	4.24⑤	4.85	114%
Wheat					
Forage (14 DAT)	0.418⑥	0.390⑥	–	0.393	101%
Hay (35 DAT)	0.691⑥	0.611⑥	–	0.440	72%
Grain (86 DAT)	0.084⑥	0.058⑥	0.050⑦	0.085	170%
Straw (86 DAT)	0.623⑥	0.508⑥	0.489⑦	0.424	87%

① Values obtained using sample preparation procedures in Method GRM 02.31.

② Extraction efficiency = 'cold' results/ ^{14}C results × 100.

③Values from Table 9 (%TRR from unrinsed samples).

④ Values from Table 9 (data from extracts of each species).

⑤ Total ^{14}C as aminopyralid +C-1+C-3 Table 9.

⑥ Values from Table 4 (total ^{14}C extractable).

⑦ Values from Table 7 (total aminopyralid equivalents).

The extraction efficiency of method GRM 02.34 was determined by extracting soil samples treated in accordance with the test conditions of the European aerobic soil degradation study (Yoder and Smith, 2003). Samples of soil were treated with ^{14}C-aminopyralid at the equivalent of 120 g ai/ha (0.016 mg/kg). Samples were extracted at 9, 21, 57 and 79 days after dosing using the extraction procedures described in method GRM 02.34. Replicate aliquots of each extract were counted by LSC to determine ^{14}C aminopyralid. Each extract was then analysed using HPLC with ESI LC/MS/MS for qualitative and quantitative analysis of aminopyralid. The resulting levels were compared to verify extraction efficiency and are shown in Table 31.

Table 29. Summary of extraction efficiency of aminopyralid residues in soil samples.

Soil sample	% recovery with LSC and HPLC				% recovery by LC/MS/MS			
	Day 9	Day 21	Day 57	Day 79	Day 9	Day 21	Day 57	Day 79
Sand	82	75	63	56	79	69	59	52
Clay	68	68	26	10	64	60	23	7
Loam	72	63	52	43	72	60	49	38

The results show that the recoveries using the “cold” method are acceptable and demonstrate that method GRM 02.34 is applicable for the determination of aminopyralid residues in soils.

Stability of pesticide residues in stored analytical samples

The storage stability of aminopyralid in pasture grass and hay and wheat grain and straw was investigated (Lindsay, 2004). Samples of hay, forage (grass), wheat grain and wheat straw were fortified with aminopyralid at a concentration of 0.1 mg/kg and placed in frozen storage at -20 °C for up to 488 days (grass) and 469 days (wheat). The conditions were consistent with the storage of actual field samples.

Samples were analysed at 0, 28, 130, 187 and 488 days after fortification for the grass samples and at 0, 113, 168, 273 and 469 days after fortification for the wheat samples (n = 3 at each time point). Concurrent (procedural) recoveries were conducted at each of the sampling intervals by freshly fortifying control samples (n = 2) with aminopyralid at a concentration of 0.1 mg/kg. Residues were then extracted and determined in all samples in accordance with method GRM 02.31 which has an LOQ of 0.01 mg/kg. The data are shown in Table 32.

Table 30. Storage stability of aminopyralid residues in wheat and grass matrices.

Matrix	Storage interval (days)	Fortification concentration (mg/kg)	Residue found Mean (n = 3) (mg/kg)	Procedural recovery (%)
Grass	0	0.1	0.0882	94
Hay	28		0.0911	92
	130		0.0712	76
	187		0.0787	82
	489		0.0865	88
Forage	0	0.1	0.0858	93
	28		0.0911	95
	130		0.0757	75
	187		0.0835	84
	489		0.0884	87
Wheat	0	0.1	0.0848	86
Grain	113		0.0866	90
	168		0.0892	95
	273		0.0977	103
	469		0.0910	89
Straw	0	0.1	0.0839	83
	113		0.0840	84
	168		0.0912	91
	273		0.0924	101
	469		0.0869	85

The data indicate that aminopyralid residues are stable under conditions of frozen storage for up to 489 days in grass hay and forage, and up to 469 days in wheat grain and straw.

The storage stability of aminopyralid residues in sandy loam soil was investigated (Lindsay 2004). The characteristics of the soil were as follows: bulk density 1.03 g/cm^3; organic matter 7.1%; CEC 17.5 meq/100g; H_2O content at ⅓ bar 39.2% and at 15 bar 21.3%; 60% sand, 28% silt and 12% clay; pH 5.4.

Samples of soil were fortified with aminopyralid at 0.015 mg/kg and were stored in both polyethylene and tin containers at -20°C for up to 497 days. The conditions were consistent with the storage of actual field samples. Samples were analysed at 0, 41, 133, 194, 460 and 497 days after fortification. Concurrent (procedural) recoveries were conducted at each interval by freshly fortifying soil samples (n = 2) with aminopyralid at a concentration of 0.0015 mg/kg. Residues were extracted and determined in accordance with method GRM 02.34, as described above, which has an LOQ of 0.015 mg/kg. The concentration of aminopyralid remaining from 0 to 497 days, ranged from 0.0091 – 0.0151 mg/kg (uncorrected) or 61% – 101% of the fortified concentration.

USE PATTERNS

Table 31. Registered uses of aminopyralid. Expressed as acid equivalents/ha (ae/ha) or acid equivalents/100L (ae/100L).

Crop/Situation	Country	Application				No.	PHI (days)		PSI/
		Form.	Type	Rate (g ae/ha)	Timing		Harvest	Graze/ Cut	ESI①
Pastures	Australia	EO	Ground foliar/spot spray	150 – 210②		1	Nil	Nil	3 days
Pastures maintenance renewal	Brazil	SL EO	Ground & aerial	40 – 100③ 40 – 80④		1 1	Not determined	Not determined	
Pastures	Canada	SL	Ground & aerial	60 – 120⑤			Nil	Nil	𝒢
Pastures	Colombia	SL	Ground	10 – 50 g ae/100L⑥	Post-emergence	1			
Pastures	Mexico	SL	Ground foliar	20 – 120			7 days	7 days	
	Mexico	SC	Ground foliar	10 – 40 g ae/100L			7 days	7 days	
Pastures	New Zealand	SC	Ground foliar/broadcast	60			Nil	Nil	4 days⑦
			Spot spray	6 – 9 g ae/100L					
Pastures	UK	EO	Ground foliar	60⑧		1		7 days	
Pastures	US	SL	Ground/aerial	53 – 123⑨			0⑩ or 7❶days	0 or 7 days	𝒢
Pastures	Venezuela	SL	Ground foliar	120 – 160❶ or 30 – 40 g ae/100L					
Wheat	Argentina	WG	Ground foliar	3.75 – 5	From 3rd leaf to end of tillering	NS	Nil		
Wheat, Barley Oats, Triticale	Australia	EO	Ground foliar	5 – 7.5❷	3-leaf to 1st node (Z13 to Z31)	1	Nil	7 days	3 days
Wheat	Canada		Ground foliar	10	2 to 6 leaf stage		50 days	Nil	𝒢

Crop/Situation	Country	Application				No.	PHI (days)		PSI/
		Form.	Type	Rate (g ae/ha)	Timing		Harvest	Graze/ Cut	ESI①
Wheat	Mexico	SL	Ground foliar	30 g ai/ha	Not stated		7 days		
Wheat	US		Ground/aerial	7.6 – 10❸	3-leaf to early jointing (Z30)	1	50 days	14 days (8.75 label low rate Nil)	☙
			Spot spray	38 g ai/100L					

① PSI/ESI = Pre-slaughter Interval or Export Slaughter Interval. ② with up to 98 g ai/ha fluroxypyr. ③ with up to 800 g ai/ha 2,4-D or 200 g ai/ha fluroxypyr. ④ with up to 640 g ai/ha 2,4-D or 160 g ai/ha fluroxypyr. ⑤ with up to 1440 g ae/ha 2,4-D. ⑥ with up to 400 g ai/100L 2,4-D. ⑦ Slaughter Interval (domestic and export). ⑧ with 200 g ai/ha fluroxypyr. ⑨ with 982 g ae/ha 2,4-D. ⑩ 0 days on Milestone label. ❶ 7 days on Forefront label. ❶ with 1280 g ae/ha 2,4-D. ❷ with up to 105 g ai/ha fluroxypyr. ❸ with 143 g ai/ha fluroxypyr. ☙3 days removal to clean feed before introducing to another sensitive broadleaf cropping area. (crop safety statement).

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials for aminopyralid uses on cereals and pastures. Tables are listed below:

All trials submitted to the meeting were conducted in accordance with the OECD principles of Good Laboratory Practice (GLP). All trials were well documented in both the analytical and field phases of the reports. Analytical reports included method validation with procedural recoveries from fortification at concentrations similar to those occurring in samples from supervised field trials. Dates of analyses and/or duration of residue sample storage were provided. Intervals of freezer storage between sampling and analysis were recorded for all trials and were covered by the conditions of the freezer storage stability studies.

All trials included analyses of control samples, however no control data are recorded in the tables except in instances where residues in the control samples exceeded the validated LOQ. Residue data reported in the following tables are not adjusted for analytical recoveries.

In most trials, field samples from an unreplicated plot were taken at each sampling interval and were analysed. For the purposes of the evaluation, where replicate samples were analysed separately, the mean of the two results is reported as the residue from the plot in following tables.

When residues were not detected and were reported as ND in the studies, they are indicated as being below the LOQ (e.g. < 0.01 mg/kg). Residues, application rates and spray concentrations have

generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from trials that reflect the maximum GAP have been used for the estimation of maximum residue levels. Residue trials conducted at exaggerated or higher than label application rates are also included in the estimation of maximum residue levels, where the resulting residues are less than the LOQ. The values that are included in the MRL estimation are underlined in the tables below.

Formulations used in the residue trials include soluble granules (SG), water dispersible granules (WG), soluble concentrates (SL), water-in-oil emulsions (EO), micro-emulsions (ME) containing salt forms of aminopyralid. Some were combination products with other herbicides such as fluroxypyr, 2,4-D and triclopyr. The types of formulations used in various trials are tabulated below.

Table 32. Formulations used in supervised trials for cereals and pastures.

Formulation Code/ Designation	g ae/kg or g ae/L	Form of active	Trials
GF-1118; SG 75%	750 g ae/kg	Potassium salt	Spain, Hungary, Poland, Italy
GF-1118; WG 750	750 g ae/kg	Not stated	Argentina
GF-871; SL 240	240 g ae/L	TIPA salt①	Australia, USA
GF-982②; EO	10 g ae/L	TIPA salt①	Australia, USA, Canada
GF-389; SL 247	247 g ae/L	Potassium salt	USA
GF-1004; SL 40	40 g ae/L	TIPA salt①③	Brazil
GF-843; EO 40	40 g ae/L	Potassium salt④	Brazil
GF-839; ME 30 #1	30 g ae/L	Potassium salt⑤	UK, Germany, Spain, France, Italy
GF-819, ME 30 #2	30 g ae/L	Potassium salt⑥	UK, Germany, France, Spain

① Triisopropanolammonium salt. ② Combination with 140 g ae/L fluroxypyr (1-methylheptyl ester or meptyl ester).
③ Combination with 320 g ae/L 2,4-D. ④ Combination with 80 g ae/L fluroxypyr (meptyl ester).
⑤ Combination with 100 g ae/L fluroxypyr (as meptyl ester) ⑥ Combination with 240 g ae/L triclopyr (as butyl

Application rates and/or spray concentrations are expressed as g acid equivalents/ha (g ae/ha) or g acid equivalents/100l (g ae/100l). In all cases residues were determined and expressed as aminopyralid. Methods used to determine residues in cereal matrices were GRM 02.31 and GRM 03.25 (Argentina) and GRM 02.31 for grass pasture and hay matrices.

Cereal grains

Residue data were provided for barley, oats and wheat from trials conducted in Argentina, Australia, Canada, Europe and USA.

Table 33. Aminopyralid residues in barley grain.

BARLEY GRAIN	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
Torredalomar, Spain, 2003 (Astoria)	SG 75%	10	302	1	BBCH 30	47	0.04	GHE-P-10576① CEMS-2063
Zaragoza, Spain, 2004 (Unia)	SG 75%	10	298	1	BBCH 30	58	0.08	GHE-P-10690② CEMS-2246
SA, Australia, 2002 (Barque)	SL 240	10 15 20	99 90 90	1 1 1	Z15 (5-leaf)	103 103 103	<u>0.07</u> 0.10 0.12	020060-03③
NSW, Australia, 2002 (Grimnett)	SL 240	10 15 20	96 96 100	1 1 1	5 – 6 leaf	134 134 134	<u>0.06</u> < 0.01 0.10	020060-06③
NSW, Australia, 2003 (Tantangara)	SL 240	7.5 15	95 95	1 1	1st node	80 80	<u>0.07</u> 0.16	030072-02④
	EO	7.5 15	95 95	1 1		80 80	<u>0.06</u> 0.11	

BARLEY GRAIN Country, Year (variety)	Application					PHI	Residues	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
QLD, Australia, 2003 (Cullum)	SL 240	7.5 15	106 105	1 1	1 – 3 tiller	88 88	0.04 0.04	030072-06④
	EO	7.5 15	106 107	1 1	1 – 3 tiller		0.03 0.05	

① Recoveries were 72% and 75% at 0.01 and 0.1 mg/kg, respectively. ② Recoveries were 71% and 101% at 0.01 and 0.1 mg/kg, respectively. ③Recoveries were 76% and 99% at 0.01 and 0.05 mg/kg, respectively. ④ Recoveries ranged 89 – 101% over concentrations 0.01 – 1 mg/kg.

Table 34. Aminopyralid residues in oat grain.

OAT GRAIN Country, Year (variety)	Application					PHI	Residues	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
NSW, Australia, 2002 (Graza)	SL 240	10 15 20	100	1	5 – 6 leaf	134 134 134	0.02 0.04 0.04	020060-07①
SA, Australia, 2003 (Euro)	SL 240	7.5 15	100	1	5 leaf 1 tiller	112 112	0.03 0.06	030071-02②
	EO	7.5 15	100	1	5 leaf 1 tiller	112 112	0.03 0.06	
NSW, Australia, 2003 (Graza 68)	SL 240	7.5 15	95 95	1	1st node	80 80	< 0.01 0.03	030072-03③
	EO	7.5 15	95 95		1st node	80 80	0.01 0.03	
SA, Australia, 2003 (Euro)	SL 240	7.5 15	100 100	1	6 leaf 2 tillers	106 106	0.03 0.05	030072-08③
	EO	7.5 15	100 100		6 leaf 2 tillers	106 106	0.03 0.07	

①Recovery 116% at 0.01 mg/kg. ② Recoveries were 94 and 97% at 1 mg/kg. ③ Recoveries ranged 89 – 101% over concentrations 0.01 – 1 mg/kg.

Table 35. Aminopyralid residues in wheat grain.

WHEAT GRAIN Country, Year (variety)	Application					PHI	Residues	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
Szolnok, Hungary, 2003 (MV Emma)	SG 75%	9.5	210	1	BBCH 30	72	< 0.01	GHE-P-10577① CEMS-2064A
Rzechino,Poland, 2003 (Candos)	SG 75%	10.5	208	1	BBCH 30	84	0.01	GHE-P-10577① CEMS-2064B
Bologna, Italy, 2003 (Soisson)	SG 75%	10	299	1	BBCH 30	69	0.01	GHE-P-10575② CEMS-2059A
Bologna, Italy, 2003 (Mieti)	SG 75%	10	298	1	BBCH 31-32	73	< 0.01	CHE-P-10575② CEMS-2059B
Zaragoza, Spain, 2003 (Scalibur)	SG 75%	10	300	1	BBCH 30	49	< 0.01	CHE-P-10575② CEMS-2059C
Zaragoza, Spain, 2004 (Kilopondio)	SG 75%	10	299	1	BBCH 30	70	< 0.01	GHE-P-10689③ CEMS-2245D

WHEAT GRAIN Country, Year (variety)	Application					PHI	Residues	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
Mainar, Spain, 2004 (Amaroc)	SG 75%	10	298	1	BBCH 30	80	< 0.01	GHE-P-10689③ CEMS-2245E
Villareal, Spain, 2004 (Amilcar)	SG 75%	10	302	1	BBCH 30	80	< 0.01	GHE-P-10689③ CEMS-2245F
Lower Saxony, Germany 2004 (Drifter)	SG 75%	11	330	1	BBCH 30	118	0.01	GHE-P-10691④ CEMS-2247A
Kolobrzeski, Poland 2004 (Ritmo)	SG 75%	11	327	1	BBCH 30	116	< 0.01	GHE-P-10691④ CEMS-2247B
Argentina, 2003 (Delfin)	WG 750	7.5 15	200 200	1 1	Z 22/23	97 97	< 0.01 < 0.01	030070⑤ GHB-P 1096
Argentina, 2003 (Don Enrique (klein))	WG 750	7.5 15	200 200	1 1	2 tillers	95 95	< 0.01 < 0.01	030070⑤ GHB-P 1096
Argentina, 2003 (Prointa granar)	WG 750	7.5 15	200 200	1 1	1 tiller	111 111	< 0.01 < 0.01	030070⑤ GHB-P 1096
Argentina, 2004 (Buck sureno)	WG 750	7.5 15	200 200	1 1	Z21	111 111	< 0.01 < 0.01	030070.01⑤ GHB-P 1109
Argentina, 2004 (Klein scorpion)	WG 750	7.5 15	200 200	1 1	BBCH 14	121 121	< 0.01 0.02	030070.01⑤ GHB-P 1109
Argentina, 2004 (Granar)	WG 750	7.5 15	200 200	1 1	1-2 tillers	86 86	< 0.01 < 0.01	030070.01⑤ GHB-P 1109
WA, Australia, 2002 (Calingiri)	SL 240	10 15 20	101 102 101	1 1 1	5-6 leaf stage	98 98 98	< 0.01 < 0.01 < 0.01	020060-01⑥
SA, Australia, 2002 (Frame)	SL 240	10 15 20	99 90 90	1 1 1	Z15	103 103 103	< 0.01 < 0.01 < 0.01	020060-02⑥
NSW, Australia, 2002 (Babbler)	SL 240	10 15 20	100 96 100	1 1 1	5 – 6 leaf	134 134 134	< 0.01 < 0.01 < 0.01	020060-05⑥
QLD, Australia, 2002 (Petrel)	SL 240	10 15 20	102 99 101	1 1 1	4 – 6 leaf	88 88 88	0.07 0.07 0.11	020060-08⑥
NSW, Australia, 2003 (Wollaroi)	SL 240	7.5 15	101 101	1 1	6-leaf	80 80	0.01 0.02	030071-01⑦
	EO	7.5 15	101 101	1 1	6-leaf	80 80	< 0.01 0.01	
NSW, Australia, 2003 (Mulgara)	SL 240	7.5 15	95 105	1 1	1st node	80 80	0.01 0.02	030072-01⑧
	EO		95 95	1 1	1st node	80 80	< 0.01 0.01	
QLD, Australia, 2003 (Strzelecki)	SL 240	7.5 15	103 102	1 1	5 leaf 1 tiller	99 99	0.02 0.04	030072-04⑧
	EO	7.5 15	102 100	1 1	5 leaf 1 tiller	99 99	0.01 0.02	
QLD, Australia, 2003 (Baxter)	SL 240	7.5 15	103 102	1 1	3 – 6 tiller	88 88	0.03 0.06	030072-05⑧
	EO	7.5 15	99 102	1 1	3 – 6 tiller	88 88	0.02 < 0.01	
SA, Australia, 2003 (Yitpi)	SL 240	7.5 15	96 100	1 1	1st tiller	107 107	< 0.01 < 0.01	030072-07⑧
	EO	7.5 15	100 100	1 1	1st tiller	107 107	< 0.01 < 0.01	
VA, USA, 2003 (Coker9835)	EO	10	135	1	BBCH 32	73	0.025	030042⑨
AR, USA, 2003 (Natchez)	EO	10	116	1	BBCH 41-45	50	0.023	

WHEAT GRAIN Country, Year (variety)	Application					PHI	Residues	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg)	
IN, USA, 2003 (Bravo)	EO	10	188	1	BBCH 31	80	< 0.01	
MN, USA, 2003 (Oxen)	EO	10	150	1	BBCH 37	72	< 0.01	
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	72	< 0.01	
ND, USA, 2003 (Oxen)	EO	10	151	1	BBCH 37	72	< 0.01	
NE, USA, 2003 (VNS HRW)	EO	10	187	1	BBCH 31	61	0.025	
OK, USA, 2003 (Coker9663)	EO EO	10 50	119 119	1 1	BBCH 33 BBCH 33	69 69	0.013 0.055	
SD, USA, 2003 (Marshall)	EO SL 240 SL 247	10 9.7 10.4	152 152 152	1 1 1	BBCH 37 BBCH 37 BBCH 38	72 72 64	< 0.01 < 0.01 0.012	
ND, USA, 2003 (Oxen)	EO SL 240 SL 247	10 9.7 10.4	152 152 152	1 1 1	BBCH 37 BBCH 37 BBCH 38	72 72 65	< 0.01 < 0.01 0.01	
ND, USA, 2003 (Alsen)	EO SL 240 SL 247	10.4 10.5 10.5	147 146 146	1 1 1	BBCH 37 BBCH 37 BBCH 37	50 50 50	0.013 0.014 0.014	
NE. USA, 2003 (Forge HRS)	EO SL 240 SL 247	10 10 10	187 188 187	1 1 1	BBCH 31 BBCH 31 BBCH 31	56 56 56	0.022 0.013 0.023	
SD, USA, 2003 (Walworth)	EO SL 240 SL 247	10 10 10	140 140 140	1 1 1	BBCH 30-31 BBCH 30-31 BBCH 30-31	64 64 64	0.011 0.01 0.01	
TX#1, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 39	57	< 0.01	
TX#2, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 37	69	< 0.01	
NM, USA, 2003 (Jagger)	EO	10	141	1	BBCH 37	62	< 0.01	
TX#4, USA, 2003 (TAM 200)	EO	10	177	1	BBCH 33	67	0.011	
TX#5, USA, 2003 (Jagger)	EO	10	174	1	BBCH 37	67	< 0.01	
KS, USA, 2003 (Ike)	EO	10	110	1	BBCH 30	80	< 0.01	
WA, USA, 2003 (Declo)	EO	10	141	1	BBCH 39	57	0.021	
SK, Canada, 2003 (ACEatonia)	EO SL 240 SL 247	10 10 9.4	107 109 107	1 1 1	BBCH 30 BBCH 30 BBCH 30	55 54 54	0.01 < 0.01 0.011	
SK, Canada, 2003 (ACEatonia)	EO SL 240 SL 247	10 10 10	109 111 113	1 1 1	BBCH 37 BBCH 37 BBCH 37	49 49 49	< 0.01 0.013 0.013	

①Recoveries 79 and 123% @ 0.01 and 0.1 mg/kg. ②Recoveries 84 and 119% @ 0.01 and 0.1 mg/kg. ③Recoveries were 71% and 89% at 0.01 and 0.1 mg/kg, respectively. ④Recoveries were 71% and 101% at 0.01 and 0.1 mg/kg. ⑤Recoveries ranged 71 – 102% at 0.01 mg/kg; 71 – 79% at 0.1 mg/kg and 71 – 107% at 1 mg/kg. ⑥ Recoveries ranged 88 – 98% over concentrations 0.01 – 0.4 mg/kg (n = 3). ⑦ Recoveries were 94 and 97% at 1 mg/kg. ⑧ Recoveries ranged 89 – 101% over concentrations 0.01 – 1 mg/kg. ⑨ Recoveries ranged 80 – 103% over concentrations over concentration 0.05 and 0.5 mg/kg (n = 18).

Livestock feeds

Residue data were provided for forage and straw from barley, oats, wheat and grass pastures from trials conducted in Argentina, Australia, Canada, Europe and USA.

Table 36. Aminopyralid residues in barley straw from trials in Europe

BARLEY STRAW Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
Torredalomar Spain, 2003 (Astoria)	SG 75%	10	302	1	BBCH 30	47	< 0.01	GHE-P-10576① CEMS-2063
Zaragoza, Spain, 2004 (Unia)	SG 75%	10	298	1	BBCH 30	58	0.06	GHE-P-10690② CEMS-2246

①Recoveries were 80 and 102% at concentrations of 0.01 and 0.1 mg/kg, respectively. ② Recoveries were 68% and 79% at concentrations of 0.01 and 0.1 mg/kg, respectively.

Table 37. Aminopyralid residues in barley straw from trials in Australia.

BARLEY STRAW Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
SA, Australia, 2002 (Barque)	SL 240	10 15 20	99 90 90	1 1 1	Z15 (5-leaf)	103 103 103	0.03 0.07 0.07	020060-03①②
NSW, Australia, 2002 (Grimnett)	SL 240	10 15 20	96 96 100	1 1 1	5 – 6 leaf	134 134 134	0.03 0.04 0.05	020060-06①③
NSW, Australia, 2003 (Tantangara)	SL 240	7.5 15	95 95	1 1	1st node	80 80	0.08 0.18	030072-02④⑤
	EO	7.5 15	95 95	1 1		80 80	0.07 0.16	
QLD, Australia, 2003 (Cullum)	SL 240	7.5 15	106 105	1 1	1 – 3 tiller	88 88	0.03 0.04	030072-06④⑥
	EO	7.5 15	106 107	1 1	1 – 3 tiller		0.04 0.06	

①Recoveries 99 and 107% @ 0.4 and 2 mg/kg. ②Moisture contents ranged 10.7 – 12.4%. ③Moisture contents ranged 25.5 – 41.3%. ④Recoveries ranged 78 – 100% over concentrations 0.01 – 1 mg/kg (n = 7). ⑤Moisture contents ranged 7.6 – 8.3%. ⑥Moisture contents ranged 55 – 68.6%.

Table 38. Aminopyralid residues in barley forage.

BARLEY FORAGE Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
SA, Australia, 2002 (Barque)	SL 240	10	99	1	Z15 (5-leaf)	0 1 3 7 14 28	3.89 2.60 1.32 0.54 0.26 0.13	020060-03①②
		15	90	1	Z15 (5-leaf)	0 1 3 7 14 28	5.18 4.19 2.15 1.04 0.47 0.21	

BARLEY FORAGE Country, Year (variety)	Application Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
		20	90	1	Z15 (5-leaf)	0 1 3 7 14 28	8.96 5.23 3.74 1.12 0.47 0.28	
NSW, Australia, 2002 (Grimnett)	SL 240	10	96	1	5 – 6 leaf	0 1 3 7 14 28	1.99 3.33 1.29 0.71 0.30 0.27	020060-06②③
		15	96	1	5 – 6 leaf	0 1 3 7 14 28	3.20 3.09 2.06 1.12 0.41 0.34	
		20	100	1	5 – 6 leaf	0 1 3 7 14 28	5.10 3.80 2.71 1.51 0.44 0.40	

①Moisture contents ranged 84.4 to 87.9%. ②Recoveries ranged 86 – 108 % over concentrations 0.01 – 5 mg/kg (n = 7). ③ Moisture contents ranged 76.3 – 86.3%.

Table 39. Aminopyralid residues in oat straw.

OAT STRAW Country, Year (variety)	Application Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
NSW, Australia, 2002 (Graza)	SL 240	10 15 20	100	1	5 – 6 leaf	134 134 134	0.11 0.11 0.17	020060-07①②
SA, Australia, 2003 (Euro)	SL 240	7.5 15	100	1	5 leaf 1 tiller	112 112	0.02 0.05	030071-02③④
	EO	7.5 15	100	1	5 leaf 1 tiller	112 112	0.03 0.10	
NSW, Australia, 2003 (Graza 68)	SL 240	7.5 15	95 95	1	1st node	80 80	0.05 0.13	030072-03④⑤
	EO	7.5 15	95 95			80 80	0.04 0.08	
SA, Australia, 2003 (Euro)	SL 240	7.5 15	100 100	1	6 leaf 2 tillers	106 106	0.04 0.07	030072-08④⑥
	EO	7.5 15	100 100		6 leaf 2 tillers	106 106	0.04 0.09	

①Recoveries 73 and 77% @ 0.4 and 2 mg/kg. ② Moisture contents ranged 25.2 – 46.7%. ③ Moisture contents ranged 12.9 – 19.5%. ④ Recoveries ranged 78 – 100% over concentrations 0.01 – 1 mg/kg (n = 7). ⑤ Moisture contents ranged 42.8 – 56.2%. ⑥ Moisture contents ranged 23.9 – 33.5%.

Table 40. Aminopyralid residues in oat forage.

OAT FORAGE	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg) dry weight	
NSW, Australia, 2002 (Graza)	SL 240	10	100	1	5 – 6 leaf	0 1 3 7 14 28	1.19 1.46 0.90 <u>0.40</u> 0.15 0.34	020060-03①②
		15	100	1	5 – 6 leaf	0 1 3 7 14 28	1.72 1.81 1.19 0.59 0.18 0.26	
		20	100	1	5 – 6 leaf	0 1 3 7 14 28	3.46 2.77 1.57 0.85 0.27 0.52	
SA, Australia, 2003 (Euro)	SL 240	7.5	100	1	5 leaf 1 tiller	0 1 3 7 14 28	1.74 1.27 0.81 <u>0.34</u> 0.29 0.18	030071-02③④
		15	100	1	5 leaf 1 tiller	0 1 3 7 14 28	3.87 2.95 1.53 0.66 0.54 0.30	
	EO	7.5	100	1	5 leaf 1 tiller	0 1 3 7 14 28	2.93 2.04 1.05 <u>0.79</u> 0.31 0.23	
		15	100	1	5 leaf 1 tiller	0 1 3 7 14 28	5.77 3.25 2.03 1.43 0.79 0.59	

① Moisture contents ranged 81.8 – 87.2%. ②Recoveries ranged 87 – 99% over concentrations 0.01 – 5 mg/kg.
③ Recoveries ranged 85 – 124% over concentrations 0.01 – 1 mg/kg (n = 15). ④ Moisture contents ranged 82.7 – 87.2%.

Table 41. Aminopyralid residues in wheat straw from Europe and USA.

WHEAT STRAW	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg) as received	
Szolnok, Hungary, 2003 (MV Emma)	SG 75%	9.5	210	1	BBCH 30	72	0.04	GHE-P-10577① CEMS-2064A
Rzechino, Poland, 2003 (Candos)	SG 75%	10.5	208	1	BBCH 30	84	0.03	GHE-P-10577① CEMS-2064B

WHEAT STRAW Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
Bologna, Italy, 2003 (Soisson)	SG 75%	10	299	1	BBCH 30	69	0.09	GHE-P-10575② CEMS-2059A
Bologna, Italy, 2003 (Mieti)	SG 75%	10	298	1	BBCH 31-32	73	0.07	CHE-P-10575② CEMS-2059B
Zaragoza, Spain, 2003 (Scalibur)	SG 75%	10	300	1	BBCH 30	49	0.13	CHE-P-10575② CEMS-2059C
Zaragoza, Spain, 2004 (Kilopondio)	SG 75%	10	299	1	BBCH 30	70	0.16	GHE-P-10689③ CEMS-2245D
Mainar, Spain, 2004 (Amaroc)	SG 75%	10	298	1	BBCH 30	80	0.03	GHE-P-10689③ CEMS-2245E
Villareal, Spain, 2004 (Amilcar)	SG 75%	10	302	1	BBCH 30	80	0.04	GHE-P-10689③ CEMS-2245F
Lower Saxony, Germany 2004 (Drifter)	SG 75%	11	330	1	BBCH 30	118	0.08	GHE-P-10691④ CEMS-2247A
Kolobrzeski, Poland 2004 (Ritmo)	SG 75%	11	327	1	BBCH 30	116	0.06	GHE-P-10691④ CEMS-2247B
VA, USA, 2003 (Coker9835)	EO	10	135	1	BBCH 32	73	0.06	030042⑤
AR, USA, 2003 (Natchez)	EO	10	116	1	BBCH 41-45	50	0.04	
IN, USA, 2003 (Bravo)	EO	10	188	1	BBCH 31	80	0.03	
MN, USA, 2003 (Oxen)	EO	10	150	1	BBCH 37	72	< 0.01	
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	72	< 0.01	
ND, USA, 2003 (Oxen)	EO	10	151	1	BBCH 37	72	< 0.01	
NE, USA, 2003 (VNS HRW)	EO	10	187	1	BBCH 31	61	0.13	
OK, USA, 2003 (Coker9663)	EO	10	119	1	BBCH 33	69	0.06	
SD, USA, 2003 (Marshall)	EO SL 240 SL 247	10 9.7 10.4	152 152 152	1 1 1	BBCH 37 BBCH 37 BBCH 38	72 72 64	< 0.01 0.02 0.06	
ND, USA, 2003 (Oxen)	EO SL 240 SL 247	10 9.7 10.4	152 152 152	1 1 1	BBCH 37 BBCH 37 BBCH 38	72 72 65	0.01 0.02 0.04	
ND, USA, 2003 (Alsen)	EO SL 240 SL 247	10.4 10.5 10.5	147 146 146	1 1 1	BBCH 37 BBCH 37 BBCH 37	50 50 50	0.13 0.07 0.07	
NE. USA, 2003 (Forge HRS)	EO SL 240 SL 247	10 10 10	187 188 187	1 1 1	BBCH 31 BBCH 31 BBCH 31	56 56 56	0.1 0.06 0.08	
SD, USA, 2003 (Walworth)	EO SL 240 SL 247	10 10 10	140 140 140	1 1 1	BBCH 30-31 BBCH 30-31 BBCH 30-31	64 64 64	0.1 0.07 0.06	
TX#1, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 39	57	0.04	
TX#2, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 37	69	0.02	
NM, USA, 2003 (Jagger)	EO	10	141	1	BBCH 37	62	0.12	
TX#4, USA, 2003 (TAM 200)	EO	10	177	1	BBCH 33	67	0.04	
TX#5, USA, 2003 (Jagger)	EO	10	174	1	BBCH 37	67	0.04	

WHEAT STRAW Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
KS, USA, 2003 (Ike)	EO	10	110	1	BBCH 30	80	0.04	
WA, USA, 2003 (Declo)	EO	10	141	1	BBCH 39	57	0.04	
SK, Canada, 2003 (ACEatonia)	EO	10	107	1	BBCH 30	55	0.07	
	SL 240	10	109	1	BBCH 30	54	0.07	
	SL 247	9.4	107	1	BBCH 30	54	0.14	
SK, Canada, 2003 (ACEatonia)	EO	10	109	1	BBCH 37	49	0.07	
	SL 240	10	111	1	BBCH 37	49	0.05	
	SL 247	10	113	1	BBCH 37	49	0.07	

①Recoveries 84 and 71% @ 0.01 and 0.1 mg/kg. ②Recoveries 87 and 88% @ 0.01 and 0.1 mg/kg. ③Recoveries were 75% and 89% at 0.01 and 0.1 mg/kg, respectively. ④ Recoveries were 68% and 79% at 0.01 and 0.1 mg/kg, respectively. ⑤Recoveries ranged 72 – 93% over concentrations 0.05, 0.5 and 5 mg/kg (n = 17).

Table 42, Aminopyralid residues in wheat straw from Australia.

WHEAT STRAW Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
WA, Australia, 2002 (Calingiri)	SL 240	10	100	1	5-6 leaf	98	0.10	020060-01③④
		15			stage		0.18	
		20					0.20	
SA, Australia, 2002 (Frame)	SL 240	10	99	1	Z15	103	0.07	020060-02③⑤
		15	90	1		103	0.1	
		20	90	1		103	0.1	
NSW, Australia, 2002 (Babbler)	SL 240	10	100	1	5 – 6 leaf	134	0.04	020060-05③⑥
		15	96	1		134	0.05	
		20	100	1		134	0.06	
QLD, Australia, 2002 (Petrel)	SL 240	10	102	1	4 – 6 leaf	88	0.07	020060-08③⑦
		15	99	1		88	0.10	
		20	101	1		88	0.14	
NSW, Australia, 2003 (Wollaroi)	SL 240	7.5	101	1	6-leaf	80	0.06	030071-01⑧⑨
		15	101	1		80	0.14	
	EO	7.5	101	1	6-leaf	80	0.08	
		15	101	1		80	0.18	
NSW, Australia, 2003 (Mulgara)	SL 240	7.5	95	1	1st node	80	0.09	030072-01⑨⑩
		15	105	1		80	0.2	
	EO		95	1	1st node	80	0.12	
			95	1		80	0.24	
QLD, Australia, 2003 (Strzelecki)	SL 240	7.5	103	1	5 leaf 1 tiller	99	0.02	030072-04⑨❶
		15	102	1		99	0.12	
	EO	7.5	102	1	5 leaf 1 tiller	99	0.02	
		15	100	1		99	0.03	
QLD, Australia, 2003 (Baxter)	SL 240	7.5	103	1	3 – 6 tiller	88	0.04	030072-05⑨❷
		15	102	1		88	0.1	
	EO	7.5	99		3 – 6 tiller	88	0.06	
		15	102			88	0.07	
SA, Australia, 2003 (Yitpi)	SL 240	7.5	96	1	1st tiller	107	0.05	030072-07⑨❸
		15	100	1		107	0.2	
	EO	7.5	100	1	1st tiller	107	0.13	
		15	100	1		107	0.23	

③ Recoveries ranged 85 – 94% over concentrations 0.05 – 1 mg/kg (n = 3). ④ Moisture contents ranged 22.2 – 26%. ⑤ Moisture contents ranged 9.9 – 12%. ⑥ Moisture contents ranged 13.7 – 18.3%. ⑦ Moisture contents ranged 11.2 – 36.3 %. ⑧ Moisture contents ranged 7.1 – 8.8% for the SL formulation and 8.2 – 9.8% for the EO formulation. ⑨ Recoveries ranged 78 – 100% over concentrations 0.01 – 1 mg/kg (n = 7). ⑩ Moisture contents ranged 7.2 – 9.3%. ❶ Moisture contents ranged 24.1 – 33.4%. ❷ Moisture contents ranged 24.1 – 55%. ❸ Moisture contents ranged 8.1 – 9.6%.

Table 43. Aminopyralid residues in wheat forage from Europe and USA.

WHEAT FORAGE	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg) as received	
Bologna, Italy, 2003 (Soisson)	SG 75%	10	299	1	BBCH 30	0 14 28 64	0.4 0.06 0.05 0.05	GHE-P-10575① CEMS-2059A
Zaragoza, Spain, 2004 (Kilopondio)	SG 75%	10	299	1	BBCH 30	0 14 28 38	0.35 0.03 0.05 0.06	GHE-P-10689② CEMS-2245D
VA, USA, 2003 (Coker9835)	EO	10	135	1	BBCH 32	0 7 14 21 28	0.79 0.26 <u>0.19</u> 0.16 0.11	030042③
AR, USA, 2003 (Natchez)	EO	10	116	1	BBCH 41-45	0 7	<u>0.30</u> 0.07	
IN, USA, 2003 (Bravo)	EO	10	188	1	BBCH 31	0 7	<u>0.52</u> 0.13	
MN, USA, 2003 (Oxen)	EO	10	150	1	BBCH 37	0 7	<u>0.19</u> 0.17	
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	0 7	<u>0.29</u> 0.19	
ND, USA, 2003 (Oxen)	EO	10	151	1	BBCH 37	0 7	<u>0.32</u> 0.16	
NE, USA, 2003 (VNS HRW)	EO	10	187	1	BBCH 31	0 7	<u>0.54</u> 0.12	
OK, USA, 2003 (Coker9663)	EO	10	119	1	BBCH 33	0 7 14 21 28	0.57 0.12 <u>0.10</u> 0.10 0.12	
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	0 7 14 21 28	0.31 0.17 <u>0.07</u> 0.04 0.03	
	SL 240	9.7	152	1	BBCH 37	0 7 14 21 28	0.25 0.05 <u>0.11</u> 0.15 0.08	
	SL 247	10.4	152	1	BBCH 38	0 7 14 21 28	0.21 0.13 <u>0.16</u> 0.28 0.11	
ND, USA, 2003 (Oxen)	EO	10	152	1	BBCH 37	0 7	<u>0.30</u> 0.16	
	SL 240	9.7	152	1	BBCH 37	0 7	<u>0.16</u> 0.16	
	SL 247	10.4	152	1	BBCH 38	0 7	<u>0.21</u> 0.09	
ND, USA, 2003 (Alsen)	EO	10.4	147	1	BBCH 37	0 7	<u>0.41</u> 0.12	
	SL 240	10.5	146	1	BBCH 37	0 7	<u>0.43</u> 0.06	
	SL 247	10.5	146	1	BBCH 37	0 7	<u>0.38</u> 0.06	

WHEAT FORAGE Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
NE. USA, 2003 (Forge HRS)	EO	10	187	1	BBCH 31	0 7	0.49 0.11	
	SL 240	10	188	1	BBCH 31	0 7	0.37 0.05	
	SL 247	10	187	1	BBCH 31	0 7	0.63 0.08	
SD, USA, 2003 (Walworth)	EO	10	140	1	BBCH 30-31	0 7	0.53 0.13	
	SL 240	10	140	1	BBCH 30-31	0 7	0.41 0.05	
	SL 247	10	140	1	BBCH 30-31	0 7	0.40 0.05	
TX#1, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 39	0 7	0.37 0.12	
TX#2, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 37	0 7	0.26 0.03	
NM, USA, 2003 (Jagger)	EO	10	141	1	BBCH 37	0 7	0.45 0.11	
TX#4, USA, 2003 (TAM 200)	EO	10	177	1	BBCH 33	0 7	0.63 0.1	
TX#5, USA, 2003 (Jagger)	EO	10	174	1	BBCH 37	0 7	0.36 0.06	
KS, USA, 2003 (Ike)	EO	10	110	1	BBCH 30	0 7	0.67 0.05	
WA, USA, 2003 (Declo)	EO	10	141	1	BBCH 39	0 7	0.16 0.05	
SK, Canada, 2003 (ACEatonia)	EO	10	107	1	BBCH 30	0 7	0.11 0.09	
	SL 240	10	109	1	BBCH 30	0 7	0.72 0.11	
	SL 247	9.4	107	1	BBCH 30	0 7	0.85 0.22	
SK, Canada, 2003 (ACEatonia)	EO	10	109	1	BBCH 37	0 7	0.49 0.05	
	SL 240	10	111	1	BBCH 37	0 7	0.53 0.05	
	SL 247	10	113	1	BBCH 37	0 7	0.42 0.04	

① Recoveries 100 and 119% @ 0.01 and 0.1 mg/kg. ②Recoveries were 70% and 86% at 0.01 and 0.1 mg/kg, respectively. ③Recoveries ranged 75 – 105% over concentrations 0.05, 0.5 and 5 mg/kg (n = 34).

Table 44. Aminopyralid residues in wheat forage from Australia.

WHEAT FORAGE Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
WA, Australia, 2002 (Calingiri)	SL 240	10	100	1	5-6 leaf stage	0 1 3 7 14 28	3.81 2.64 1.21 0.71 0.42 0.37	020060-01①②
		15	100	1	5-6 leaf stage	0 1 3 7 14 28	5.26 4.80 1.35 1.33 0.79 0.62	

WHEAT FORAGE Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
		20	100	1	5-6 leaf stage	0 1 3 7 14 28	7.86 5.77 2.84 1.40 0.96 0.70	
SA, Australia, 2002 (Frame)	SL 240	10	99	1	Z15 (5-leaf)	0 1 3 7 14 28	3.81 2.82 ND *c 1.35* 0.48 0.32 0.11	020060-02①③
		15	90	1	Z15 (5-leaf)	0 1 3 7 14 28	4.33 4.41 1.01 0.50 0.37 0.11	
		20	90	1	Z15 (5-leaf)	0 1 3 7 14 28	7.43 4.89 2.47 0.83 0.47 0.20	
NSW, Australia, 2002 (Babbler)	SL 240	10	100	1	5 – 6 leaf	0 1 3 7 14 28	2.59 2.90 2.11 1.02 0.33 0.44	020060-05①④
		15	96	1	5 – 6 leaf	0 1 3 7 14 28	4.53 3.38 2.44 1.09 0.38 0.53	
		20	100	1	5 – 6 leaf	0 1 3 7 14 28	7.18 4.56 3.72 1.57 0.36 0.68	
QLD, Australia, 2002 (Petrel)	SL 240	10	102	1	4 – 6 leaf	0 1 3 7 14 28	4.50 3.02 1.42 0.77 0.49 0.34	020060-08①⑤
		15	99	1	4 – 6 leaf	0 1 3 7 14 28	9.57 5.68 1.93 1.27 0.78 0.43	
		20	101	1	4 – 6 leaf	0 1 3 7 14 28	13.3 10 3.22 1.88 1.08 0.55	

WHEAT FORAGE	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg) dry weight	
NSW, Australia, 2003 (Wollaroi)	SL 240	7.5	101	1	6-leaf	0 1 3 6 14 28	1.58 1.26 0.95 <u>0.16</u> 0.08 0.14	030071-01⑥⑦
		15	101	1	6-leaf	0 1 3 6 14 28	2.38 2.99 2.29 0.45 0.31 0.26	
	EO	7.5	101	1	6-leaf	0 1 3 6 14 28	1.63 0.89 0.72 <u>0.45</u> 0.35 0.22	
		15	101	1	6-leaf	0 1 3 6 14 28	2.66 1.44 0.88 0.99 0.56 0.33	

①Recoveries ranged 87 – 106% over concentrations 0.01 – 5 mg/kg (n = 17). ②Moisture contents ranged 82.2–86.6%. ③Moisture contents ranged 75.1 – 85.6%. ④Moisture contents ranged 77.1 – 81.4%. ⑤Moisture contents ranged 73.5 – 88.5%. ⑥Moisture contents ranged 70.6 – 84.1%. ⑦ Recoveries ranged 85 – 124% over concentrations 0.01 – 1 mg/kg (n = 15).

Table 45. Aminopyralid residues in wheat hay from USA; wheat hay was allowed to dry for 2 to 7 days to obtain proper moisture for hay, prior to freezing for analysis.

WHEAT HAY	Application					PHI	Residues	Ref./Study No.
Country, Year (variety)	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing	(days)	(mg/kg) as received	
VA, USA, 2003 (Coker9835)	EO	10	135	1	BBCH 32	0 7 14 21 28	1.99 0.99 <u>0.61</u> 0.45 0.41	030042①
AR, USA, 2003 (Natchez)	EO	10	116	1	BBCH 41-45	0 7	<u>0.76</u> 0.28	
IN, USA, 2003 (Bravo)	EO	10	188	1	BBCH 31	0 7	<u>1.31</u> 0.33	
MN, USA, 2003 (Oxen)	EO	10	150	1	BBCH 37	0 7	<u>0.45</u> 0.39	
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	0 7	<u>0.69</u> 0.56	
ND, USA, 2003 (Oxen)	EO	10	151	1	BBCH 37	0 7	<u>0.69</u> 0.46	
NE, USA, 2003 (VNS HRW)	EO	10	187	1	BBCH 31	0 7	<u>0.98</u> 0.23	
OK, USA, 2003 (Coker9663)	EO	10	119	1	BBCH 33	0 7 14 21 28	1.08 0.29 <u>0.34</u> 0.24 0.22	

WHEAT HAY Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
SD, USA, 2003 (Marshall)	EO	10	152	1	BBCH 37	0 7 14 21 28	0.86 0.45 c *0.017* <u>0.25</u> 0.044 0.044	
	SL 240	9.7	152	1	BBCH 37	0 7 14 21 28	0.37 0.24 *c 0.017* <u>0.26</u> 0.18 0.06	
	SL 247	10.4	152	1	BBCH 38	0 7 14 21 28	0.35 0.27 *c 0.017* <u>0.21</u> 0.24 0.06	
ND, USA, 2003 (Oxen)	EO	10	152	1	BBCH 37	0 7	<u>0.76</u> 0.32	
	SL 240	9.7	152	1	BBCH 37	0 7	<u>0.34</u> 0.36	
	SL 247	10.4	152	1	BBCH 38	0 7	<u>0.54</u> < 0.01	
ND, USA, 2003 (Alsen)	EO	10.4	147	1	BBCH 37	0 7	<u>1.67</u> 0.28	
	SL 240	10.5	146	1	BBCH 37	0 7	<u>1.32</u> 0.19	
	SL 247	10.5	146	1	BBCH 37	0 7	<u>0.87</u> 0.16	
NE. USA, 2003 (Forge HRS)	EO	10	187	1	BBCH 31	0 7	<u>1.23</u> 0.37	
	SL 240	10	188	1	BBCH 31	0 7	<u>0.71</u> 0.17	
	SL 247	10	187	1	BBCH 31	0 7	<u>1.24</u> 0.23	
SD, USA, 2003 (Walworth)	EO	10	140	1	BBCH 30-31	0 7	<u>1.88</u> 0.44	
	SL 240	10	140	1	BBCH 30-31	0 7	<u>1.38</u> 0.19	
	SL 247	10	140	1	BBCH 30-31	0 7	<u>1.33</u> 0.16	
TX#1, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 39	0 7	<u>0.98</u> 0.33	
TX#2, USA, 2003 (TAM 105)	EO	10	143	1	BBCH 37	0 7	<u>0.83</u> 0.06	
NM, USA, 2003 (Jagger)	EO	10	141	1	BBCH 37	0 7	<u>1.02</u> 0.32	
TX#4, USA, 2003 (TAM 200)	EO	10	177	1	BBCH 33	0 7	<u>0.54</u> 0.19	
TX#5, USA, 2003 (Jagger)	EO	10	174	1	BBCH 37	0 7	<u>0.43</u> 0.14	
KS, USA, 2003 (Ike)	EO	10	110	1	BBCH 30	0 7	<u>1.46</u> 0.12	
WA, USA, 2003 (Declo)	EO	10	141	1	BBCH 39	0 7	<u>0.38</u> 0.18	
SK, Canada, 2003 (ACEatonia)	EO	10	107	1	BBCH 30	0 7	<u>0.37</u> 0.13	
	SL 240	10	109	1	BBCH 30	0 7	<u>2.32</u> 0.62	
	SL 247	9.4	107	1	BBCH 30	0 7	<u>2.36</u> 0.64	

WHEAT HAY Country, Year (variety)	Application					PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.	Timing			
SK, Canada, 2003 (ACEatonia)	EO	10	109	1	BBCH 37	0 7	1.28 0.13	
	SL 240	10	111	1	BBCH 37	0 7	1.48 0.08	
	SL 247	10	113	1	BBCH 37	0 7	1.46 0.12	

① Recoveries ranged 70 – 107% over concentrations 0.05, 0.5 and 5 mg/kg (n = 35).

Pastures

Hay samples in the European trials were cut at the PHI indicated and left to dry for 3 to 5 days prior to analysis. In the US and Canadian trials, hay samples were dried for 2 to 5 days after cutting at the PHI. All results are expressed on an as received basis. Samples for silage were cut at the PHI indicated in the tables below and left to silage prior to collection for analysis at 115 days after application.

Table 46. Aminopyralid residues in pastures and hay from trials conducted in Europe and USA.

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
Mogi Mirim, Brazil, 2002 (*Brachiaria decumbens*)	SL 40	120	250	1	Grass	0 7 14 21 28	1.9, 1 2.1, 1.7 1.7, 2.7 1.6, 2.8 2.1, 1.2	020131①②
		240	250	1	Grass	0 7 14 21 28	4.9, 5.6 6.5, 6 8.6, 6.4 8, 6.4 7.2, 6.5	
Cedral, Brazil, 2002 (*Brachiaria brizantha*)	SL 40	120 240	250	1 1	Grass	0 0	11.2, 12 15.5, 15.6	
Londrina, Brazil, 2002 (*panicum maximum*)	SL 40	120 240	200	1 1	Grass	0 0	12.2, 13.5 11.6, 11.8	
Mogi Mirim, Brazil, 2002 (*Brachiaria decumbens*)	EO 40	100	250	1	Grass	0 7 14 21 28	2.1, 0.6 2.8, 2.8 1.8, 2.6 2.3, 2.6 1.7, 3	020132①③
		200	250	1	Grass	0 7 14 21 28	0.2, 1 4.2, 1.4 4.3, 4.3 8.2, 2.5 3.4, 3.5	
Cedral, Brazil, 2002 (*Brachiaria brizantha*)	EO 40	100 200	250	1 1	Grass	0 0	8.9, 3.8 12.7, 26.6	
Londrina, Brazil, 2002 (*panicum maximum*)	EO 40	100 200	200	1 1	Grass	0 0	2.4, 4.8 20.2, 16.3	
Derbyshire, UK, 2002 (Italian and periennial Ryegrass ley)	ME 30 #1	60	301	1	Grass	0	4.22	GHE-P-10448 295/155/1
Lamstedt, Germany, 2002 (*Lolium perenne*)	ME 30 #1	65	327	1	Grass	0	4	295/155/2
Derbyshire, UK, 2002 (Italian ryegrass)	ME 30 #2	60	299	1	Grass Hay	0 3	1.7 1.18	GHE-P-10449④ 295/153/9

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
Lamstedt, Germany, 2002 (*Lolium perenne*)	ME 30 #2	63	313	1	Grass Hay	0 3	1.62 1.42	295/153/2
Emilia Romagna, Italy 2002 (*Lolium multiflorum*, *Avene spp*)	ME 30 #2	60	302	1	Hay	3	4	295/153/3
Noilhan, France, 2002 (*Dactylis spp*)	ME 30 #2	62	310	1	Hay	3	8	295/153/4
Derbyshire, UK, 2002 (Long term ryegrass ley)	ME 30 #2	60	299	1	Grass	0 1 3 7 14 21	3.15 2.56 3.2 <u>1.53</u> 1.46 1.93	295/153/5
Lower Saxony, Germany 2002 (*Lolium spp*)	ME 30 #2	60	299	1	Grass	0 1 4 7 14 21	2.95 1.97 1.31 <u>1.81</u> 0.91 0.71	295/153/6
Tarn-et-Garonne, France, 2002 (*Vicia spp Trifolium spp.)*	ME 30 #2	61	303	1	Grass	0 1 3 7 14 21	3.92 2.15 0.96 <u>0.84</u> 0.55 0.81	295/153/7
Montardon, France, 2002 (*Festuca arundinacea*)	ME 30 #2	61	255	1	Grass	0 1 3 7 15 21	4.25 3.04 2.65 <u>2.18</u> 1.38 1.10	295/153/8
Neidersachsen, Germany, 2003 (*Lolium*)	ME 30 #1	66	330	1	Grass Hay	0 3	13.65 8.5	GHE-P-10578⑤ CEMS-2065A
Sheffield, UK, 2003 (Perennial ryegrass)	ME 30 #1	58	289	1	Grass Hay	0 3	9.47 6.59	CEMS-2065B
Rabastens, France, 2003 (*Festuca, Lolium spp*)	ME 30 #1	60	301	1	Grass Hay	0 3	4.55 1.68	CEMS-2065C
Pastriz, Spain, 2003 (Fuego)	ME 30 #1	60	302	1	Grass Hay	0 3	7.06 8.85	CEMS-2065D
Chesterfield, UK, 2003 (Ryegrass, fescue and pasture mixture)	ME 30 #1	60	300	1	Grass Silage	0 1 3 7 14 21 3	2 1.83 1.69 <u>1.03</u> 0.63 0.41 1.45	GHE-P-10579 CEMS-2066A⑥
Maine-et-Loire, France, 2003 (*Festuca spp*)	ME 30 #1	60	302	1	Grass	0 1 3 7 14 21	8.86 5 3.21 <u>2.97</u> 0.79 0.4	CEMS-2066B
Maine-et-Loire, France, 2003 (*Dactyle spp*)	ME 30 #1	58	292	1	Grass Hay	0 0	5.49 13.08	CEMS-2066C
Niedersachsen, Germany, 2003 (*Lolium perenne*)	ME 30 #1	63	210	1	Grass Hay	0 3	3.22 2.02	CEMS-2066D

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
Montardon, France, 2003 (*Festuca spp*.)	ME 30 #1	61	305	1	Grass	0	6.48	GHE-P-10580⑦
						1	3.56	CEMS-2067A
						3	3.75	
						7	1.96	
						14	2.11	
						21	1.37	
Olaeta-Aramaio, Spain, 2003 (Ryegrass Barsilo)	ME 30 #1	61	306	1	Grass	0	2.34	CEMS-2067B
						1	2.4	
						3	1.91	
						7	1.32	
						14	1.07	
						21	0.95	
Tournan, France, 2003 (Italian ryegrass)	ME 30 #1	55	273	1	Grass	0	1.65	CEMS-2067C
					Hay	3	3.37	
Bologna, Italy, 2003 (*Festuca spp, Dacus spp, Digitaria spp*)	ME 30 #1	60	302	1	Grass	0	7.24	CEMS-2067D
					Hay	3	5.79	
AB, Canada, 2002 (Brome fescue mix)	SL 240	118	148	1	Grass	0	13.7	020018①⑧
						3	5.2	
						7	4.1	
						14	1.9	
						21	2	
						28	2.2	
					Hay	0	15.9	
						14	3.8	
						21	4.2	
						28	4.6	
	SL 240*	118	149	1	Grass	0	13.2	* +2,4-D tank mix
						3	6.9	
						7	5.9	
						14	2.3	
						21	1.6	
						28	2.1	
					Hay	0	25.1	
						14	4.7	
						21	3.3	
						28	5.5	
AB, Canada, 2002 (Fescue Timothy mix)	SL 240	116	97	1	Grass	0	14.6	
						3	6.7	
						7	3.8	
						14	2.3	
						22	2.6	
						28	1.9	
					Hay	0	16.8	
						14	3.2	
						22	4.5	
						28	3.7	
	S 240*	125	104	1	Grass	0	13.8	* +2,4-D tank mix
						3	6.3	
						7	4.8	
						14	1.7	
						22	2.1	
						28	1.9	
					Hay	0	21.6	
						14	3	
						22	3.3	
						28	3.4	
SK, Canada, 2002 (Brome grass mix)	SL 240	119	150	1	Grass	0	10.7	
						7	1.5	
						14	1.4	
					Hay	0	26.2	
						14	2.9	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
						22	2.8	
AB, Canada, 2002 (Fescue Brome mix)	SL 240	119	149	1	Grass	0	12.2	
						7	4.4	
						14	2.6	
					Hay	0	22.2	
						14	5.1	
						21	5.1	
AB, Canada, 2002 (Orchard Fescue Timothy mix)	SL 240	121	101	1	Grass	0	9.1	
						7	4.6	
						13	2.9	
					Hay	0	15.1	
						13	3.9	
						21	5.3	
MB, Canada, 2002 (Brome grass)	SL 240	121	101	1	Grass	0	12.7	
						7	3.5	
						14	2.3	
					Hay	0	55	
						14	6.6	
						20	4.2	
SK, Canada, 2003 (Native grasses)	SL 240	120	150	1	Grass	0	12.8	
						8	3.8	
						14	3.7	
					Hay	0	30	
						14	9.2	
						21	7.8	
VA, USA, 2002 (Fescue/orchard grass)	SL 240	120	140	1	Grass	0	4.8	
						3	4.6	
						7	3.6	
						14	2.8	
						21	1.8	
						28	2.3	
					Hay	0	17.9	
						14	8.6	
						21	7.8	
						28	6.4	
	SL 240*	120	140	1	Grass	0	8.7	
						3	6.4	
						7	4.5	
						14	5.8	
						21	3.4	
						28	3.5	
					Hay	0	26.3	
						14	11	
						21	16.6	
						28	4.8	
WA, USA, 2002 (Fescue)	SL 240	120	140	1	Grass	0	4.8	
						3	1.1	
						7	1.2	
						14	1.1	
						21	1.1	
						28	1	
					Hay	0	10.6	
						14	3.1	
						21	3.2	
						28	3	
	SL 240*	120	140	1	Grass	0	6.1	
						3	1.3	
						7	1.8	
						14	1.6	
						21	1.2	
						28	1	
					Hay	0	12.4	
						14	3.8	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
						21 28	4.1 3	
GA, USA, 2002 (Bermuda grass)	SL 240	120	164	1	Grass Hay	0 7 14 0 14 21	12.5 5.9 2 25.8 8.8 5.6	
ID, USA, 2002 (Mixture)	SL 240	120	163	1	Grass Hay	0 7 14 0 14 20	6.9 0.7 0.9 18.2 2.4 2.3	
MS, USA, 2002 (Bermuda grass)	SL 240	125	148	1	Grass Hay	0 7 14 0 14 21	10 2.2 3 18.6 7.1 3.6	
MT-1, USA, 2002 (Crested wheat)	SL 240	122	190	1	Grass Hay	0 7 14 0 14 21	11.1 7.1 2.4 15.9 5 4.4	
MT-2, USA, 2002 (Orchard grass)	SL 240	121	188	1	Grass Hay	0 6 13 0 13 20	9.4 1.5 1.3 15.7 2.2 1.3	
ND, USA, 2002 (Brome grass)	SL 240	120	151	1	Grass Hay	0 7 14 0 14 22	11.2 4.4 1.4 18.1 3.4 1	
NY, USA, 2002 (Orchard grass)	SL 240	115	181	1	Grass Hay	0 7 14 0 14 21	4.6 3 2.8 10.9 10 7.8	
OH, USA, 2002 (Fescue/orchard grass)	SL 240	123	175	1	Grass Hay	0 7 15 0 15 21	5 2. 2.1 16 10.4 5.6	
PA, USA, 2002 (Tall fescue)	SL 240	125	157	1	Grass Hay	0 7 14 0 14 21	10.1 2 2.8 32.2 5.9 5.9	
TX, USA, 2002 (Tall fescue)	SL 240	121	171	1	Grass Hay	0 7 14 0 14 21	16 1.5 2 18.2 2.1 3.9	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) as received	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
WI, USA, 2002 (Reed canary grass)	SL 240	121	176	1	Grass	0	6.5	
						7	3.7	
						14	2	
					Hay	0	20.3	
						14	10	
						21	5.9	

① Joint oil or adjuvant added to sprays. ②Recoveries ranged 78 – 108% over concentrations 1, 50, 100 and 200 mg/kg. ③Recoveries ranged 78 – 107% over concentrations 1, 50 and 100 mg/kg. ④ Recoveries ranged 84 – 122% over concentrations 0.01, 1 and 5 mg/kg in pastures and 78% and 87% at 0.01 mg/kg and 5 mg/kg in hay, respectively. ⑤ Recoveries were 77 and 112% at 0.01 and 0.1 mg/kg in grass and 72% and 93% at 0.01 and 0.1 mg/kg in hay. ⑥ Recoveries were 84% and 70% at 0.01 mg/kg and 93% and 113% at 0.1 mg/kg in grass, 75% at 0.01 mg/kg and 88% at 0.1 mg/kg in hay and 95% at 0.01 mg/kg and 90% at 0.1 mg/kg in silage. ⑦ Recoveries were 84% and 94% at 0.01 mg/kg and 0.1 mg/kg in grass respectively; 105% and 93% at 0.01 mg/kg and 0.1 mg/kg in hay, respectively. ⑧Mean recoveries ranged 79 – 92% over concentrations 0.01, 0.1, 20, 30 and 60 mg/kg in forage; mean recoveries ranged 84 – 100% over concentrations 0.01, 0.02, 0.1, 1, 20, 30 and 60 mg/kg.

Table 47. Aminopyralid residues in pastures from trials conducted in Australia and New Zealand.

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
NSW, Australia, 2004 (Native pasture)	SL 240	270	245	1	Forage	0	37.1	030103-01①②
						3	18.2	
						7	14.5	
						14	6.1	
						30	6.9	
						56	2.6	
		540	253	1	Forage	0	86.5	
						3	30	
						7	28.2	
						14	12.5	
						30	12.8	
						56	9.6	
NSW, Australia, 2004 (Native pasture)	SL 240	270	253	1	Forage	0	52.5	030103-02①③
						3	8.4	
						7	7.9	
						14	4.3	
						30	3.4	
						56	3.2	
		540	253	1	Forage	0	76.7	
						3	12.4	
						7	15.4	
						14	9.9	
						30	9.3	
						56	7.3	
VIC, Australia, 2004 (Kangaroo grass)	SL 240	270	238	1	Forage	0	103	030103-03①④
						3	90.6	
						7	13.8	
						14	13.3	
						28	11.5	
						56	1.2	
		540	241	1	Forage	0	212	
						3	26	
						7	28.7	
						14	25.7	
						28	25.1	
						56	2.5	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
QLD, Australia, 2004 (Kikuyu grass)	SL 240	210	240	1	Forage	0 3 7 14 28 56	9 5.3 4.4 1.4 1.3 0.85	030102-01❷❸
		420	253	1	Forage	0 3 7 14 28 56	19 5.3 7.7 6.4 2.3 2.4	
	EO	210	243	1	Forage	0 3 7 14 28 56	0.7 4.6 4.6 3.3 2.1 0.7	
QLD, Australia, 2004 (Qld blue grass)	SL 240	210	241	1	Forage	0 3 7 14 28 56	19 5.5 8.3 6.6 3.1 2.4	030102-02❷❹
		420	253	1	Forage	0 3 7 14 28 56	36 11 9.1 2.6 4.8 2.2	
	EO	210	255	1	Forage	0 3 7 14 28 56	12 5.3 4.4 5.5 2.3 2.2	
QLD, Australia, 2004 (Native pasture)	SL 240	210	249	1	Forage	0 3 7 14 28 56	12 1.5 1.5 0.61 0.44 0.46	030102-03❷❺
		420	251	1	Forage	0 3 7 14 28 56	21 2.8 2.6 1.8 1.1 0.9	
	EO	210	260	1	Forage	0 3 7 14 28 56	12 3.3 3.3 1.7 1.3 1.6	
Leeston, NZ, 2003 (Perennial ryegrass & clover) (5 cm height)	SL 240	60	192	1	Forage	0 1 3 7 14 28	38.8 22.4 11.3 9.6 10.9 7.4	030028-01⑤⑥

PASTURES/HAY Country, Year (variety)	Application Form.	Rate (g ae/ha)	Water (L/ha)	No.	Sample	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
		120	198	1	Forage	0 1 3 7 14 28	96.6 56.9 28.8 30.1 25.5 15.7	
		300	390	1	Forage	0 1 3 7 14 28	245 150 40 53 64 41	
		600	381	1	Forage	0 1 3 7 14 28	482 294 139 125 4.6 77	
Leeston, NZ, 2003 (Perennial ryegrass & clover) (15 cm height)	SL 240	60	182	1	Forage	0 1 3 7 14 28	11.3 21.9 15 11.7 12.8 6.5	030028-02⑤⑦
		120	191	1	Forage	0 1 3 7 14 28	– 47 3.1 28 24 17	
		300	371	1	Forage	0 1 3 7 14 28	221 24 75 80 51 42	
		600	375	1	Forage	0 1 3 7 14 28	430 268 156 139 84 75	
Oakura, NZ, 2003 (Ryegrass and white clover)	SL 240	60	156	1	Forage	0 1 3 7 14 28	48 29 11 10 7 5	030028-03⑤⑧
		120	162	1	Forage	0 1 3 7 14 28	75 60 20 19 17 11	
		300	299	1	Forage	0 1 3 7 14 28	238 111 51 55 51 27	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
		600	299	1	Forage	0 1 3 7 14 28	402 244 71 87 89 7	
Okato, NZ, 2003 (Ryegrass)	SL 240	60	157	1	Forage	0 1 3 7 14 28	42.4 1.5 13.2 9.5 8.7 2.3	030028-04⑤⑨
		120	154	1	Forage	0 1 3 7 14 28	77 54 20 56 13 8	
		300	309	1	Forage	0 1 3 7 14 28	141 87 76 46 41 23	
		600	299	1	Forage	0 1 3 7 14 28	5.6 324 125 82 71 45	
Dunsandel, Canterbury, NZ, 2002 (Browntop, white clover	SL 240	60	218	1	Forage	0 7 14 28	6.2 2.1 1.4 1.7	020049-01⑩❶
		120	204	1	Forage	0 7 14 28	11 3.3 3.3 8.9	
		240	204		Forage	0 7 14 28	24 7.3 7 4.5	
		480	189		Forage	0 7 14 28	37 14.5 15 12	
Leeston, NZ, 2002 (Perennial ryegrass and white clover)	SL 240	60	204	1	Forage	0 7 14 28	7.3 1.5 0.8 < 0.01	020049-02⑩❶
		120	218	1	Forage	0 7 14 28	13 2.9 2 1.2	
		240	204	1	Forage	0 7 14 28	31 5.3 4.1 1.7	

PASTURES/HAY Country, Year (variety)	Application				Sample	PHI (days)	Residues (mg/kg) dry weight	Ref./Study No.
	Form.	Rate (g ae/ha)	Water (L/ha)	No.				
		480	204	1	Forage	0 7 14 28	64 14 12 4.7	

①Recoveries ranged 77 – 137% over concentrations 0.01, 1 and 10 mg/kg. ②Moisture contents ranged 41 – 63%. ③Moisture contents ranged 33 – 62%. ④Moisture contents ranged 8 – 28%. ⑤Recoveries ranged 40 – 166% at 0.01 mg/kg; recoveries ranged 67 – 103% over concentrations 0.1, 1, 10 and 100 mg/kg. ⑥Moisture contents ranged 80 – 87%. ⑦Moisture contents ranged 82 – 89%. ⑧Moisture contents ranged 85 – 90%. ⑨Moisture contents ranged 83 – 90%. ⑩Recoveries ranged 79 - 129% at concentrations of 1, 10 and 100 mg/kg. ⓫Moisture contents ranged 71 – 77%. ⓬Moisture contents ranged 78 – 83%. ⓭ Recoveries ranged 73 -97% over concentrations of 1 and 10 mg/kg. ⓮Moisture contents ranged 70 – 83%. ⓯ Moisture contents ranged 45 –70%. ⓰Moisture contents ranged 41 – 75%.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

As part of a supervised field trial study (Roberts, Schelle and Knuteson, 2004), wheat crops at a site in Oklahoma were treated at 50 g ae/ha (equivalent to 5× the US GAP) at crop stage BBCH 33, and bulk grain was collected at 69 days after application for processing into various wheat fractions (Figure 5).

Method GRM 02.31 was used to determine aminopyralid residues in whole grain and wheat fractions. A summary of the results is shown below.

Table 48. Aminopyralid residues in processed wheat fractions.

Application rate	Sample/Fraction	Aminopyralid residues (mg/kg)	Processing Factor (PF)
50 g ae/ha	Whole (bulked) wheat	0.055	–
	Bran	0.133 *c 0.016*	2.4
	Flour	<LOQ	0.2
	Shorts①	0.067	1.2
	Middlings②	0.032	0.58
	Germ	0.02	0.36
	Aspirated grain fractions	0.338 *c 0.03*	6.1

① Low grade mill product containing principally germ and fine bran particles.

② Also known as semolina.

Recoveries in various wheat fractions are shown below.

Table 49. Recoveries in various wheat fractions.

Sample matrix	% Recovery at Fortification Levels	
	0.05 mg/kg	2.5 mg/kg
Wheat grain	96, 102	
Aspirated grain fractions	104	102
Bran	109	102
Middlings	115	104
Shorts	127	109
Flour	112	109
Germ	97	104

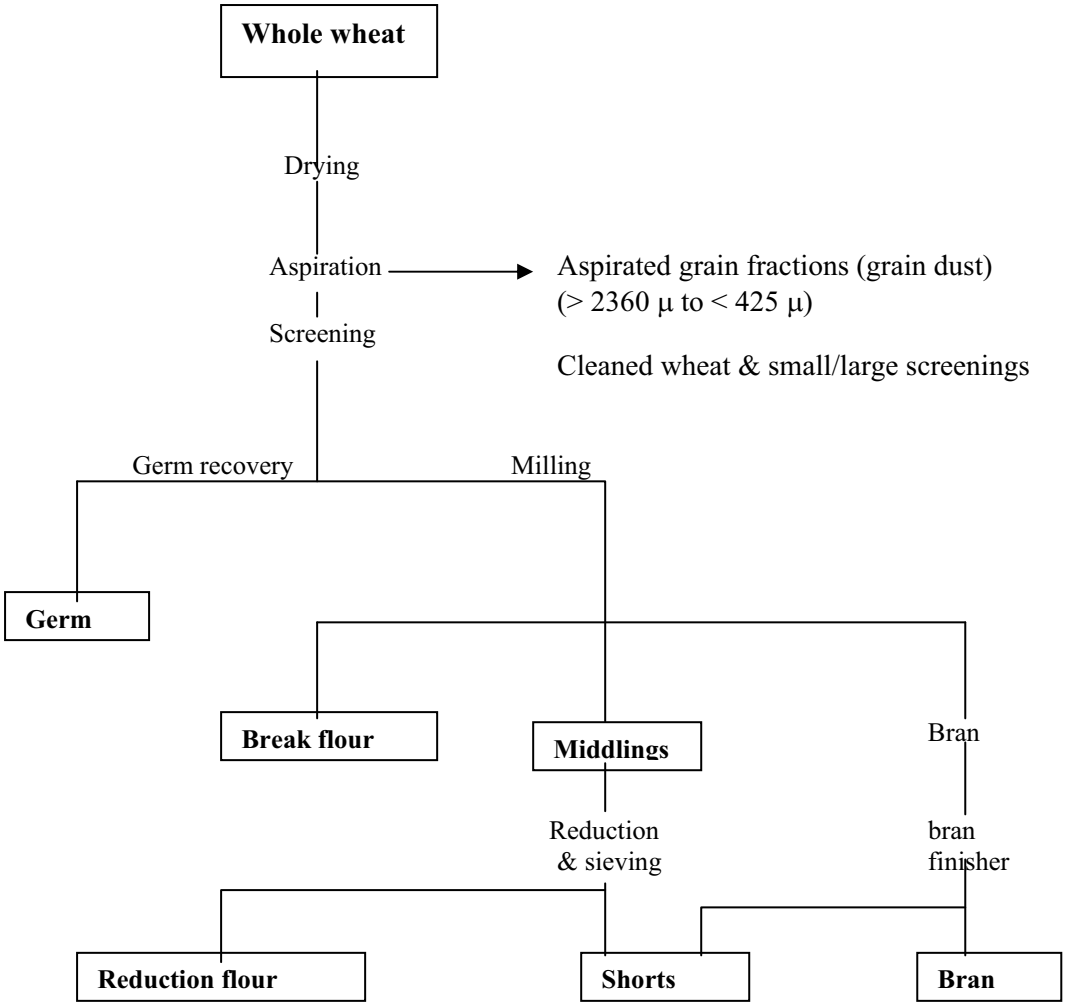


Figure 5. Schematic of wheat grain processing as described by Roberts, Schelle and Knuteson, 2004.

Residues in Animal Commodities

Farm Animal (Livestock) Feeding Studies

Lactating Cow Feeding Study

The meeting received a lactating dairy cow feeding study, which provided information on likely residues resulting in animal tissues and milk from residues in the animal diet (Rosser, Rutherford and McFarlane, 2004).

In this study, Holstein dairy cows were divided into a control group I and four treatment groups (T-I–T-IV). The four treatment groups corresponded to nominal doses of 0.5×, 1×, 3× and 10×, where 1× was 64.5 ppm in the feed. Summaries of bodyweight ranges, feed intakes and actual doses are shown in Table 54. There were four animals in the control group (C-1–C-4) and three animals per dose group for T-I to T-III (0.5× to 10×). In the T-IV (or 10×) group, an additional six animals were included to allow for a withdrawal or depuration phase following the 28 days dosing period; two animals included for slaughter at 3, 7 and 14 days after dosing had ceased. Bodyweights in the control group ranged 502 – 590 kg at the commencement of the study and 501 – 600 kg on day 28 of the study.

Table 50. Summary of dosing regime, animal bodyweights and feed consumption.

Treatment Group	Animal No.	Mean mg aminopyralid /day	Mean Feed consumption① (kg)	Dose in the feed (ppm)②	Bodyweight (kg)③	Dose (mg/kg bw)④
T-I-1	2	466.3	17.2	27.1	522	0.89
T-I-2	5	567.5	17.1	33.2	608	0.93
T-I-3	14	821.5	22.2	37	565	1.46
Mean		*618.4*	*18.8*	*32.8*	*565*	*1.10*
T-II-1	20	1333.6	22.8	58.5	499	2.67
T-II-2	11	1577.1	23.3	67.7	656	2.40
T-II-3	17	1312.7	19.4	67.7	550	2.38
Mean		*1407.8*	*21.8*	*64.5*	*569*	*2.48*
T-III-1	26	3482.8	19.5	178.6	553	6.29
T-III-2	7	3334.4	19.3	172.8	592	5.63
T-III-3	15	4365.4	22.8	191.5	602	7.25
Mean		*3727.7*	*20.5*	*181.5*	*583*	*6.40*
T-IV-1	24	14028.9	21.6	649.5	513	27.34
T-IV-2	10	15007.1	21.6	694.8	570	26.35
T-IV-3	23	14550.3	20.8	699.5	612	23.78
T-IV-4	13	11747.3	18.4	638.4	547	21.49
T-IV-5	16	12991.8	21.1	615.7	714	18.19
T-IV-6	21	12725.8	19.0	669.8	565	22.52
T-IV-7	1	14870.6	23.2	641.0	586	25.36
T-IV-8	22	14737.6	23.2	635.2	579	25.45
T-IV-9	12	12227.2	21.7	563.5	595	20.54
Mean		*13654.1*	*21.2*	*644.7*	*587*	*23.27*

① Mean daily feed consumption on a dry weight basis for the 4 weeks during dosing.

② Dose of aminopyralid expressed as mg aminopyralid per kg feed dry weight consumed.

③ Mean of bodyweights recorded on days 8, 15, 22 and 28 of the study.

④ Dose of aminopyralid expressed as mg aminopyralid per kg bodyweight.

The actual mean dose levels were 32.8, 64.5, 181.5 and 644.7 ppm in the feed.

Milk from each cow was collected at morning and afternoon milkings (AM and PM) and both milkings were pooled to form a single whole milk sample for each day for each animal. Samples of whole milk were collected for analysis the day before dosing began and during the first 7 days of the study, then every third day until the end of the dosing period (study days 10, 13, 16, 19, 22, 25 and 28). In addition, samples of whole milk were collected from each cow in the depuration phase of the study from the time that dosing has ceased until slaughter. On days 13 and 28 of the study, additional samples of pooled milk were collected and separated into cream and skim milk from 3 cows in the control group, three cows in the 1× group and three cows in 10× group that were not used in the depuration phase of the study.

Cows in the control group and groups T-I, T-II and T-III and three animals in group T-IV were slaughtered within 24 hours after receiving the final dose (day 29). The remaining animals in group T-IV were slaughtered on days 32, 36 and 43 or 3, 7 and 14 days after dosing has ceased. Samples of liver, kidney, muscle (equal portions flank, loin and leg composited) and fat (equal portions perirenal, abdominal and subcutaneous composited) were collected from each animal. All samples (tissues and milk) were stored frozen at -17°C prior to analysis. All samples were analysed within 1 month of sampling (4 to 26 days); control samples were analysed after 17 to 33 days after storage.

Residues in liver, kidney, muscle, fat, whole milk, skim milk and cream were determined using method GRM 03.18. Residue levels in milk and tissues and concurrent recoveries are shown in Tables 55, 56 and 57.

Table 51. Recovery of aminopyralid in milk, skim milk, cream and edible tissues.

Matrix	Fortification level (mg/kg)	Number of samples (n)	Recovery Range (%)	Mean Recovery (%)
Milk	0.01	34	74 – 116	89 ± 10
	0.1	15	83 – 103	93 ± 6
	1	8	77 – 92	86 ± 5
Mean	0.01 – 1	57	74 – 116	90 ± 9
Skim milk	0.01	4	80 – 91	85 ± 5
	0.1	2	77, 89	83 ± 8
Mean	0.01 – 0.1	6	77 – 91	84 ± 6
Cream	0.01	4	80 – 90	85 ± 5
	0.1	2	82, 92	87 ± 7
Mean	0.01 – 0.1	6	80 – 92	86 ± 5
Fat	0.01	8	70 – 93	80 ± 7
	0.1	3	85 – 91	88 ± 3
	1	2	91, 92	91 ± 1
Mean	0.01 – 1	13	70 – 93	84 ± 8
Muscle	0.01	6	68 – 83	78 ± 5
	0.1	3	86 – 89	87 1
	1	2	82, 92	87 ± 7
Mean	0.01 – 1	11	68 – 92	82 ± 7
Liver	0.01	4	73 – 89	81 ± 7
	0.1	1	87	87
	1	2	93, 94	94 ± 1
Mean	0.01 – 1	7	73 – 94	85 ± 8
Kidney	0.01	6	81 – 102	92 ± 8
	0.1	1	83	83
	1	2	89	89
	3	2	92, 99	96 ± 5
Mean	0.01 – 3	11	81 – 102	92 ± 7

Table 52: Aminopyralid residues in skim milk and cream for dose levels T-II and T-IV.

Study Day	Skim milk		Cream	
	T-II (64.5 ppm)	T-IV (644.7 ppm)	T-II (64.5 ppm)	T-IV (644.7 ppm)
13	< 0.01 (2), 0.015	0.058, 0.054, 0.068	< 0.01 (2), 0.012	0.052, 0.046, 0.059
28	< 0.01 (3)	0.043, 0.048, 0.074	< 0.01 (3)	0.037, 0.043, 0.065

Following dosing at 32.8 ppm in the feed, aminopyralid residues in milk were < 0.01 mg/kg over the 28 days of dosing. Residues reached plateau within 2 to 3 days of dosing. Residues in milk ranged < 0.01–0.024 mg/kg and 0.011–0.028 mg/kg following dosing at 64.5 and 181.5 ppm, respectively. Aminopyralid residues ranged 0.023–0.127 mg/kg following dosing at 644.7 ppm. There was little difference between the residues found in skim milk and cream indicating that aminopyralid is not fat soluble.

Residues had declined to < 0.01 mg/kg within 2 days of withdrawal from dosing at the highest level of 644.7 ppm.

Table 53. Aminopyralid residues in tissues at the end of the dosing period.

Sample/Tissue	Aminopyralid residues in tissues at day 29 at each dose level (mg/kg)			
	T-I (32.8 ppm)	T-II (64.5 ppm)	T-III (181.5 ppm)	T-IV (644.7 ppm)
Muscle	< 0.01 (3)	< 0.01 (3)	0.01, 0.017, 0.046	0.012, 0.021, 0.029
Fat	< 0.01 (2), 0.011	< 0.01 (2), 0.013	0.016, 0.073, 0.095	0.025, 0.039, 0.042
Liver	< 0.01 (3)	< 0.01 (2), 0.014	0.026, 0.033, 0.054	0.059, 0.064, 0.116
Kidney	0.043, 0.052, 0.102	0.099, 0.139, 0.202	0.456, 0.507, 1.537	0.902, 1.242, 2.549

Highest residues were found in kidney at all dose levels; the magnitude of residues were muscle < fat < liver < kidney. The depuration data show that following withdrawal from dosing for 3 days, residues in all tissues, including kidney, decline to < 0.01 mg/kg.

Table 54. Aminopyralid residues in tissues following depuration up to 14 days after dosing.

Aminopyralid residues in tissues following depuration (mg/kg)		
Sample/Tissue	Days of study	T-IV (644.7 ppm)
Muscle	29 (0)	0.012, 0.021, 0.029
	32 (+3)	< 0.01, < 0.01
	36 (+7)	< 0.01, < 0.01
	43 (+14)	< 0.01, < 0.01
Fat	29 (0)	0.025, 0.039, 0.042
	32 (+3)	< 0.01, 0.01
	36 (+7)	< 0.01, < 0.01
	43 (+14)	< 0.01, < 0.01
Liver	29 (0)	0.059, 0.064, 0.116
	32 (+3)	< 0.01, < 0.01
	36 (+7)	ND, ND
	43 (+14)	ND, ND
Kidney	29 (0)	0.902, 1.242, 2.549
	32 (+3)	< 0.01, < 0.01
	36 (+7)	ND, < 0.01
	43 (+14)	< 0.01, < 0.01

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was available on residues monitoring data for aminopyralid as it is a new compound.

NATIONAL MAXIMUM RESIDUE LIMITS

The meeting was aware that the following national MRLs had been established.

Table 55. National MRLs for aminopyralid.

Country	Commodity	MRL (mg/kg)
Argentina	Wheat, grain	0.04
Australia	Cereal grains	0.1
	Edible offal (mammalian)[except kidney]	0.02
	Eggs	*0.01
	Kidney (mammalian0	0.3
	Meat (mammalian)	*0.01
	Milks	*0.01
	Poultry meat	*0.01
	Poultry, edible offal of	*0.01
	Wheat bran, unprocessed	0.3
	Forage of cereal grains (green)	3
	Mixed pastures (leguminous/grasses)	200
	Straw and fodder of cereal grains (dry)	0.2
USA	Grass, forage	25
	Grass, hay	50
	Wheat, forage	2.0
	Wheat, hay	4.0
	Wheat, grain	0.04
	Wheat, straw	0.25
	Wheat, bran	0.1
	Wheat, aspirated grain fractions	0.2
	Milk	0.03
	Cattle, meat	0.02
	Goat, meat	0.02
	Horse, meat	0.02

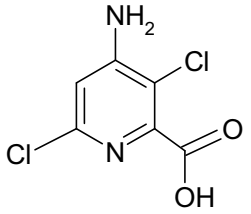
Country	Commodity	MRL (mg/kg)
	Sheep, meat	0.02
	Cattle, fat	0.02
	Goat, fat	0.02
	Horse, fat,	0.02
	Sheep, fat	0.02
	Cattle, meat by-products, except kidney	0.02
	Goat, meat by-products, except kidney	0.02
	Horse, meat by-products, except kidney	0.02
	Sheep, meat by-products, except kidney	0.02
	Cattle, kidney	0.3
	Goat, kidney	0.3
	Horse, kidney	0.3
	Sheep, kidney	0.3
Canada	Hay or fodder (dry) of grasses	65
	Wheat grain	0.05
	Wheat straw and fodder, dry	0.5
	Wheat bran, processed	0.1
	Wheat flour	0.01
	Wheat germ	0.02
	Milk of cattle, goat, and sheep	0.02
	Milk, cream of cattle, goats, and sheep	0.02
	Meat from mammals other than marine mammals	0.05
	Fat from mammals other than marine mammals	0.05
	Liver from mammals other than marine mammals	0.05
	Kidney from mammals other than marine mammals	1.0
Japan	Wheat, grain	0.04
Colombia (has adopted US-EPA MRLs):	Almond hulls	25
	Grass, forage	25
	Grass, hay	50
	Wheat, forage	2.0
	Wheat, hay	4.0
	Wheat, grain	0.04
	Wheat, straw	0.25
	Wheat, bran	0.1
	Wheat, aspirated grain fractions	0.2
	Milk	0.03
	Cattle, meat	0.02
	Goat, meat	0.02
	Horse, meat	0.02
	Sheep, meat	0.02
	Cattle, fat	0.02
	Goat, fat	0.02
	Horse, fat,	0.02
	Sheep, fat	0.02
	Cattle, meat by-products, except kidney	0.02
	Goat, meat by-products, except kidney	0.02
	Horse, meat by-products, except kidney	0.02
	Sheep, meat by-products, except kidney	0.02
	Cattle, kidney	0.3
	Goat, kidney	0.3
	Horse, kidney	0.3
	Sheep, kidney	0.3
United Kingdom (tMRLs)	Milk	0.01*
	Meat, muscle	0.01*
	Meat, fat	0.01*
	Meat, liver	0.01*
	Meat, kidney	0.1

* MRL set at or about LOQ.

APPRAISAL

Aminopyralid is a new herbicide that is used for the control of broadleaf weeds in pastures and cereal crops. It was advanced to the 2006 JMPR schedule of new compounds by the 37th session of the CCPR. The manufacturer submitted studies on metabolism in plants and animals, analytical methods, storage stability, environmental fate and degradation, supervised field trials, processing and farm animal (livestock) feeding.

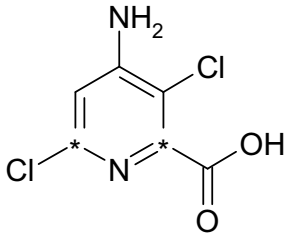
Chemical name and structure:



4-amino-3, 6-dichloropyridine-2-carboxylic acid

Animal metabolism

The meeting received metabolism studies in lactating goats and laying hens. In both studies, aminopyralid was labelled in the 2- and 6-positions of the pyridine ring, as shown below.



A single lactating goat was orally dosed for 6 days with [^{14}C] aminopyralid at the equivalent of 14 ppm in the feed (0.26 mg/kg bw/day). Total radioactivity was measured in samples of milk, urine, faeces, cage wash and tissues. A large proportion of the administered dose was eliminated via urine and faeces, with each accounting for approximately 46% of the total administered dose; the total eliminated was 92% of the administered dose. Approximately 3% of the administered dose was present in cage wash and < 0.1% was present in milk and tissues.

The radioactivity in milk was found to plateau within 24 to 48 hours after dosing had commenced. The total radioactivity in milk was approximately 0.05% of the total administered dose, with concentrations ranging 0.003–0.008 mg/kg aminopyralid equivalents.

TRR in tissues were 0.008 mg/kg equivalents in liver, 0.071 mg/kg equivalents in kidneys, 0.001 mg/kg equivalents in composite fat and non-detectable in composite muscle.

Methanol extraction of milk followed by partitioning with ether and hexane resulted in recovery of 71% TRR. Methanol extraction of liver and kidney samples followed by partitioning with hexane resulted in release of 58% and 80% TRR, respectively. Further characterisation was not conducted in milk or liver due to very low levels of radioactivity being present.

One radiolabelled component representing approximately 80% ^{14}C in kidney was identified by HPLC analysis of kidney extracts; this was parent aminopyralid present at 0.057 mg/kg. In summary, aminopyralid was rapidly excreted from the goat, with detectable residues of 0.06 mg/kg present in kidneys only.

Ten laying hens of 45 weeks age were orally dosed for 7 days with ^{14}C aminopyralid at the equivalent of 10.5 ppm in the feed. TRR in excreta collected daily ranged from 55% to 87% of the nominal daily dose over 1 to 6 days of the study. All eggs contained low levels of radioactivity that gradually increased to a plateau level of 0.004 mg/kg aminopyralid equivalents within 5 to 7 days of the study. TRR in all eggs collected over the study period accounted for < 0.01% of the total administered dose.

TRR in tissues were < 0.01% of the total administered dose. TRR in muscle and fat were comparable, corresponding to 0.0018 and 0.0017 mg/kg aminopyralid equivalents, respectively. TRR in skin (with fat) and liver were 0.0029 and 0.0024 mg/kg aminopyralid equivalents, respectively. The levels of radioactivity in eggs and tissues were low and were not further characterised.

Residues in excreta were readily extracted into $CH_3CN:H_2O$ with approximately 96% TRR being recovered. HPLC analysis of the excreta extracts indicated that 93% of the radioactivity was composed of unchanged aminopyralid.

In summary, aminopyralid is readily excreted by hens following oral dosing for 7 days at 10 ppm in the feed. TRR in eggs on days 6 and 7 of the study were 0.004 mg/kg aminopyralid equivalents. TRR in muscle and fat were non-detectable (< 0.002 mg/kg aminopyralid equivalents), while TRR in liver and skin/fat were 0.002–0.003 mg/kg aminopyralid equivalents.

The Meeting concluded that aminopyralid is readily eliminated by lactating goats and laying hens following oral dosing, and that it does not undergo any significant metabolism. Most of the eliminated radioactivity was recovered as unchanged aminopyralid.

Plant metabolism

Metabolism studies for aminopyralid applying to wheat and grass/pastures were submitted to the Meeting. In both studies, aminopyralid was labelled in the 2- and 6-positions of the pyridine ring, as shown above.

^{14}C aminopyralid was applied to spring wheat at rates of 40 and 80 g ai/ha. The wheat was at growth stages BBCH 26 – 28 (6 to 8 tillers detectable) at the time of application. Samples of plant material (forage) were taken at 0 and 14 days after application; hay was sampled at 35 days after application and grain and straw at 86 days after application. Homogenised samples were extracted with $CH_3CN:H_2O$ followed by partitioning with CH_3CN/CH_2Cl_2 prior to HPLC analysis. In forage and hay 88–96% of the extracted radioactivity was composed of free and/or conjugated forms of aminopyralid. Similarly in straw and grain 89 and 69%, respectively, of the extracted radioactivity was composed of free and conjugated aminopyralid. Acid/base treatment of the extracted solids and aqueous phase extracts released another 4% and 7% of the TRR in straw and grain, respectively.

Three types of pasture grasses (perennial ryegrass, big bluestem and *Panicum maximum*) were treated with a single application of ^{14}C aminopyralid at a rate of 360 g ai/ha. Samples of grass were collected for analysis at 0, 7, 14, 21 and 42 days after application.

During the first 7 days after application, aminopyralid comprised approximately 49–97% of the TRR. After 7 days, the amount of extracted aminopyralid decreased and large proportions of other metabolites formed, ranging 18–60% of the TRR at 7 to 42 days after application in grass forage. Acid/base hydrolysis of the metabolites released radioactivity that was subsequently identified by HPLC analysis as aminopyralid. The metabolites were glucose conjugates of aminopyralid that were easily released by base and/or acid hydrolysis. Overall, 87–96% of the TRR in grass forage and hay was identified as aminopyralid and conjugates of aminopyralid.

In summary, the two plant metabolism studies demonstrated that aminopyralid forms the major proportion of the radioactivity when applied to wheat and pasture grasses. With time, the plant converts aminopyralid to glucose conjugates that are easily released by base and/or acid hydrolysis to parent compound.

Environmental fate

The meeting received information on the environmental fate of aminopyralid in soil, including studies on photodegradation on soil, aerobic soil degradation and crop rotation studies (confined and field). ^{14}C aminopyralid was labelled in the 2- and 6-positions of the pyridine ring in all soil studies.

In a photodegradation study on soil, aminopyralid degraded into non-extracted ^{14}C and CO_2. The half-life (DT_{50}) for photodegradation of aminopyralid was 61 days and DT_{90} was 203 days.

Aerobic soil degradation of ^{14}C aminopyralid was investigated in a range of European and US soils. As found in the soil photodegradation study, aminopyralid degrades to CO_2 and non-extracted residues under aerobic conditions; no other residues were identified. Reported DT_{50} values ranged from 18 – 343 days and DT_{90} values ranged 45 – 1141 days.

Data were reported from field dissipation studies that were conducted in Europe, US and Canada. The reported DT_{50} values from the field studies ranged from 8 to 54 days with the majority of values approximating 30 to 35 days. DT_{90} values ranged 26 to 430 days.

Crop rotation studies were conducted in a leafy vegetable (lettuce), a root crop (turnip) and a cereal crop (sorghum). The crops were grown in soil treated with ^{14}C aminopyralid either 90 or 120 days prior to sowing. The results from the different crops were similar, with radioactivity ranging 0.002 – 0.007 mg/kg equivalents in lettuce, turnip roots and tops and sorghum grain and 'late forage'. The highest levels of radioactivity were present in 'early forage' of sorghum at 0.03 mg/kg equivalents from sorghum sown at 90 days after application. Extraction of the radioactivity led to results similar to those in the wheat and grass metabolism studies, i.e. the radioactivity was composed of aminopyralid and conjugates that were easily released by base hydrolysis of extracted phases and non-extracted solids.

Methods of analysis

The Meeting received details of analytical methods for the determination of residues of aminopyralid in agricultural commodities (namely grass pastures, cereal grains, cereal forage and straw), bovine tissues and milk and soil.

Methods for the quantitative determination of aminopyralid residues in barley, sorghum, wheat and grass pasture were provided to the Meeting (method GRM 02.31). Residues are determined using LC/MS/MS. The validated LOQ for all matrices is reported as 0.01 mg/kg. Residues of aminopyralid and its conjugates are extracted from the sample matrices by homogenisation with mild base, followed by acidification and purification on an SPE column. Aminopyralid in the purified extract is derivatized to its butyl ester form and quantified using LC/MS/MS.

In the method validation component of the study, untreated control samples of barley, sorghum and wheat grain; barley, sorghum and wheat forage; barley straw, sorghum stover and wheat straw; pasture grass forage and hay were fortified with aminopyralid at concentrations ranging 0.01–0.5 mg/kg for grain, 0.01–5 mg/kg for forage and straw and 0.01–20 mg/kg for grass forage and hay. Mean recoveries in all samples ranged 92–109% over all concentrations tested. Independent laboratory validation confirmed the LOQ of 0.01 mg/kg, and mean recoveries ranged 93–120% over all matrices tested.

The extraction efficiency of aminopyralid was determined by extracting wheat grain, forage, straw, hay and pasture grass samples from the metabolism studies in accordance with method GRM 02.31. The extraction efficiencies of the pasture grass samples ranged 88 – 114% and of the wheat matrices ranged 72–101% when calculated based on the total radioactivity.

A GC/MS method for the determination of aminopyralid, fluroxypyr and 2,4-D residues in pastures was provided, which was a modified version of the method described above and has a validated LOQ of 1 mg/kg. Recoveries were validated over a range of concentrations (1–100 mg/kg) and ranged 78–115% with a mean recovery of 95%. The reported LOD was 0.2 mg/kg in grass pasture samples.

Aminopyralid residues in animal tissues and milk are also determined by LC/MS/MS with a validated limit of quantitation of 0.01 mg/kg (method GRM 03.18). Residues are extracted with MeOH/$NaHCO_3$ solution, purified using a SPE plate and derivatized to form the 1-butyl ester. The method was validated over the concentration range of 0.01–2.5 mg/kg in kidney and 0.01–1 mg/kg for all other tissues and milk. The mean recoveries in bovine fat, muscle, liver and kidney ranged 79–96% and in whole milk, skim milk and cream ranged 73–89%. In an independent laboratory validation, the LOQ of 0.01 mg/kg was confirmed for aminopyralid in bovine milk and kidneys using LC/MS/MS. The mean recoveries in bovine milk and kidney were 83% and 87%, respectively.

Methods were provided for the determination of aminopyralid residues in soil (Method GRM 02.34). The soil method was validated with recoveries being conducted in four soil types at concentrations ranging 0.0015–0.1 mg/kg with a mean recovery of 88%; the validated LOQ was 0.0015 mg/kg.

Stability of pesticide residues in stored analytical samples

The storage stability of aminopyralid in pasture grass and hay and wheat grain and straw was investigated. Samples of hay, forage (grass), wheat grain and wheat straw were fortified with aminopyralid at a concentration of 0.1 mg/kg and placed in frozen storage at –20 °C. Aminopyralid residues are stable under conditions of frozen storage for up to 489 days in grass hay and forage, and up to 469 days in wheat grain and straw, with 86% and 88% aminopyralid remaining in fortified grass hay and forage, respectively and 91% and 87% remaining in wheat grain and straw, respectively

Storage stability in animal tissues and milk was not conducted as samples from the metabolism and livestock feeding study were analysed within 3 months of sample collection.

Residue definition

The results of the plant metabolism studies on wheat and pasture grasses indicate that aminopyralid is not significantly metabolised and is transformed to glucose conjugates. Greater than 90% extracted TRR is identified as aminopyralid and conjugates with no metabolites formed to any extent.

In goats and hens, administered aminopyralid is readily eliminated following oral dosing, and it does not undergo any significant metabolism. Greater than 93% of the eliminated radioactivity was recovered as unchanged aminopyralid. Detected radioactivity in goat kidney was identified as aminopyralid.

Analytical methods for plant and animal matrices and soil determine aminopyralid and any conjugates that are hydrolysed by acid/base as the butyl ester derivative of aminopyralid.

On the basis of the metabolism in plants and animals and the analytical methodology submitted, the Meeting recommended a residue definition for aminopyralid for plants and animals.

Definition of the residue (for compliance with the MRL for all commodities and for estimation of dietary intake for plant and animal commodities): aminopyralid and its conjugates that can be hydrolysed, expressed as aminopyralid.

The residue is not fat-soluble.

Results of supervised trials on crops

In all supervised field trials, commercial formulations containing either the potassium salt or triisopropanolammonium (TIPA) salt were used. In several trials both salt forms were used and in addition many formulations included combinations of the aminopyralid salts with other herbicides such as 2,4-D, fluroxypyr and triclopyr. The aminopyralid TIPA salt dissociates rapidly in water to the aminopyralid acid at pH values greater than 2.56.

Supervised trials for the foliar application of aminopyralid on cereals, namely barley, oats and wheat, and pasture grasses were provided to the Meeting.

Cereal grains

Barley

Data for barley was received from trials conducted in Australia. The registered use in Australia allows a single application between 3-leaf to 1st node (BBCH 13-31) at a rate of 5–7.5 g ai/ha with a nil PHI for harvest and a non-grazing interval of 7 days after application.

The residues in barley grain from four trials in Australia are in rank order: 0.03, 0.04, 0.06, 0.06, and 0.07 (2) mg/kg.

Data for barley was received from two trials conducted in Spain, however there is no GAP for barley in Spain.

The Meeting considered that there were insufficient trials to estimate a maximum residue level for barley.

Oats

Data for oats were received from trials conducted in Australia where two different formulations were used. The registered use in Australia allows a single application between 3-leaf to 1st node (BBCH 13-31) at a rate of 5–7.5 g ai/ha with a nil PHI and grazing at 7 days after application.

The residues in oat grain from four trials in Australia are in rank order: < 0.01, 0.01, 0.02 and 0.03 (4) mg/kg.

The Meeting considered that there were insufficient trials to estimate a maximum residue level for oats.

Wheat

Trials on wheat were conducted in Argentina, Australia, Canada, Hungary, Italy, Poland, Spain and the USA. GAP in Argentina is a single application at rates of 3.75–5 g ai/ha from 3rd leaf to end of tillering, with a nil PHI for harvest. Residues in wheat grain from trials in Argentina were: < 0.01 (6) mg/kg.

GAP for wheat in Australia is the same as that for barley and oats; a single application between 3-leaf to 1st node (BBCH 13-31) at a rate of 5–7.5 g ai/ha with a nil PHI and grazing at 7 days after application. Residues in wheat grain from the Australian trials are in rank order were: < 0.01 (7), 0.01 (3), 0.02 (2), 0.03 and 0.07 mg/kg.

In the US, GAP allows a single application from 3-leaf to early jointing (BBCH 13 to 30–31) at rates of 7.6–10 g ai/ha, with a PHI of 50 days for harvest and 14 days for grazing/cutting. GAP in Canada is a single application from 2 to 6-leaf stage at a rate of 10 g ai/ha with a PHI of 50 days for harvest and no restrictions for grazing. The Meeting considered that as the GAP in both Canada and USA is specified as an application timing as well as PHI, the stage of crop growth at which the spray is applied is the important determinant compared to the PHI in relation to the final residues in grain. Therefore, trials where the application timings were within the specified GAP for Canada and USA were considered relevant, even though the actual PHIs may have been longer than 50 days.

Residues in wheat grain from the Canadian and US trials are in rank order: < 0.01 (8), 0.01 (14) and 0.02 (5) mg/kg.

Although there are no registered uses of aminopyralid on wheat in Europe, the Meeting considered that the data from the European trials may be included in the estimation of the maximum residue level for wheat as the application rates and application timings are similar to those registered uses in Argentina, Australia, Canada and the USA. The Meeting made reference to the outcomes of the OECD/FAO Zoning project and considered that cropping practices and herbicide use in broadacre crops such as wheat are similar in many regions and therefore the European trials may be considered as being supportive of GAP in other regions, in this case specifically Argentina, Australia, Canada and USA. The residues from the European trials are in rank order: < 0.01 (7) and 0.01 (3) mg/kg.

The Meeting agreed that the data sets for wheat from trials in Argentina, Australia, Canada, Europe and the USA could be combined, therefore the residues in wheat grain in ranked order were: < 0.01 (23), 0.01 (10), 0.011 (3), 0.12, 0.013, (4), 0.014(2), 0.02 (2), 0.021, 0.022, 0.023, 0.025(2), 0.03 and 0.07 mg/kg.

The Meeting also agreed that the data set for wheat could support the data sets for barley and oats, thereby allowing maximum residue levels to be estimated for barley and oats. In addition, registered uses in Australia apply to the minor crop triticale, therefore the combined data set for barley, oats and wheat may also be applied to triticale by crop extrapolation.

Residues for the combined data sets for barley, oats and wheat in ranked order were: < 0.01 (24), 0.01 (11), 0.011 (3), 0.012, 0.013 (4), 0.014 (2), 0.02 (3), 0.021, 0.022, 0.025, 0.025, 0.023, 0.03 (6), 0.04, 0.06 (2), and 0.07 (3)

The Meeting recommended a maximum residue level of 0.1 mg/kg for aminopyralid in barley, oats, triticale and wheat, with an STMR of 0.01 mg/kg.

Livestock feed commodities

In trials conducted in Australia and New Zealand, residues in livestock feed commodities were reported on a 'dry weight' basis with associated moisture contents reported for samples at harvest and therefore require no correction for the estimation of MRLs. However the data from trials conducted in all other regions are reported on an 'as received' basis and require correction for moisture content by using default factors that are presented in the FAO Manual 2002. The default factors used are indicated and the 'as received' figures are adjusted for moisture content in the relevant sections below.

Cereal Straw

The registered use of aminopyralid on barley and oats in Australia allows a single application between 3-leaf to 1st node (BBCH 13-31) at a rate of 5–7.5 g ai/ha with a nil PHI and grazing at 7 days after application.

The data from the Australian trials are reported on a dry weight basis and therefore require no correction for moisture content. Residues in barley straw from trials that correspond to Australian GAP in ranked order were: 0.03 (3), 0.04, 0.07 and 0.08 mg/kg.

Residues in oat straw from trials that correspond to Australian GAP in ranked order were: 0.02, 0.03, 0.04 (3), 0.05 and 0.11 mg/kg.

Data for barley were received from two trials in Spain; these trials corresponded to Australian GAP. Residues when corrected for moisture content (88%) were 0.01 and 0.07 mg/kg.

Wheat straw

The registered use of aminopyralid on wheat in Australia allows a single application between 3-leaf to 1st node (BBCH 13–31) at a rate of 5–7.5 g ai/ha with a nil PHI and grazing at 7 days after application.

The data from the Australian trials are reported on a 'dry weight' basis and therefore require no correction for moisture content. Residues in wheat straw from trials that correspond to Australian GAP in ranked order were: 0.02 (2), 0.04 (2), 0.05, 0.06 (2), 0.07 (2), 0.08, 0.09, 0.1, 0.12 and 0.13 mg/kg.

In the US, GAP allows a single application from 3-leaf to early jointing (BBCH 13-30) at rates of 7.6–10 g ai/ha, with a PHI of 50 days for harvest and 14 days for grazing/cutting. GAP in Canada is a single application from 2 to 6-leaf stage at a rate of 10 g ai/ha with a PHI of 50 days for harvest and a nil PHI for grazing. The Meeting considered that as the GAP in both Canada and USA is specified as application timing as well as PHI, the stage of crop growth at which the spray is applied is the important determinant when compared to the PHI in relation to the final residues in

grain. Therefore, trials where the application timings were within the specified GAP for Canada and USA were considered relevant, even though the actual PHIs may have been longer than 50 days. Residues in wheat straw on an 'as received' basis from the Canadian and US trials in ranked order were: 0.02, 0.03, 0.04 (6), 0.05, 0.06 (4), 0.07 (7), 0.08, 0.1 (2), 0.12, 0.13 (2) and 0.14 mg/kg. When corrected for moisture content (12%), residues in wheat straw in ranked order were: 0.02, 0.03, 0.04 (6), 0.06, 0.07 (4), 0.08 (7), 0.09, 0.11 (3), 0.15 (2) and 0.16 mg/kg.

As with the wheat grain, there are no registered uses of aminopyralid on wheat straw in Europe, however the data from the European trials may be included in the estimation of the maximum residue level for wheat as the application rates and application timings are similar to those for registered uses in Argentina, Australia, Canada and USA. In addition, cropping practices and herbicide use in broadacre crops such as wheat are similar in many regions and therefore the European trials may be considered as being supportive of GAP in Argentina, Australia, Canada and USA. Residues in wheat straw from the European trials were reported on an 'as received' basis and in ranked order were: 0.03 (2), 0.04 (2), 0.06, 0.07, 0.08, 0.09, 0.13 and 0.16 mg/kg. When corrected for moisture content (12%), residues in wheat straw in ranked order were: 0.03 (2), 0.04 (2), 0.07, 0.08, 0.09, 0.1, 0.15 and 0.21 mg/kg.

The Meeting agreed that the data sets for wheat straw from trials in Argentina, Australia Canada, Europe and the US were from a single population and could be combined, therefore the residues in ranked order were: 0.02 (3), 0.03 (3), 0.04 (10), 0.05, 0.06 (3), 0.07 (7), 0.08 (9), 0.09 (3), 0.1 (5), 0.12, 0.13, 0.15 (3), 0.16 and 0.21 mg/kg.

The Meeting also agreed that the data set for wheat straw could support the data sets for barley and oat straw. In addition, registered uses in Australia apply to the minor crop triticale; therefore the combined data set for barley, oats and wheat may also be applied to triticale straw by crop extrapolation.

Residues from the combined data sets for barley, oat and wheat straw in rank order were: 0.01, 0.02 (4), 0.03 (7), 0.04 (14), 0.05 (2), 0.06 (3), 0.07 (9), 0.08 (10), 0.09 (3), 0.1 (6), 0.12, 0.13, 0.15 (3), 0.16 and 0.21 mg/kg. The Meeting recommended a maximum residue level of 0.3 mg/kg for aminopyralid in straw of barley, oats, triticale and wheat, with a highest residue of 0.21 mg/kg and an STMR of 0.07 mg/kg.

Cereal forage

GAP in Australia for barley and oats allows grazing of forage at 7 days after an application between 3-leaf to 1st node (BBCH 13–31) at a rate of 5–7.5 g ai/ha. Residues in barley forage (as reported on a dry weight basis) from trials that correspond to GAP were 0.54 and 0.71 mg/kg. Residues in oat forage were 0.34, 0.4 and 0.79 mg/kg.

The Meeting considered that the trials for barley and oat forage could be combined with the data set for wheat forage for the purposes of estimating the livestock dietary burden.

GAP in Australia for wheat allows application between 3-leaf to 1st node (BBCH 13–31) at a rate of 5–7.5 g ai/ha, with grazing of forage at 7 days after application. Residues in wheat forage (as reported on a dry weight basis) from trials that corresponded to GAP were 0.16, 0.45, 0.48, 0.71, 0.77, 1.02 mg/kg.

In the US, GAP allows a single application from 3-leaf to early jointing (BBCH 30-31) at rates of 7.6–10 g ai/ha, with an interval of 14 days after application for grazing or cutting. Residues in wheat forage that correspond to US GAP (as reported on an 'as received' basis) in ranked order were: 0.07, 0.1 (2), 0.16 and 0.19 mg/kg. When corrected for moisture content (75%), residues in wheat forage were: 0.28, 0.4 (2), 0.64 and 0.76 mg/kg.

GAP in Canada is a single application from 2 to 6-leaf stage at a rate of 10 g ai/ha with no restrictions on grazing. Residues in wheat forage (on an 'as received' basis) from trials that corresponded to Canadian GAP were: 0.11, 0.42, 0.49, 0.53, 0.72 and 0.85 mg/kg. An additional 25 US trials corresponded to GAP in Canada and residues in ranked order were: 0.16 (2), 0.19, 0.21,

0.26, 0.29, 0.3 (2), 0.32, 0.36, 0.37 (2), 0.38, 0.4, 0.41 (2), 0.42, 0.45, 0.49, 0.52, 0.53, 0.54, 0.63 (2) and 0.67 mg/kg. When corrected for moisture content (75%), residues were: 0.64 (2), 0.76, 0.84, 1.04, 1.16, 1.2 (2), 1.28, 1.44, 1.48 (2), 1.52, 1.6, 1.64 (2), 1.68, 1.8, 1.96, 2.08, 2.12, 2.16, 2.52 (2), and 2.68 mg/kg.

The Meeting considered that the trials corresponding to GAP in Australia, Canada and the US were from the same population and decided to combine the data for the purposes of estimating the livestock dietary burden. The residues in barley, oat and wheat forage in ranked order were: 0.16, 0.28, 0.34, 0.4 (2), 0.4, 0.45, 0.48, 0.54, 0.64 (3), 0.71, 0.71, 0.76 (2), 0.77, 0.79, 0.84, 1.02, 1.04, 1.16, 1.2 (2), 1.28, 1.44, 1.48 (2), 1.52, 1.6, 1.64 (2), 1.68, 1.8, 1.96, 2.08, 2.12, 2.16, 2.52 (2) and 2.68 mg/kg. The highest residue is 2.7 mg/kg and the STMR is 1.03 mg/kg.

Wheat hay

Residues in wheat hay were reported from trials conducted in the US and Canada. The GAP for wheat in the US is single application from 3-leaf to early jointing (BBCH 13–30) at rates of 7.6–10 g ai/ha, with a PHI of 50 days for harvest and 14 days after application for grazing or cutting. The GAP for wheat in Canada is a single application from 2 to 6-leaf stage at a rate of 10 g ai/ha with a PHI of 50 days for harvest and no restrictions for grazing.

Residues in wheat hay from US trials that correspond to US GAP (as reported on an 'as received' basis) were: 0.21, 0.25, 0.26, 0.34 and 0.61 mg/kg. When corrected for moisture content (88%), residues on a dry weight basis were: 0.24, 0.28, 0.29, 0.39 and 0.69 mg/kg.

Residues from Canadian trials that correspond to Canadian GAP were: 0.37, 1.28, 1.46, 1.48, 2.32 and 2.36 mg/kg. When corrected for moisture content (12%), residues on a dry weight basis were: 0.42, 1.45, 1.66, 1.68, 2.64, 2.68 mg/kg.

An additional 25 US trials corresponded to Canadian GAP and residues on an 'as received' basis were: 0.34, 0.38, 0.43, 0.45, 0.54 (2), 0.69 (2), 0.71, 0.76 (2), 0.83, 0.87, 0.98 (2), 1.02, 1.23, 1.24, 1.31, 1.32, 1.33, 1.37, 1.46, 1.67 and 1.88 mg/kg. When corrected for moisture content (12%), residues on a dry weight basis were: 0.38, 0.43, 0.49, 0.51, 0.61 (2), 0.78, 0.81, 0.86 (2), 0.94, 0.99, 1.1 (2), 1.16, 1.39, 1.41, 1.49, 1.5 (2), 1.56, 1.66, 1.89, 2.14 mg/kg.

The Meeting agreed to combine the data sets from Canada and the USA and residues in wheat hay on a dry weight basis were: 0.24, 0.28, 0.29, 0.38, 0.39, 0.42, 0.43, 0.49, 0.51, 0.61 (2), 0.69, 0.78, 0.81, 0.86 (2), 0.94, 0.99, 1.1 (2), 1.16, 1.39, 1.41, 1.45, 1.49, 1.5 (2), 1.56, 1.66 (2), 1.68, 1.89, 2.14, 2.64 and 2.68 mg/kg. The Meeting recommended a maximum residue level of 3 mg/kg in wheat hay (n = 36), with a highest residue of 2.7 mg/kg and an STMR of 1 mg/kg.

The Meeting decided that wheat forage (when expressed on a dry weight basis) is similar to wheat hay for the purposes of estimating the livestock dietary burden. Therefore only one of the two commodities is considered necessary for inclusion in the livestock dietary burden tables. The highest residue in cereal forage/hay is 2.7 mg/kg and the STMR is 1 mg/kg.

Grass Pastures: forage and hay

The meeting received data for grass pastures (forage) and hay from trials conducted in Australia, Brazil, Canada, France, Germany, Italy, New Zealand, Spain, the UK and USA.

GAP in Brazil allows a single application at rates of 40–100 g ae/ha with no specified interval to harvest or for grazing. Forage residue data, calculated as the average of replicate measurements that correspond to Brazilian GAP expressed on an 'as received' basis were: 1.3, 1.4, 3.6, 6.3 and 11.6 mg/kg. When corrected for moisture content (75%) residues were: 5.2, 5.6, 14.4, and 46.4 mg/kg.

Trials from Europe were evaluated against UK GAP, which allows a single application at 60 g ae/ha with a 7 days interval for grazing/cutting. Forage data from trials in France, Germany, Italy, Spain and the UK that correspond to UK GAP expressed on an as received basis were: 0.8, 1, 1.3, 1.5, 1.8, 2.0, 2.2, and 3 mg/kg. Correcting for moisture content (75%), residues in forage on a dry weight

basis were: 3.2, 4, 5.2, 6, 7.2, 7.6, 8.8 and 12 mg/kg. The sampling intervals for hay did not correspond to the PHI of 7 days.

GAP in Canada allows application at 60–120 g ae/ha with no restrictions for grazing/cutting. Residues in forage as expressed on an as received basis were: 9.1, 10.7, 12.2, 12.7, 12.8, 13.2, 13.7, 13.8 and 14.6 mg/kg. Correcting for moisture content (75%), residues on a dry weight basis were: 36.4, 42.8, 48.8, 50.8, 52.1, 52.8, 54.8, 55.2 and 58.4 mg/kg. Residues in hay that correspond to GAP are on an as received basis were: 15.1, 15.9, 16.8, 21.6, 22.2, 25.1, 26.2, 30, and 55 mg/kg. When corrected for moisture content (12%), residues were: 17.1, 18.1, 19.1, 24.5, 25.2, 29.8, 34.1 and 62.5 mg/kg.

GAP in the US allows application at 50–120 g ae/ha with no restrictions for grazing/cutting of forage and hay. Residues in forage as expressed on an as received basis were: 4.6, 4.8 (2), 5, 6.1, 6.5, 6.9, 8.7, 9.4, 10, 10.1, 11.1, 11.2, 12.5, and 16 mg/kg. Correcting for moisture content (75%), residues on a dry weight basis were: 18.4, 19.2 (2), 20, 24.4, 26, 27.6, 34.8, 37.6, 40 (2), 44 92), 50 and 64 mg/kg.

Residues in hay on an 'as received' basis were: 10.6, 10.9, 12.4, 15.7, 15.9, 16, 17.9, 18.1, 18.2 (2), 18.6, 20.3, 25.8, 26.3 and 32.2 mg/kg. Correcting for moisture content (12%), residues on a dry weight basis were: 12, 12.4, 14.1, 17.8, 18.1, 18.2, 20.3, 20.5, 20.7, 21.1, 23.1, 29.3, 29.9 and 36.6 mg/kg.

GAP in New Zealand is application at 60 g ae/ha with a nil PHI for gazing/cutting. Forage data from trials that correspond to GAP expressed on a dry weight basis were: 6.2, 7.3, 11.3, 38.8, 42.4, and 48 mg/kg.

GAP in Australia is application at rates ranging 150–210 g ae/ha with a nil PHI for grazing/cutting. Forage data from trials that correspond to GAP were (as expressed on a 'dry weight' basis): 9, 12 (3), 19, 37.1, 52.5, and 103 mg/kg.

The Meeting agreed that for the purposes of estimating livestock dietary burden, the GAP from Australia led to the highest residues in grass pasture. However the data from the US and Canadian trials also fall within the spread of the values from the limited Australian trials. The Meeting therefore agreed to combine the data sets from Australia, Canada and the US; residues in forage on a dry weight basis were: 18.4, 19.2 (2), 20, 24.4, 26, 27.6, 34.8, 36.4, 37.1, 37.6, 40 (2), 42.8, 44 (2), 48.8, 50, 50.8, 52.1, 52.5, 52.8, 54.8, 55.2, 58.4, 64 and 103 mg/kg. The Meeting recommended a highest residue of 103 mg/kg for the purposes of estimating the livestock dietary burden, with an STMR of 41 mg/kg.

Residues in hay from trials conducted in Canada and the US can also be combined on the basis of application rate and nil PHI. Residues are in rank order and on a dry weight basis: 12, 12.4, 14.1, 17.1, 17.8, 18.1 (2), 18.2, 19.1, 20.3, 20.5, 20.7, 21.2, 23.1, 24.5, 25.2, 29.3, 29.8, 29.9, 34.1, 36.6 and 62.5 mg/kg. The Meeting recommended a maximum residue level of 70 mg/kg for grass hay, with a highest residue of 63 mg/kg and an STMR of 21 mg/kg for the purposes of estimating livestock dietary burden.

Fate of residues during processing

A processing study for wheat was provided to the Meeting. A summary of the processing factors and the resulting STMR-P values is provided.

Raw Agricultural Commodity				Processed Commodity			
Commodity	MRL (mg/kg)	STMR (mg/kg)	HR (mg/kg)	Commodity	PF	MRL (mg/kg)	STMR-P (mg/kg)
Wheat	0.1	0.01	0.07	Wheat bran	2.4	0.3	0.024
				Flour	0.2	–	0.002
				Germ	0.36	–	0.0036
				Aspirated grain fraction	6.1	–	0.06

Data from the processing study indicate that there is concentration of aminopyralid residues in wheat bran and aspirated grain fractions, with processing factors of 2.4 and 6.1, respectively. The Meeting agreed to recommend a maximum residue level of 0.3 mg/kg for wheat bran. An HR-P of 0.17 mg/kg is estimated for wheat bran (wheat milled by-products) and 0.43 mg/kg is estimated for aspirated grain fractions for inclusion in the livestock dietary burden. The corresponding STMR-P values for livestock burden are 0.024 mg/kg for wheat bran (wheat milled by-products) and 0.06 mg/kg for aspirated grain fractions.

Farm animal feeding studies

Groups of lactating dairy cows received the equivalent of 0, 32.8, 64.5, 181.5 and 644.7 ppm in the feed for 28 days. Following the dosing period, there was an additional depuration phase of 14 days, with slaughter intervals of 3, 7 and 14 days after withdrawal from dosing.

Residues were determined in liver, kidney, muscle, fat, whole milk, skim milk and cream.

Residues in whole milk following dosing at 32.8 ppm in the feed were < 0.01 mg/kg over the 28 days period. Residues reached plateau within 2 to 3 days of dosing. Residues in milk ranged < 0.01–0.024 mg/kg and 0.011–0.028 mg/kg following dosing at 64.5 and 181.5 ppm, respectively. Aminopyralid residues ranged 0.023–0.127 mg/kg following dosing at 644.7 ppm. Residues had declined to < 0.01 mg/kg within 2 days of withdrawal from dosing at the highest level of 644.7 ppm.

The highest aminopyralid residues in tissues following dosing at 32.8 ppm level were: muscle < 0.01 mg/kg, fat 0.01 mg/kg, liver < 0.01 mg/kg, and kidney 0.1 mg/kg. Following dosing at 64.5 ppm, aminopyralid residues were < 0.01 mg/kg in muscle, 0.01 mg/kg in fat and liver and 0.2 mg/kg in kidney.

The highest aminopyralid residues in tissues following dosing at 181.5 ppm level were 0.05 mg/kg in muscle and liver, 0.09 mg/kg in fat, and 1.5 mg/kg in kidney. The highest aminopyralid residues in tissues following dosing at 644.7 ppm level were 0.03 mg/kg in muscle, 0.04 mg/kg in fat, 0.06 mg/kg in liver, and 2.5 mg/kg in kidney.

As there is no hen or poultry feeding study, the hen metabolism study is used to recommend appropriate maximum residue levels in hen tissues and eggs. The dose level in the hen metabolism study was 10.5 ppm in the feed and hens were dosed daily for 7 days. TRR in muscle, skin/fat, fat, liver and eggs were < 0.01 mg/kg which is the limit of quantitation in the method used to determine aminopyralid residues in animal tissues and milk. Although the method was not validated for eggs, the Meeting considered that as aminopyralid is not fat-soluble and that the method had been validated for bovine tissues and milk, it would also be applicable to eggs.

Farm animal dietary burden

The Meeting estimated the dietary burden of aminopyralid residues in livestock (farm animals) on the basis of the livestock diets listed in the FAO Manual 2002.

The maximum dietary burden calculations include the highest residues (HR) and STMR-P values which are used for the estimation of maximum residue levels in animal commodities such as milk, eggs, meat and offal. The STMR dietary burden calculations for livestock allow an estimate of the median residues in milk, eggs, meat and offal that can be used in the chronic dietary assessments and there STMR and STMR-P values for feeds are used.

The percentage dry matter is taken as 100% when highest residues and STMR values are already expressed on a dry weight basis.

Estimated maximum dietary burden of farm animals

Commodity	*Group*	*Residue (mg/kg)*	*HR/STMR*	Diet content (%)			*Residue Contribution (mg/kg)*		
				Beef cattle	Dairy cattle	Poultry	*Beef cattle*	*Dairy cattle*	*Poultry*
Cereal forage	*AF*	*2.7*	*HR*	100	60	10	*2.7*	*1.62*	*0.27*
Cereal straw	*AS*	*0.21*	*HR*	80	20	10	*0.17*	*0.04*	*0.02*
Grass forage	*AF*	*103*	*HR*	**100**	**100**	**10**	***103***	***103***	***10.3***
Grass hay	*AS*	*63*	*HR*	100	60	10	*63*	*37.8*	*6.3*
Cereal grain	*GC*	*0.01*	*HR*	80	40	**40**	*0.06*	*0.03*	***0.03***
Wheat milled by-products	*CF*	*0.02*	*STMR-P*	40	40	**50**	*0.07*	*0.07*	***0.08***
*AGF**	*–*	*0.06*	*STMR-P*	5	–		*0.003*		
Total				**100**	**100**	**100**	***103***	***103***	***10.4***

* Aspirated grain fractions

The calculated highest dietary burdens for beef cattle, dairy cattle and poultry are 103, 103, and 10.4 ppm, respectively.

Estimated STMR dietary burden of farm animals

Commodity	*Group*	*Residue (mg/kg)*	*STMR/ STMR-P*	Diet content (%)			*Residue Contribution (mg/kg)*		
				Beef cattle	Dairy cattle	Poultry	*Beef cattle*	*Dairy cattle*	*Poultry*
Cereal forage	*AF*	*1*	*STMR*	100	60	10	*1*	*0.6*	*0.1*
Cereal straw	*AS*	*0.07*	*STMR*	80	20	10	*0.06*	*0.01*	*0.01*
Grass forage	*AF*	*37*	*STMR*	**100**	**100**	**10**	***37***	***37***	***3.7***
Grass hay	*AS*	*21*	*STMR*	100	60	10	*21*	*12.6*	*2.1*
Cereal grain	*GC*	*0.01*	*STMR*	80	40	**40**	*< 0.01*	*< 0.01*	***< 0.01***
Wheat milled by-products	*CF*	*0.02*	*STMR-P*	40	40	**50**	*0.01*	*0.01*	***0.01***
*AGF**	*–*	*0.06*	*STMR-P*	5	–	–	*0.003*	–	–
Total				**100**	**100**	**100**	***37***	***37***	***3.7***

* Aspirated grain fractions

The STMR dietary burdens for beef cattle, dairy cattle and poultry are 37, 37 and 3.7 mg/kg, respectively.

Animal commodity maximum residue levels

The livestock dietary burdens used for the estimation of the maximum residue levels for animal commodities were 103 ppm for beef and dairy cattle and 10.4 ppm for poultry. The livestock dietary burdens used for the STMR estimation for dietary risk assessment were 37 ppm for beef and dairy cattle and 3.7 ppm for poultry.

For poultry, the maximum dietary burden of 10.3 ppm is very similar to the dose level of 10.5 ppm in the hen metabolism study. Residues in hen tissues and eggs were < 0.01 mg/kg following dosing for 7 consecutive days. On the basis of the hen metabolism study, the Meeting recommended maximum residue levels of *0.01 mg/kg poultry meat, poultry offal and eggs. These values of *0.01 mg/kg were also used in the dietary risk assessment.

For cattle, the maximum dietary burden of 103 ppm is between the dose levels of 64.5 ppm and 181.5 ppm. The residues in kidney are the highest of all tissues and range 0.45–2.5 mg/kg

between these two feed levels. On the basis of interpolation between the two feed levels, the Meeting recommended a maximum residue level of 1 mg/kg for mammalian kidney. For liver and other offal, the Meeting recommended a maximum residue level of 0.05 mg/kg. For milk, the meeting recommended a maximum residue level of 0.02 mg/kg. For meat, the Meeting recommended a maximum residue level of 0.1 mg/kg on the basis of higher levels being present in fat compared to muscle at the same dose levels.

Dietary burden (ppm)			*Residues (mg/kg)*					
Feed level [ppm]	*Milk*		*Meat (fat)*		*Liver*		*Kidney*	
	Highest	*Mean*	*Highest*	*Mean*	*Highest*	*Mean*	*Highest*	*Mean*
MRL estimate (beef and dairy cattle)								
(103 ppm)		*0.016*	*0.026, (0.054)*		*0.031*		*0.87*	
[64.5/181.5]	*[0.024, 0.028]*		*[< 0.01, 0.046]*		*[0.014, 0.054]*		*[0.202, 1.537]*	
STMR estimate (beef and cattle)								
(37 ppm)		*0.01*		*0.01*		*0.01*		*0.1*
[32.8 ppm]								

For the purposes of the dietary risk assessment, the STMR estimate for the livestock dietary burden is 37 ppm for beef and dairy cattle and 3.7 ppm for poultry. Based on the poultry metabolism study, the STMR values for poultry and eggs are 0.01 mg/kg. In the lactating cattle study, the feed level of 32.8 is close to the STMR level of 37 ppm. The STMR values for milk, meat (fat) and liver are 0.01 mg/kg and 0.1 mg/kg for kidney.

Conclusions

On the basis of the data from supervised trials and farm animal feeding studies, the Meeting provisionally estimated maximum residue levels, but these are not recommended for use as maximum residue limits (MRLs) because of the deferred toxicological evaluation.

DIETARY RISK ASSESSMENT

Long-term intake and short-term intake

As the Meeting received an incomplete toxicology data submission, the dietary risk assessment for aminopyralid could not be finalised.

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Hastings, M.J.	011159	2003
Hastings, M.J.	011159	2003
Kalvan, H.C.	030070	2005
Kalvan, H.C.	030070.01	2005
Lindsay, D.A.	030002.01	2004
Lindsay, D.A.	030004.01	2004
Lindsey, A.E. and Hastings, M.J.	021295	2004
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Madsen, S.	FOR01009	2003
Magnussen, J.D.	030008	2004
Magnussen, J.D.	030009	2004
Magnussen, J.D. and Balcer, J.L.	010071	2004
McCormick, R.W., Schelle, G.E. and Dolder, S.C.	020018	2004
Mollica, J. and West, S.	031005	2003
Nelson, R.M.	FOR01015	2002
Olberding, E.L. and Hastings, M.J.	021310	2004
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Pinheiro, A.C.	020131	2003
Pinheiro, A.C.	020132	2003
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Rawle, N.W.	GHE-P-10575	2003
Rawle, N.W.	GHE-P-10576	2003
Rawle, N.W.	GHE-P-10577	2003
Rawle, N.W.	GHE-P-10578	2004
Rawle, N.W.	GHE-P-10579	2004
Rawle, N.W.	GHE-P-10580	2004
Rawle, N.W.	GHE-P-10689	2005
Rawle, N.W.	GHE-P-10690	2005
Rawle, N.W.	GHE-P-10691	2005
Reed, R.L.	020157	2005
Reed, R.L.	030098	2004
Robaugh, D. and Randolph, R.	031005	2003
Roberts, D.W. and Schelle, G.E.	020031	2004
Roberts, D.W. and Schelle, G.E.	020032	2004
Roberts, D.W., Schelle, G.E. and Knuteson, J.A.	030042	2004
Rosser, S.W., Rutherford, L.A. and McFarlane, J.H.	030061	2004
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Rutherford, L.A.	020080	2004
Rutherford, L.A. and Hastings, M.J.	021327	2003
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Yoder, R.N. and Smith, K.P.	010091	2002
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