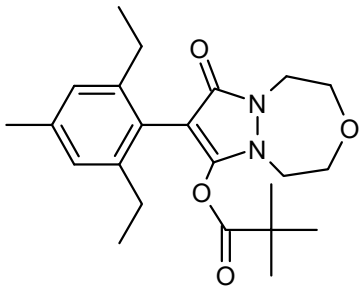
PINOXADEN (293)

The first draft was prepared by Ms Monique Thomas, Pest Management Regulatory Agency, Canada

EXPLANATION

Pinoxaden is a selective post-emergence herbicide for the control of annual grass weeds in cereal crops. Pinoxaden belongs to the phenylpyrazole class of herbicides which acts by inhibiting the enzyme acetyl-CoA carboxylase (ACCase). At the 47th Session of the CCPR (2015), pinoxaden was scheduled for evaluation as a new compound by the 2016 JMPR.

IDENTITY

ISO common name:	Pinoxaden
Chemical name:	
IUPAC:	8-(2,6-diethyl-*p*-tolyl)-1,2,4,5-tetrahydro-7-oxo-7*H*-pyrazolo[1,2-*d*][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropionate
CAS:	8-(2,6-diethyl-4-methylphenyl)-1,2,4,5-tetrahydro-7-oxo-7*H*-pyrazolo[1,2-*d*][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropanoate
CAS Registry. No.:	243973-20-8
CIPAC No.:	776
Trade Name:	NOA 407855
Structural formula:	
	
Molecular formula:	$C_{23}H_{32}N_2O_4$
Molecular weight:	400.5 g/mol

Physical and chemical properties

Pure active ingredient			
Parameter	Value		Reference
Density (24 °C)	1.16 g/cm^3		L01-004888
Physical state, colour	fine powder, white		107875
Odour	odourless		
Vapour pressure	Temperature (°C)	Vapour pressure (Pa)	L01-006961
	20	2.0×10^{-7} (extrapolated)	
	25	4.6×10^{-7} (extrapolated)	
Solubility in water	200 mg/L		107876
Solubility in organic solvents	Solvent	Solubility (g/L)	109861
	Methanol	104.3	
	Acetone	163.5	
	Ethyl acetate	130	
	Dichloromethane	> 500	

Pure active ingredient			
Parameter	Value		Reference
	Toluene	130	
	Octanol	140	
	Hexane	1.0	
Partition coefficient	1800 (log P_{ow} = 3.2) at 25 °C		107877
pKa	none		L01-004889
Hydrolysis rate (15 °C)	pH	DT_{50} (days)	
	7	23.3	
	9	0.6	
Hydrolysis rate (25 °C)	4	17.2	00RP05
	5	17.5	
	7	9.9	
	9	0.2	
Thermal stability in air	Stable at room temperature; no decomposition is observed in air or nitrogen below 150 °C		HT03/068
Technical grade material			
Physical state, colour	powder, light beige		109860
Odour	sweet		

Formulation

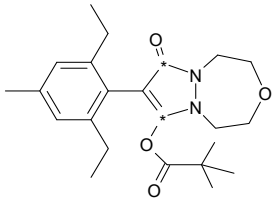
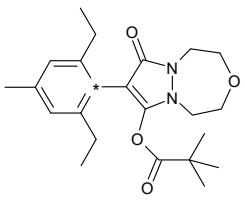
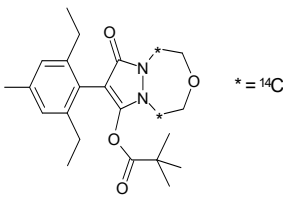
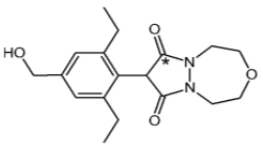
Pinoxaden is primarily available as emulsifiable concentrate formulations (EC) containing 100 g/L pinoxaden or 92.7 g/L pinoxaden and 7.7 g/L florasulam. All pinoxaden formulations contain the safener cloquintocet-mexyl (CGA185072) in a 4:1 ratio of pinoxaden to safener.

Specification

Pinoxaden has not been evaluated by the Joint Meeting of Pesticide Specifications.

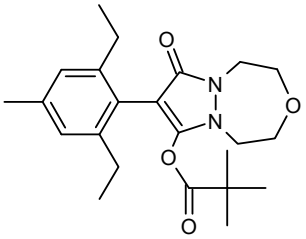
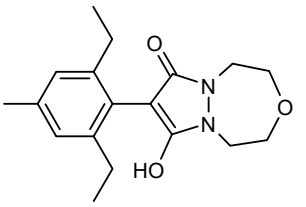
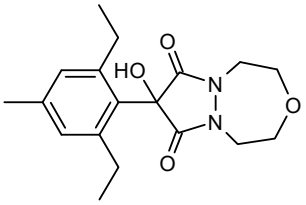
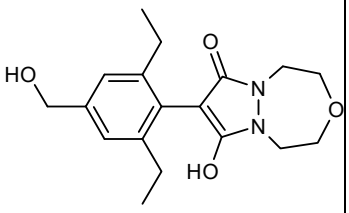
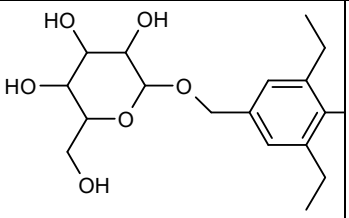
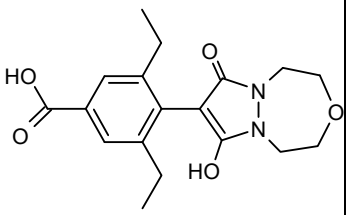
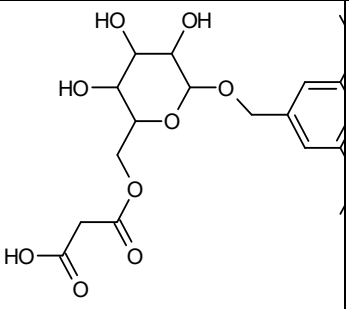
METABOLISM AND ENVIRONMENTAL FATE

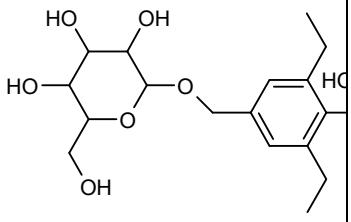
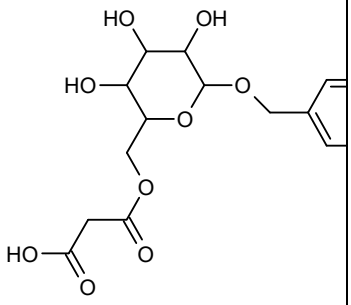
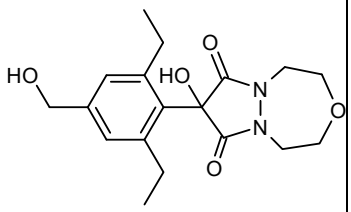
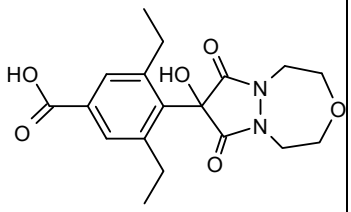
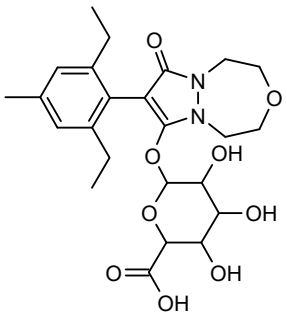
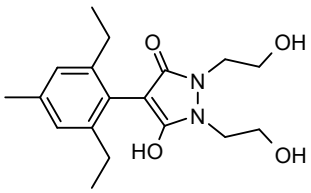
The metabolism and distribution of pinoxaden in plants, and pinoxaden and the metabolite M4 in animals, was investigated using ^{14}C-labelled test material as shown below:

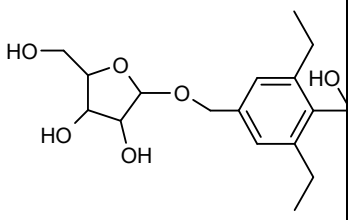
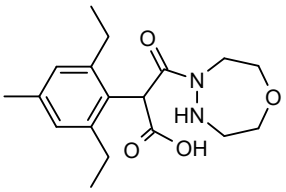
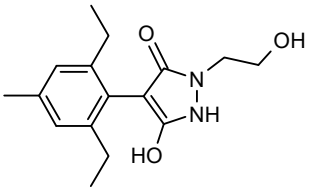
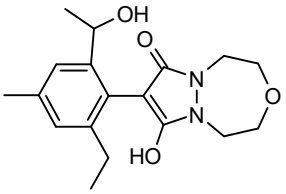
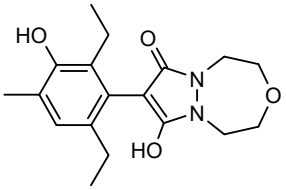
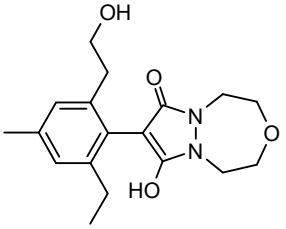
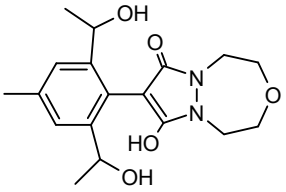
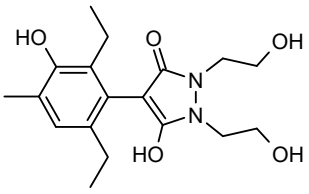
Pinoxaden			M4
[Pyrazol-3,5-^{14}C] label	[Phenyl -1-^{14}C] label	[Oxadiazepin-3,6-^{14}C] label	[Pyrazol-5-^{14}C] label
			
* indicates position of radiolabel			

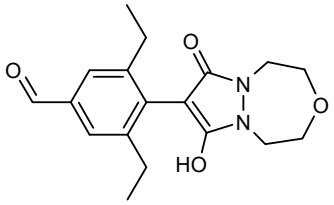
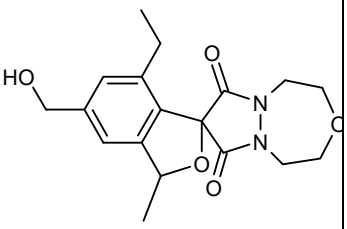
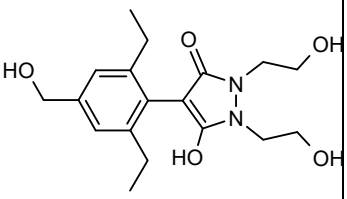
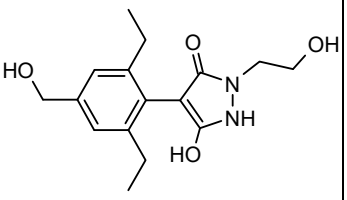
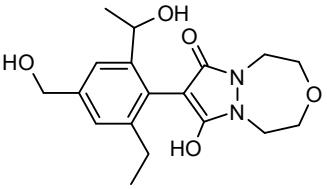
Chemical names, structures and code names of metabolites and degradation products of pinoxaden are summarized in the following table. Compounds are referred to primarily by the code name.

Code names, chemical names and structures of pinoxaden related substances:

Compound Name	Structure	IUPAC-Name	Occurrence in
Pinoxaden NOA 407855 = M1		8-(2,6-diethyl-p-tolyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropionate	Plants and animals
NOA 407854 = M2		8-(2,6-Diethyl-4-methyl-phenyl)-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Spring Wheat Goat Hen Rat
NOA 447204 = M3		8-(2,6-Diethyl-4-methyl-phenyl)-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Hen Rotational Wheat Rotational Lettuce
SYN 505164 = M4		8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Goat Hen Rat
M5 (glucose conjugate of M4)		8-[2,6-Diethyl-4-(3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-yloxymethyl)-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Rat
SYN 502836 = M6		3,5-Diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzoic acid	Winter Wheat Spring Wheat Hen Goat Rat
M7 (malonyl-glucose conjugate of M4)		Malonic acid mono-{6-[3,5-diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzyloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-ylmethyl} ester	Winter Wheat Spring Wheat

Compound Name	Structure	IUPAC-Name	Occurrence in
M8 (glucose conjugate of M10)		8-[2,6-Diethyl-4-(3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-yloxymethyl)-phenyl]-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Spring Wheat
M9 (malonyl-glucose conjugate of M10)		Malonic acid mono-{6-[3,5-diethyl-4-(8-hydroxy-7,9-dioxo-hexahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzyloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-ylmethyl} ester	Winter Wheat
SYN 505887 = M10		8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Spring Wheat Goat Rat
SYN 504574 = M11 = ME7		3,5-Diethyl-4-(8-hydroxy-7,9-dioxo-hexahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzoic acid	Winter Wheat Spring Wheat Rat Rotational crop forage
M12		6-[8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-yloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-carboxylic acid	Goat Rat
M13		4-(2,6-diethyl-4-methyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat Rat

Compound Name	Structure	IUPAC-Name	Occurrence in
M14 (pentose conjugate of M4)		8-[4-(3,4-Dihydroxy-5-hydroxymethyl-tetrahydro-furan-2-yloxymethyl)-2,6-diethyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d] [1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Rat
M19		2-(2,6-diethyl-4-methyl-phenyl)-3-[1,4,5]oxadiazepan-4-yl-3-oxo-propionic acid	Goat Rat
M20		4-(2,6-diethyl-4-methyl-phenyl)-5-hydroxy-1-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat Rat
M22		8-[2-ethyl-6-(1-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M23		8-(2,6-diethyl-3-hydroxy-4-methyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M24		8-[2-ethyl-6-(2-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M26		8-[2,6-bis-(1-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M27		4-(2,6-diethyl-3-hydroxy-4-methyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat

Compound Name	Structure	IUPAC-Name	Occurrence in
M31		3,5-Diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d] [1,4,5]oxadiazepin-8-yl)-benzaldehyde	Winter Wheat Hen
M32		7-ethyl-5-(hydroxymethyl)-3-methyl-3H-spiro[2-benzofuran-1,8'-pyrazolo[1,2-d][1,4,5]oxadiazepine]-7',9'-dione	Winter wheat Spring Wheat Rotational Crops
M33		4-(2,6-diethyl-4-hydroxymethyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Hen
M34		4-(2,6-diethyl-4-hydroxymethyl-phenyl)-5-hydroxy-1-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Hen Rat
M35		8-[2-ethyl-6-(1-hydroxy-ethyl)-4-hydroxymethyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Hen Rat

Plant metabolism

The Meeting received information on the fate of pinoxaden labelled in the [pyrazol-3,5-^{14}C], [phenyl-1-^{14}C] and the [oxadiazepin-3,6-^{14}C] rings following foliar application to wheat.

Study 1(Sandmeier, 2001)

Cell culture experiment

Wheat cell cultures were used to investigate the metabolism of pinoxaden and to isolate metabolites for use as reference compounds to confirm the identity of the metabolites in the foliar experiment. Five cell culture flasks were treated with pinoxaden at 5×10^{-5} mol/L. Cell cultures were harvested as whole; one flask after two days and all others, nine days after treatment. Cells were separated from the medium by filtration and subsequently washed with water.

Harvested cells were homogenized in the presence of acetonitrile/water (80:20 v/v). The homogenates were centrifuged and re-extracted. The pooled extracts as well as the media were subjected to TLC analyses.

Foliar application experiment

Winter wheat (variety Galaxie) grown under outdoor conditions was treated as an autumn application with pinoxaden, labelled in the [pyrazol-3,5-^{14}C] ring (specific activity: 52.97 µCi/mg) and formulated as an emulsifiable concentrate formulation, containing the safener cloquintocet-mexyl. The test material was applied once at growth stage BBCH 13 (three leaves unfolded) as a foliar spray at a rate of 68.5 g ai/ha. Samples of forage (immature plant) were harvested 0, 14, 42, and 209 days after application. Mature plants were harvested 264 days after application and separated into grain, straw and husk.

The total radioactive residues (TRRs) were determined by combustion and liquid scintillation counting (LSC). The unextracted radioactivity was determined by combustion.

The radioactive residues in forage declined rapidly from 6.73 mg eq/kg on Day 0 to 0.30 mg eq/kg 14 DAT (days after treatment) and 0.011 mg eq/kg at 209 DAT. Residues in grain, husks and straw at maturity were low.

Table 1 Summary of the Total Radioactive Residues in Winter Wheat Samples

Total Radioactive Residues [mg eq/kg]						
Mature Crop (DAT 264)			Forage			
Grain	Husks	Straw	DAT 0	DAT 14	DAT 42	DAT 209
0.004	0.03	0.04	6.73	0.30	0.11	0.01

As the residues in grain were very low (0.004 mg eq/kg), no further identification was conducted. The nature of the residue in forage, husks and straw was investigated by sequential extraction using acetonitrile:water (80:20 v/v) for two hours and repeated five times or until the radioactivity extracted was less than 5% compared to the radioactivity extracted in the first extraction step. The extracts were combined and analysed by radio-TLC.

Identification of metabolites was achieved either by co-chromatographing metabolite fractions scraped off the TLC plates with cold synthetic standards, or with metabolite fractions isolated and identified by LC-MS/MS or LC-NMR spectroscopy from the cell culture experiment, or with compounds prepared by oxidation of purified metabolite fractions.

Table 2 Summary of the characterization and identification of residues in forage, husks and straw following foliar application

DAT	0	14	42	209	264	
Plant Part	Forage	Forage	Forage	Forage	Husks	Straw
TRR [mg eq/kg]	6.73	0.30	0.11	0.01	0.03	0.04
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted	107.6	94.4	93.8	81.7	78.5	63.6
Pinoxaden	36.2 (2.44)	4.0 (0.01)	n.d.	n.d.	n.d.	n.d.
M2	66.3 (4.46)	5.4 (0.02)	1.4 (0.002)	n.d.	n.d.	n.d.
M3	1.9 (0.13)	5.7 (0.02)	3.0 (0.003)	19.2 (0.002)	31.4 (0.009)	11.1 (0.004)
M4	n.d.	25.6 (0.08)	9.3 (0.01)	1.4 (0.0002)	2.3 (0.0007)	3.4 (0.001)
M5 (glucose conjugate of M4)	n.d.	16.3 (0.05)	30.2 (0.03)	n.d.	n.d.	n.d.
M6	n.d.	3.4 (0.01)	4.5 (0.005)	n.d.	n.d.	n.d.
M7 (malonyl-glucose conjugate of M4)	n.d.	4.6 (0.01)	9.8 (0.01)	n.d.	n.d.	n.d.
M8	n.d.	1.5 (0.004)	3.3 (0.004)	10.8 (0.001)	5.0 (0.002)	1.9 (0.0007)
M9	n.d.	3.2 (0.01)	15.1 (0.02)	7.6 (0.0008)	n.d.	3.5 (0.001)

DAT	0	14	42	209	264	
Plant Part	Forage	Forage	Forage	Forage	Husks	Straw
M10	n.d.	n.d.	n.d.	8.9 (0.001)	12.6 (0.004)	14.2 (0.005)
M11	n.d.	0.9 (0.003)	0.5 (0.0005)	2.7 (0.0003)	0.9 (0.0003)	2.5 (0.0009)
Unknowns (up to 10)	none	12.4 (0.04)	11.2 (0.012)	16.3 (0.002)	11.4 (0.003)	14.8 (0.006)
Unresolved	3.2 (0.22)	12.0 (0.04)	5.5 (0.006)	14.9 (0.002)	15.0 (0.004)	12.2 (0.004)
Unextracted	1.0 (0.07)	11.1 (0.03)	12.8 (0.014)	22.5 (0.002)	26.6 (0.008)	35.1 (0.013)
Total	108.6 (6.73)	105.5 (0.30)	106.6 (0.11)	104.2 (0.011)	105.1 (0.03)	98.7 (0.04)

n.d.= not detected

[a] In % of the total radioactivity found in the plant part, determined by combustion

All homogenised field samples were analysed within *ca*.2.5 months of sampling. Therefore, the determination of the storage stability is not required

In straw, unextracted radioactivity accounted for 35% of the TRR (0.013 mg eq/kg). Acid hydrolysis of the fraction released 13% of the TRR. The only metabolite observed following radio-TLC analysis of the organo-soluble fraction obtained after partitioning was M10 (< 3.3% of the TRR).

Stem injection experiment

A stem injection experiment was also conducted to generate grain and straw samples containing higher measurable residues to aid in metabolite identification. At early booting stage (BBCH 41), 50 µg of [pyrazol-3,5-^{14}C] -pinoxaden was directly injected into the stem, approximately 1–2 cm above the first node, of each spring wheat plant (variety Toronit) grown in a growth chamber. Wheat was sampled after 14, 28 and 56 days, but only the mature plants (56 DAT) were separated into grain, husk and straw and used for analysis.

Samples were extracted in a very similar manner to foliar-treated samples but the residue remaining following acetonitrile/water extraction was subjected to Soxhlet extraction. The remaining unextracted radioactivity in grain was further investigated by initial extraction with a 0.05 N NaOH solution at room temperature for 8 hours. The sample was filtered, the extract neutralised with HCl to pH 6 and the proteins were precipitated with ethanol. The precipitate was removed by centrifugation, air dried and combusted. The filtrate was further hydrolysed with 1 N HCl for 3 hours at 100 °C. The hydrolysate was centrifuged, filtered and the residue was dried prior to combustion. The extract was adjusted to pH 4.8 with 50% NaOH and partitioned with dichloromethane. Phenylhydrazine-hydrochloride and sodium acetate were added to the water phase to produce an osazone fraction to determine if any radioactivity had been incorporated into starch.

Separate samples of whole grain were also directly hydrolysed using 1 N HCl at 100 °C for 6 hours. The hydrolysate was filtered and the extract fractionated using a cartridge eluted with water followed by 50% acetonitrile/water.

In the stem injection experiment, the TRR in grain was considerably higher (1.52 mg eq/kg) than that in grain collected from the foliar experiment. Soxhlet extraction of the residue remaining following acetonitrile extraction, released a further 12% of the TRR, with M4 and M6 being the only metabolites observed (concentrations not reported in the study). Further hydrolysis work on the unextracted residue (23% of the TRR) indicated that a low amount of the radioactivity (about 2% of the TRR) was incorporated into starch, as analysed by osazone derivatisation of the hydrolysate. Further to this, when the unextracted radioactivity released by 0.05 N NaOH was hydrolysed by 1 N HCl at 100 °C for 6 hours, 2D-TLC analysis of the hydrolysate demonstrated the presence of the metabolites M4 and M6 (both accounting for < 16% of the TRR; < 0.24 mg eq/kg).

Conversely, direct acid hydrolysis of whole grain released 100% of the TRRs. After clean-up, most of the radioactivity was shown to be M4 (86% of the TRR) with a small amount of M6 (8% of the TRR). This demonstrated that most of the radioactivity in grain consisted of conjugates of M4.

Table 3 Quantification of metabolite fractions in grain, husks and straw following stem injection experiment

DAT	56					
Plant Part (TRR)	Grain (1.52 mg eq/kg)		Husks (5.82 mg eq/kg)		Straw (34.34 mg eq/kg)	
Metabolite Fraction	%TRR [a]	mg eq/kg [b]	%TRR [a]	mg eq/kg [b]	%TRR [a]	mg eq/kg [b]
Extracted	72.9	1.11	65.3	3.80	66.3	22.76
Pinoxaden	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M2	n.d.	n.d.	n.d.	n.d.	10.0	3.43
M3	n.d.	n.d.	3.4	0.20	4.0	1.38
M4	1.7	0.03	7.3	0.42	30.4	10.44
M5 (glucose conjugate of M4)	6.6	0.10	34.1	1.98	9.1	3.14
M6	12.3	0.19	7.6	0.44	3.2	1.09
M7 (malonyl-glucose conjugate of M4)	21.8	0.33	2.1	0.12	0.2	0.61
M8	n.d.	n.d.	n.d.	n.d.	0.8	0.27
M9	n.d.	n.d.	n.d.	n.d.	0.3	0.11
M10	n.d.	n.d.	0.9	0.54	1.7	0.58
M11	n.d.	n.d.	2.3	0.14	0.4	0.15
Unknowns (up to 4)	26.8	0.417	5.3	0.31	3.1	0.86
Unresolved	3.7	0.06	2.4	0.14	3.2	1.09
Unextracted	37.5	0.57	32.7	1.90	25.6	8.79
Total	110.4	1.52	98.0	5.82	91.9	34.34

[a] As % total radioactivity found in the plant part, determined by combustion

[b] Pinoxaden equivalents

n.d. = not detected

The major metabolic pathways in winter wheat proceeded via ester hydrolysis of pinoxaden to M2, followed by hydroxylation to M4. Conjugation of M4 with glucose formed the conjugate M5 followed by malonyl conjugation to the malonyl glucose conjugate M7. An alternative step was the hydroxylation of M2 to M3 and subsequently to M10. Oxidation of M4 to M10 or M5 to M8, and M7 to M9 were also potential routes of metabolism. Further oxidation of the methyl-hydroxy function of M4 leads to the corresponding carboxylic acids M6 and M11. Conjugation of M10 with glucose to M8 followed by malonyl conjugation to the malonyl glucose conjugate M9 were also observed.

Study 2

Winter wheat (variety Galaxie) grown under outdoor conditions was treated as an autumn application with [phenyl-1-^{14}C] ring-labelled pinoxaden (specific activity: 52.43 µCi/mg) formulated as an emulsifiable concentrate formulation (Sandmeier, 2003). The test material was applied once at growth stage BBCH 49 as a foliar spray at rates of 64 g ai/ha (1× rate) and 318 g ai/ha (5× rate) and as a stem injection with a solution containing 47 µg radiolabelled-pinoxaden.

Samples of forage (immature plant) were harvested 0 (3 hours), 7, 14, and 28 days after treatment (DAT). At the 28 DAT interval, ears were also sampled. Mature plants were harvested at 55 DAT and were separated into grain, straw and husks.

The total radioactive residues (TRRs) were determined by combustion and LSC. The unextracted radioactivity was determined by combustion.

For the 1× experiment, measurable residues were observed in mature grain (0.25 mg eq/kg) and straw (5.49 mg eq/kg). Whilst not proportional, residues in the 5× grain and straw were significantly higher than those from the 1× experiment accounting for 0.84 mg eq/kg and 15.90 mg eq/kg respectively. Following stem injection, TRRs in all tested matrices were comparable to those from the 1× experiment, except for grain and straw which were greater than 3-fold higher. Despite the measurable residues in wheat matrices from the stem injection experiment, none of these were further analysed.

Table 4 Summary of the total radioactive residues in winter wheat samples

Total Radioactive Residues [mg eq/kg]							
Mature Crop (DAT 55)			Forage				
Grain	Husks	Straw	DAT 0	DAT 7	DAT 14	DAT 28 Forage	DAT 28 Ears
1× Experiment							
0.25	3.13	5.49	1.91	1.95	1.43	2.40	0.74
5× Experiment							
0.84	11.84	15.90	n.a.	n.a.	8.91	7.70	2.84
Stem Injection							
0.84	4.25	18.13	n.a.	n.a.	n.a.	4.66	0.74

n.a. Not analysed

The nature of the residues in all wheat matrices (1× experiment: forage, ears, grain, husks and straw; 5× experiment: ears, grain, husks and straw) were investigated by extraction using acetonitrile:water (80:20, v/v) for 2 hours and repeated five times or until the radioactivity extracted was less than 5% compared to the radioactivity extracted in the first extraction step. The extracts were combined and analysed by radio-TLC.

The unextracted radioactivity in grain was investigated by hydrolysing with 1 N HCl under reflux for 6 hours (temperature not specified. The sample was filtered, the extract neutralised and the proteins precipitated with ethanol. The resulting extract was centrifuged, filtered and an aliquot of the filtrate was applied to a C_{18} cartridge rinsed with water and eluted with 50% acetonitrile.

The unextracted residue in straw was investigated by hydrolysing with 1 N HCl at 105 °C for 6 h. The sample was filtered and the extract partitioned with dichloromethane. The residue was hydrolysed with 2 N NaOH at about 105 °C for 3 h. The mixture was filtered and the extract partitioned with dichloromethane. The resulting aqueous phase was adjusted to pH 2 and partitioned again with dichloromethane. The residue was combusted.

In the case of husks, the unextracted residues were hydrolysed under reflux with 1 N HCl for 6 h (temperature not provided). The mixture was filtered and the extract partitioned with dichloromethane. The resulting aqueous phase was hydrolysed under reflux with 10% NaOH for 3 h and filtered. The extract was adjusted to pH 1 and the precipitated lignin filtered off. The remaining residue was combusted.

Extracts and washings were analysed by radio-TLC, HPLC, mass spectrometry and high voltage electrophoresis (HVE). The unextracted radioactivity was determined by combustion.

For the 1× study, identification of metabolites was achieved by co-chromatography using metabolites isolated by LC-MS/MS and/or LC-NMR from samples of the 5× experiment. For the 5× study, major metabolites in grain were identified by co-chromatography with metabolites isolated from the cell culture experiment from a previous study (Sandmeier, 2001).

Table 5 Quantification of metabolites in forage including ears

Experiment	1×					5×
DAT	0 (3 hours)	7	14	28	28	28
Plant Part	Forage	Forage	Forage	Forage	Ears	Ears
TRR [mg eq/kg]	1.91	1.95	1.43	2.40	0.74	2.84
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted	105.3 (2.01)	96.0 (1.87)	99.6(1.42)	89.3 (2.14)	95.9 (0.71)	81.4 (2.31)
Pinoxaden	9.8 (0.19)	1.0 (0.02)	0.4 (0.006)	n.d.	n.d.	n.d.
M2	22.8 (0.44)	1.8 (0.04)	1.4 (0.02)	n.d.	n.d.	n.d.
M3	1.1 (0.02)	1.3 (0.03)	1.2 (0.02)	0.2 (0.005)	n.d.	0.4 (0.012)
M4	64.2 (1.22)	43.4 (0.85)	39.2 (0.56)	7.3 (0.18)	42.7 (0.32)	26.7 (0.76)
M5 (glucose conjugate of M4)	0.5 (0.009)	29.5 (0.58)	29.1 (0.42)	56.3 (1.35)	19.2 (0.14)	21.1 (0.60)

Experiment	1×					5×
DAT	0 (3 hours)	7	14	28	28	28
Plant Part	Forage	Forage	Forage	Forage	Ears	Ears
TRR [mg eq/kg]	1.91	1.95	1.43	2.40	0.74	2.84
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
M6	0.3 (0.005)	7.5 (0.15)	9.8 (0.14)	8.4 (0.20)	6.4 (0.05)	4.5 (0.13)
M7 (malonyl-glucose conjugate of M4)	n.d.	3.6 (0.07)	1.0 (0.01)	3.9 (0.09)	n.d.	0.4 (0.01)
M8	n.d.	0.9 (0.02)	1.2 (0.02)	1.1 (0.03)	1.0 (0.007)	1.2 (0.035)
M9	n.d.	n.d.	0.5 (0.008)	0.5 (0.01)	0.4 (0.003)	n.d.
M10	n.d.	0.6 (0.01)	0.6 (0.009)	0.4 (0.01)	1.3 (0.01)	0.8 (0.02)
M11	0.3 (0.006)	n.d.	0.2 (0.003)	n.d.	n.d.	n.d.
M14	n.d.	n.d.	0.6 (0.009)	n.d.	1.3 (0.009)	1.8 (0.05)
Unknowns (up to 12)	4.1 (0.08)	5.2 (0.10)	6.5 (0.09)	8.4 (0.20)	15.3 (0.11)	11.0 (0.31)
Unresolved	2.1 (0.04))	1.3 (0.02)	7.7 (0.11)	2.7 (0.06)	8.3 (0.06)	13.4 (0.38)
Unextracted	2.2 (0.04)	4.4 (0.08)	6.0 (0.09)	7.1 (0.17)	8.8 (0.06)	15.0 (0.43)
Total	107.5 (1.91)	100.4 (1.95)	105.6 (1.43)	96.4 (2.40)	104.7 (0.74)	96.4 (2.74)

n.d. = Not detected

[a] As % of the total radioactivity found in the plant part, determined by combustion

Table 6 Quantification of metabolites in grain, husks and straw at 55 DAT

Experiment	1×			5×		
Plant Part	Grain	Husks	Straw	Grain	Husks	Straw
TRR [mg eq/kg]	0.25	3.13	5.49	0.84	11.84	15.90
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted	59.8 (0.15)	67.0 (2.10)	79.4 (4.34)	76.5 (0.64)	72.6 (8.60)	77.8 (12.37)
Pinoxaden	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M3	n.d.	1.6 (0.05)	1.5 (0.08)	n.d.	0.9 (0.14)	1.5 (0.18)
M4	19.7 (0.05)	14.3 (0.45)	36.8 (2.02)	18.2 (0.15)	24.9 (3.96)	15.1 (1.78)
M5 (glucose conjugate of M4)	5.1 (0.01)	13.2 (0.42)	6.0 (0.33)	8.8 (0.07)	8.7 (1.38)	8.2 (0.97)
M6	9.6 (0.02)	5.4 (0.17)	3.2 (0.17)	13.2 (0.11)	6.1 (0.96)	3.6 (0.43)
M7 (malonyl-glucose conjugate of M4)	4.3 (0.01)	n.d.	0.2 (0.009)	10.5 (0.09)	1.3 (0.21)	0.7 (0.09)
M8	n.d.	2.7 (0.08)	2.3 (0.13)	1.4 (0.001)	1.1 (0.17)	1.3 (0.16)
M9	n.d.	1.2 (0.04)	n.d.	n.d.	0.6 (0.07)	n.d.
M10	0.7 (0.002)	4.4 (0.14)	12.8 (0.70)	0.7 (0.006)	6.7 (1.06)	5.6 (0.67)
M11	n.d.	n.d.	1.9 (0.10)	n.d.	1.1 (0.18)	0.8 (0.10)
M14 (Pentose conjugate of M4)	n.d.	2.2 (0.07)	0.4 (0.02)	n.d.	1.2 (0.19)	1.3 (0.15)
M31	n.d.	n.d.	1.7 (0.09)	n.d.	1.4 (0.23)	0.9 (0.11)
M32	n.d.	n.d.	n.d.	n.d.	1.4 (0.23)	0.7 (0.08)
Unknowns (up to 5)	7.4 (0.02)	15.1 (0.47)	3.9 (0.22)	11.8 (0.10)	10.8 (1.73)	16.9 (1.99)
Unresolved	13.0 (0.03)	6.3 (0.20)	6.6 (0.36)	12.0 (0.10)	12.1 (1.93)	15.5 (1.84)
Unextracted	45.9 (0.11)	30.2 (0.95)	17.0 (0.93)	19.4 (0.16)	24.9 (2.95)	19.4 (3.08)
Total	105.7 (0.25)	97.2 (3.13)	96.4 (5.49)	95.9 (0.80)	97.5 (11.55)	97.2 (15.45)

n.d. = Not detected

a As % of the total radioactivity found in the plant part, determined by combustion

Samples of forage (1× experiment) were analysed within less than 10 months of sampling. Other samples were stored frozen for the following maximum periods: ears less than 10 months, grain approximately 1 month, and husks and straw were both stored for less than 2 months.

Storage stability was investigated at the end of the study by re-extraction and re-analysis of stored straw and grain samples from the 1× application rate. Analysis of the initial extracts and those stored frozen for a storage period of 21 months showed similar qualitative profiles. The storage stability of forage samples was demonstrated in the autumn application study.

Extractability of TRRs in grain was relatively higher (76% of the TRR) for the 5× samples in comparison with the 1× samples (60% of the TRR). The predominant metabolites in grain were M4 (18–20% of the TRR; 0.05–0.15 mg eq/kg), the malonyl-glucose conjugate of M4 (4–11% of the TRR; 0.01–0.09 mg eq/kg) and M6 (9.6–12% of the TRR; 0.02–0.11 mg eq/kg). The metabolite M7 from the 5× experiment was found at greater than 2-fold the levels observed in the 1× experiment (10% of the TRR vs 4.3% of the TRR), yet M10 was found at comparable levels (0.7% of the TRR; 0.002–0.006 mg/kg). Other minor metabolites included M5 and M8 (each representing ≤ 10% of the TRR; ≤ 0.10 mg eq/kg), the latter being detected in 5× grain only. The unextracted residue was relatively high in the 1× grain accounting for 46% of the TRR (0.113 mg eq/kg) while it only accounted for 19% of the TRR (0.16 mg eq/kg) in the 5× grain.

In grain samples from the 1× experiment, metabolites M4 and M6 accounted for most the radioactivity in the acid hydrolysate accounting for 79% of the TRR and 11% of the TRR, respectively, indicating that the grain unextracted residues predominantly consisted of M4 and M6 or conjugates thereof.

Approximately 78% of the TRRs in straw were extracted with an 80% acetonitrile solution. The predominant metabolites were M4 (15–37% of the TRR; 1.8–2.0 mg eq/kg) and M10. (1× experiment only: 13% of the TRR; 0.7 mg eq/kg). Several minor metabolites were found in straw from both the 1× and 5× experiments including M3, M6, M7, M8, M11, M14 and M31 with M32 only found in the straw sample from the 5× rate none of which accounted for > 10% of the TRR. Unextracted radioactivity in the straw sample from the 1× experiment accounted for 17% of the TRR (0.93 mg eq/kg). Acid hydrolysis of this fraction released 6.2% of the TRR and subsequent base hydrolysis released a further 8.2% of the TRR. The major metabolites identified in the organo-soluble fractions associated with these hydrolyses were M4 (29–60% of the TRR) and M6 (17–18% of the TRR). The unextracted residues of the straw sample from the 5× experiment (25% of the TRRs, 3.1 mg eq/kg) were not further subjected to identification/characterisation procedures.

The major metabolic pathways proceeded via ester hydrolysis of pinoxaden to M2, followed by hydroxylation to M4, conjugation with pentose to form M14 or with glucose to form M5 and malonylation to M7. Alternatively, the pathway proceeded by hydroxylation of M2 to M3 and subsequently to M10 or oxidation of M4 to M10. Further oxidation of the methyl-hydroxy function of M4 leads to the corresponding carboxylic acids M6 and M11, conjugation of M10 with glucose to M8 followed by malonylation to M9.

Study 3

Spring wheat (variety Toronit) grown under outdoor conditions was treated with pinoxaden, labelled in the [phenyl-1-^{14}C] (specific activity: 53.51 µCi/mg) and [oxadiazepin-3,6-^{14}C] (specific activity: 81.08 µCi/mg) and formulated as an emulsifiable concentrate formulation containing the safener cloquintocet-mexyl (Stingelin, 2002). The test material was applied once at growth stage BBCH 37–39 (flag leaf just visible to flag leaf fully unrolled) as a foliar spray at a rate of 62 g ai/ha for the phenyl label and 66 g ai/ha for the oxadiazepine label. For the phenyl label, samples of forage (immature plant) were harvested 0 and 14 days after application, while for oxadiazepine label the forage was sampled 0, 7, 14 days after application, and both forage and ears were sampled 28 days after application. Samples of grain, husk and straw were collected 67 DAT for both labels.

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

The radioactive residues in forage declined significantly from 3.4 mg eq/kg on Day 0 to 1.0 mg eq/kg at 14 DAT for the phenyl label and 3.9 mg eq/kg on Day 0 to 1.0 mg eq/kg on Day 14

with a subsequent increase to 1.2 mg eq/kg by 28 DAT for the oxadiazepine label. In general, total radioactive residues were similar for both labels, especially at maturity for grain, husk and straw.

Table 7 Summary of the total radioactive residues in spring wheat samples

Radiolabel	Total Radioactive Residues [mg eq/kg]							
	DAT 67 Grain	DAT 67 Husk	DAT 67 Straw	DAT 0 Forage	DAT 7 Forage	DAT 14 Forage	DAT 28 Forage	DAT 28 Ears
Phenyl	0.14	0.43	0.91	3.45	n.a.	1.02	n.a.	n.a.
Oxadiazepine	0.16	0.38	1.30	3.88	1.95	1.05	1.21	0.28

n.a. = Not analysed

The nature of the residue in forage, husk, straw and grain was investigated by sequential extraction with acetonitrile:water (80:20, v/v) for 6 hours and centrifuged. The procedure was repeated five times or until the radioactivity extracted was less than 5% compared to the radioactivity extracted in the first extraction step. The extracts were combined and analysed by radio-TLC and HPLC with radio detection. An aliquot of these extracts was then subjected to microwave extraction with 1-propanol:water (80:20, v/v; 10 min. at 100 °C, 20 min. at 120 °C, and 20 min. at 150 °C). The resulting unextracted residue was determined by combustion. Microwave extraction was not performed on the forage samples from the 0 ([phenyl-1-^{14}C] and [oxadiazepin-3,6-^{14}C]) and 7 ([oxadiazepin-3,6-^{14}C]) DAT samples.

The unextracted residue in straw ([oxadiazepin-3,6-^{14}C]), which was not released following acetonitrile:water (80:20 v/v) and microwave extractions, was hydrolysed with 1 N HCl for 6 hours at 100 °C under reflux. After filtration, the hydrolysate was partitioned with dichloromethane, the organic fraction was analysed by radio-TLC and the aqueous fraction was further purified by solid phase extraction. The residue remaining after hydrolysis with 1 N HCl was subsequently hydrolysed with 10% NaOH under reflux. The hydrolysate (lignin containing fraction) was filtered and the residue (cellulose containing fraction) washed, dried and combusted. The extract was adjusted to pH 1 with concentrated HCl and kept overnight at 5 °C. The sample was centrifuged and the extract was analysed by radio-TLC, and the residue (lignin fraction) was combusted.

To improve metabolite identification in grain, individual extracts (cold extracts and microwave extracts) of grain were separately hydrolysed with 1 N HCl under reflux for 6 hours. The samples were filtered and the extracts fractionated using cartridges which were washed with water and eluted with 50% acetonitrile/water. An aliquot of the residue, following microwave extraction, was hydrolysed by refluxing with 1 N HCl for 6 hours at 100 °C. The hydrolysate was fractionated using a cartridge which was washed with water and eluted with 50% acetonitrile/water.

Identification of metabolites was achieved by co-chromatographing metabolite fractions with cold or ^{14}C-labeled reference compounds.

Table 8 Quantification of metabolites in forage, grain, husk and straw—phenyl label

DAT	0 (1 hour)	14	67		
Plant Part	Forage	Forage	Grain	Husk	Straw
TRR [mg eq/kg]	3.45	1.02	0.14	0.43	0.91
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted residue [b]	95.4	95.3	78.1	79.4	78.7
Pinoxaden	7.3 (0.25)	0.4 (0.004)	n.d.	n.d.	n.d.
M2	71.9 (2.48)	0.8 (0.008)	n.d.	n.d.	n.d.
M3	1.0 (0.03)	1.7 (0.02)	n.d.	5.0 (0.02)	7.9 (0.07)
M4	9.6 (0.33)	30.5 (0.31)	9.4 (0.01)	29.8 (0.13)	36.5 (0.33)
M5 (glucose conjugate of M4)	n.d.	38.3 (0.39)	15.7 (0.02)	3.5 (0.02)	3.5 (0.03)
M6	n.d.	8.2 (0.08)	12.0 (0.02)	12.6 (0.05)	8.7 (0.08)
M7 (malonyl-glucose conjugate of M4)	n.d.	2.8 (0.03)	3.6 (0.005)	0.7 (0.003)	n.d.
M8	n.d.	1.4 (0.01)	n.d.	n.d.	n.d.
M10	n.d.	n.d.	n.d.	5.6 (0.02)	2.4 (0.02)

DAT	0 (1 hour)	14	67		
M11	n.d.	n.d.	n.d.	3.9 (0.02)	2.8 (0.02)
M14	n.d.	2.5 (0.03)	n.d.	n.d.	1.5 (0.01)
M32	n.d.	n.d.	n.d.	1.6 (0.007)	1.0 (0.009)
Unknowns (up to 10)	2.3 (0.08)	7.3 (0.07)	27.7 (0.04)	9.4 (0.04)	7.3 (0.06)
Unresolved	3.2 (0.11)	1.3 (0.01)	9.7 (0.01)	7.2 (0.03)	7.1 (0.06)
Unextracted	1.4 (0.05)	5.9 (0.06)	21.8 (0.03)	23.8 (0.10)	22.2 (0.20)
Total	96.8 (3.45)	101.2 (1.02)	99.9 (0.14)	103.2 (0.43)	100.8 (0.91)

n.d. = Not detected

[a] As % of the total radioactivity found in the plant part, determined by combustion

[b] Total extracted residue following cold extraction with 80% aqueous acetonitrile and hot microwave extraction with 80% aqueous 1-propanol

Table 9 Quantification of metabolites in forage, grain, husk and straw—oxadiazepine label

DAT	0 (1 hour)	7	14	28	28	67		
Plant Part	Forage	Forage	Forage	Forage	Ears	Grain	Husk	Straw
TRR [mg eq/kg]	3.88	1.95	1.05	1.21	0.28	0.16	0.38	1.30
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted [b]	99.3	101.5	93.0	97.3	96.2	79.1	69.2	70.2
Pinoxaden	5.4 (0.21)	1.7 (0.03)	0.7 (0.007)	n.d.	n.d.	n.d.	n.d.	n.d.
M2	79.0 (3.07)	1.8 (0.04)	0.8 (0.04)	n.d.	n.d.	n.d.	n.d.	n.d.
M3	1.2 (0.05)	3.7 (0.07)	0.8 (0.008)	0.7 (0.008)	2.0 (0.006)	n.d.	2.6 (0.01)	4.4 (0.06)
M4	8.6 (0.33)	52.2 (1.02)	31.0 (0.33)	5.6 (0.07)	47.8 (0.14)	7.7 (0.01)	27.4 (0.10)	34.0 (0.44)
M5 (glucose conjugate of M4)	n.d.	24.5 (0.48)	36.3 (0.38)	64.4 (0.78)	24.1 (0.07)	13.3 (0.02)	4.2 (0.02)	2.2 (0.03)
M6	n.d.	6.6 (0.13)	7.0 (0.07)	7.4 (0.09)	10.5 (0.03)	13.6 (0.02)	10.0 (0.04)	9.2 (0.12)
M7 (malonyl-glucose conjugate of M4)	n.d.	n.d.	4.4 (0.05)	5.0 (0.06)	n.d.	6.7 (0.01)	0.4 (0.002)	n.d.
M8	n.d.	2.2 (0.04)	1.7 (0.02)	2.4 (0.03)	n.d.	n.d.	n.d.	n.d.
M10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.6 (0.02)	1.5 (0.02)
M11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.9 (0.007)	0.8 (0.01)
M14	n.d.	2.2 (0.04)	0.2 (0.002)	0.8 (0.01)	0.8 (0.002)	n.d.	n.d.	1.0 (0.01)
M32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1 (0.004)	0.7 (0.009)
Unknowns (up to 10)	3.3 (0.13)	0.5 (0.01)	5.7 (0.06)	10.0 (0.12)	7.1 (0.20)	35.6 (0.06) [c]	13.1 (0.05)	10.3 (0.13)
Unresolved	1.8 (0.07)	6.2 (0.12)	4.7 (0.05)	1.21 (0.02)	3.8 (0.01)	2.1 (0.003)	4.0 (0.02)	6.0 (0.08)
Unextracted	0.8 (0.03)	4.3 (0.08)	5.3 (0.06)	5.2 (0.06)	8.6 (0.02)	18.7 (0.03)	27.0 (0.10)	27.8 (0.36)
Total	100.1 (3.88)	105.8 (1.95)	98.2 (1.05)	102.5 (1.21)	104.8 (0.28)	97.9 (0.16)	96.2 (0.38)	98.0 (1.30)

n.d. = Not detected

[a] In % of the total radioactivity found in the plant part, determined by combustion

[b] Total extracted residue following cold extraction with 80% aqueous acetonitrile and hot microwave extraction with 80% aqueous 1-propanol

[c] Fraction I1 (34.5%, 0.06 mg eq/kg) released after hydrolysis with 1 N HCl was almost quantitatively M4 and M6.

As analysis of the extracts for all samples was performed within six months of sampling, a determination of the storage stability is not required.

Up to 79% of the TRR was extracted from straw. The major metabolite was M4 accounting for 34–36% of the TRR (0.33–0.44 mg eq/kg). The metabolite M6 was also found at levels up to 9.2% of the TRR as well as the minor metabolites M5, M7, M10 and M11. Trace amounts of M3 and M32 were also detected, each representing ≤ 8% of the TRR; ≤ 0.07 mg eq/kg). Unextracted radioactivity in straw accounted for 22% of the TRR (0.20 mg eq/kg) for the phenyl label and 28% of the TRR (0.36 mg eq/kg) for the oxadiazepine label. A significant amount of this residue was released by acid hydrolysis, a major part of which partitioned into dichloromethane and was attributed to metabolites M4 (0.8–1.3% of the TRR) and M6 (2.4–2.7% of the TRR). Furthermore, 2.8% and 7.1% of the TRR, released by base hydrolysis, was characterised as cellulose and lignin, respectively.

In grain, nearly 80% of the radioactivity was extracted using acetonitrile:water followed by microwave extraction with 80% n-propanol. The metabolites identified were M4, M5, M6 and M7. A predominant metabolite fraction, I_1, initially remained unidentified. To characterise metabolite fraction I_1 and the unextracted residue (which accounted for 20% of the TRR for both radiolabels), individual extracts and unextracted residues from both the phenyl and oxadiazepine labels were hydrolysed with 1 N HCl and subjected to microwave extraction. This released 92% of the TRR, and about 66% of this partitioned into the organic phase. In the case of the phenyl label, the released radioactivity consisted almost entirely of M4 (58% of the TRR) and M6 (6.8% of the TRR). For the oxadiazepine label, the metabolites M4, M5 and M6 accounted for 65%, 7.4% and 12% of the TRRs, respectively.

The major metabolic pathway in spring wheat proceeded via ester hydrolysis of pinoxaden to M2, hydroxylation of M2 to M4, conjugation of M4 with pentose to form M14 or with glucose to M5 followed by malonylation to M7. A further step included hydroxylation of M2 to M3 and subsequently M10, or alternatively oxidation of M4 to M10, or of M5 to M8. Conjugation of M10 with glucose to M8 was followed by malonylation to M9. Further oxidation of the methyl-hydroxy function of M4 leads to the corresponding carboxylic acids M6 and M11. A minor pathway is hydroxylation of the ethyl-side chain of M10 followed by cyclisation to M32, See Figure 1.

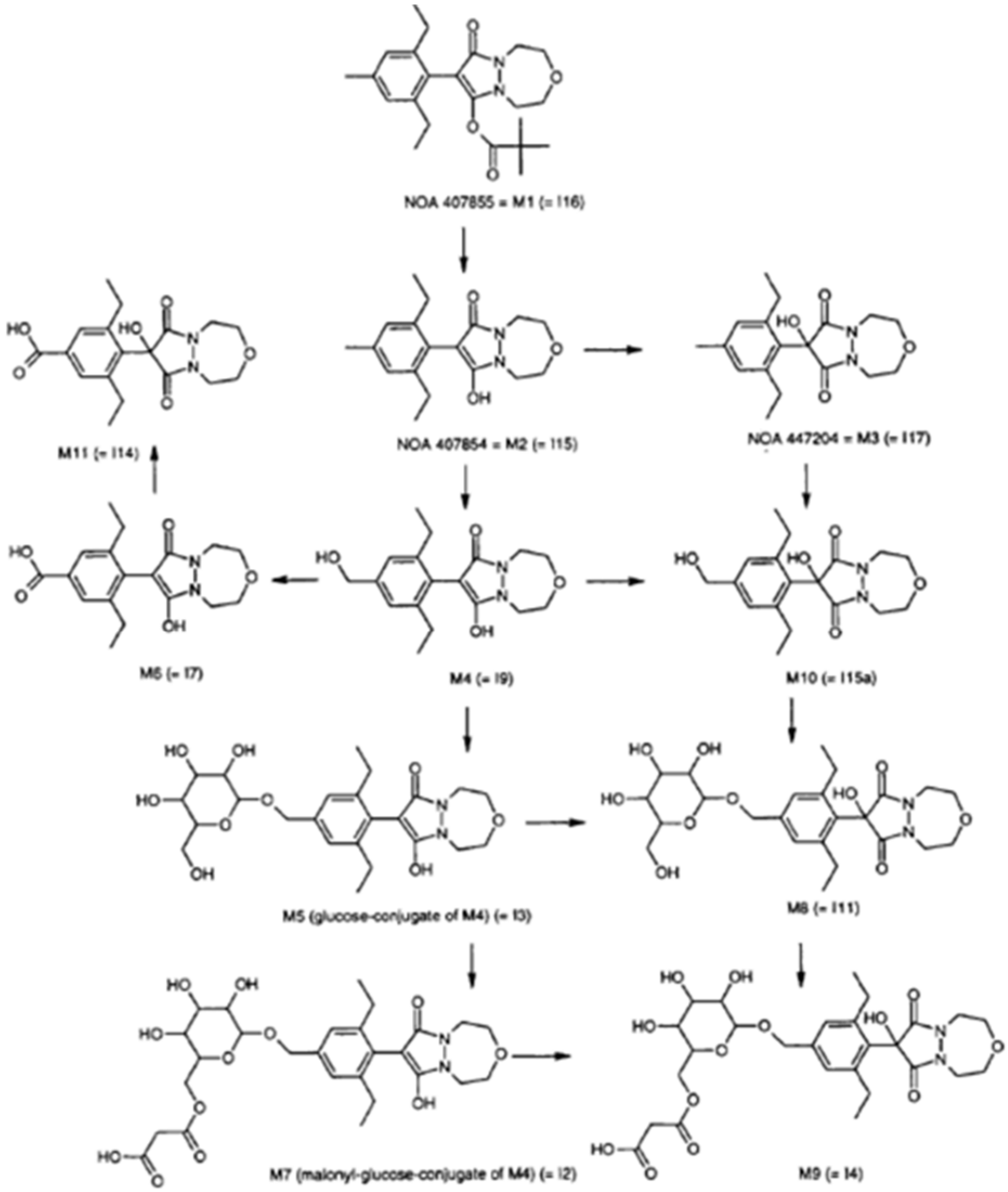


Figure 1 Metabolic pathway of pinoxaden in winter and spring wheat

Farm animal metabolism

The Meeting received information on the fate of ^{14}C- labelled pinoxaden, and the major plant metabolite ^{14}C-labelled M4, in lactating goat and ^{14}C- labelled pinoxaden in laying hens. Metabolism in laboratory animals (rat) was summarized and evaluated by the WHO panel of the 2016 JMPR.

Lactating goat

The metabolism of [phenyl-1-^{14}C]-labelled pinoxaden (specific activity: 16.8 µCi/mg) was investigated in two lactating goats (*Capra hircus*), weighing 38.5 kg and 48.5 kg, dosed orally once daily for 4 consecutive days, by a balling gun, at a dose level of 150 mg/day equivalent to 115–126 ppm in the diet (Rumbeli, 2002b). Milk production ranged from 1.0–1.5 L/day. During the treatment period, milk was collected twice daily while urine and faeces were collected once daily. At sacrifice (within 6 hours after the final dose) samples of liver, kidney, muscle (loin and leg), fat (omental and perirenal), blood, bile and GI tract were collected.

The total radioactive residues (TRRs) were determined by LSC) for liquid samples and by combustion/LSC or tissue solubilisation/LSC for solid samples.

The major route of elimination of the radioactivity was via the urine which accounted for 45–48% of the total administered radioactivity (AD), while faeces accounted for 15–21% of the AD and milk accounted for ≤ 0.01% of the AD. The tissue burden was very low (< 1% of the AD) considering the dosing levels. The overall recovery of administered radioactivity averaged 86%.

The total radioactive residues (TRRs) were highest in kidney (1.70–4.55 mg eq/kg) followed by liver (0.94–1.39 mg eq/kg), muscle (0.06–0.11 mg eq/kg for both leg muscle and loin muscle), fat (0.01–0.04 mg eq/kg) and milk (0.01–0.02 mg eq/kg).

Table 10 Balance of radioactivity in goats following oral administration of [phenyl-1-^{14}C]-pinoxaden for 4 days

Sample	Goat 1		Goat 2	
	%AD	mg eq/kg	%AD	mg eq/kg
Milk (0–78 h)	0.011	0.02	0.008	0.01
Liver	0.17	1.39	0.12	0.94
Kidney	0.08	4.55	0.04	1.70
Omental fat	0.004	0.02	0.002	0.01
Perirenal fat	0.004	0.04	0.002	0.01
Leg muscle	0.05	0.11	0.03	0.06
Loin muscle	0.003	0.11	0.003	0.06
GI tract/Rumen	17.74	–	19.25	–
Blood	0.06	0.29	0.05	0.14
Bile	0.15	53.66	0.09	52.18
Urine	47.58	–	44.74	–
Faeces	14.97	–	20.95	–
Cage wash	3.85	–	1.55	–
Total Recovery	84.7		86.8	

TRRs in milk seemed to plateau by the 2nd day of dosing.

Table 11 TRRs in goat milk following oral administration of [phenyl-1-^{14}C]-pinoxaden for 4 days

Collection Day	Goat 1	Goat 2
	mg eq/kg	mg eq/kg
Day 1	0.016	0.010
Day 2	0.018	0.012
Day 3	0.018	0.013
Day 4	0.018	0.012

The nature of the residue in milk, fat, muscle, kidney and liver samples was investigated following homogenisation with acetonitrile and extraction using acetonitrile:water (80:20 v/v) which

was repeated until the radioactivity extracted was less than 5% compared to the radioactivity extracted in the first extraction step.

Identification of metabolites was accomplished by isolation using SPE, HPLC and TLC followed by MS and ^{1}H-NMR or by co-chromatography with authentic reference standards.

Table 12 Characterization and identification of radioactivity in goat milk, kidney and liver (115–126 ppm in the diet)

Fraction	Muscle		Fat		Liver		Kidney		Milk (0–78 h)	
	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
Extracted	0.078	95.7	0.017	92.8	1.12	97.0	2.93	99.2	0.015	98.4
M2	0.073	89.8	0.0014	78.6	0.100	85.9	2.67	90.4	0.013	87.8
M3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.067	2.3	0.0001	0.4
M4	0.0005	0.7	0.0002	1.1	0.019	1.6	0.014	0.5	0.0003	1.7
M12	0.004	4.4	0.002	8.5	0.080	6.9	0.12	4.2	0.0009	6.2
M13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.010	0.3	n.d.	n.d.
Unextracted	0.004	4.3	0.001	7.2	0.035	3.0	0.024	0.8	0.0002	1.6
Total	0.081	100	0.018	100	1.16	100	2.95	100	0.015	100

n.d. = Not detected

All homogenised samples were extracted and analysed within three months of collection. Therefore, the determination of storage stability is not required.

Pinoxaden was rapidly and completely metabolized in lactating goats. The hydrolysis product of the parent compound, M2, was the major metabolite in all tissue and milk samples accounting for 79–90% of the TRRs. The glucuronide acid conjugate of M2, metabolite M12, accounted for 4.4–8.5% of the TRRs followed by the minor metabolites M4 (0.5–1.7% of the TRRs) and M3 (0.4–2.3% of the TRRs), the latter being observed only in kidney and milk. Lastly, the minor metabolite M13 was the only other metabolite detected in liver (0.3 % of the TRR), see Figure 2.

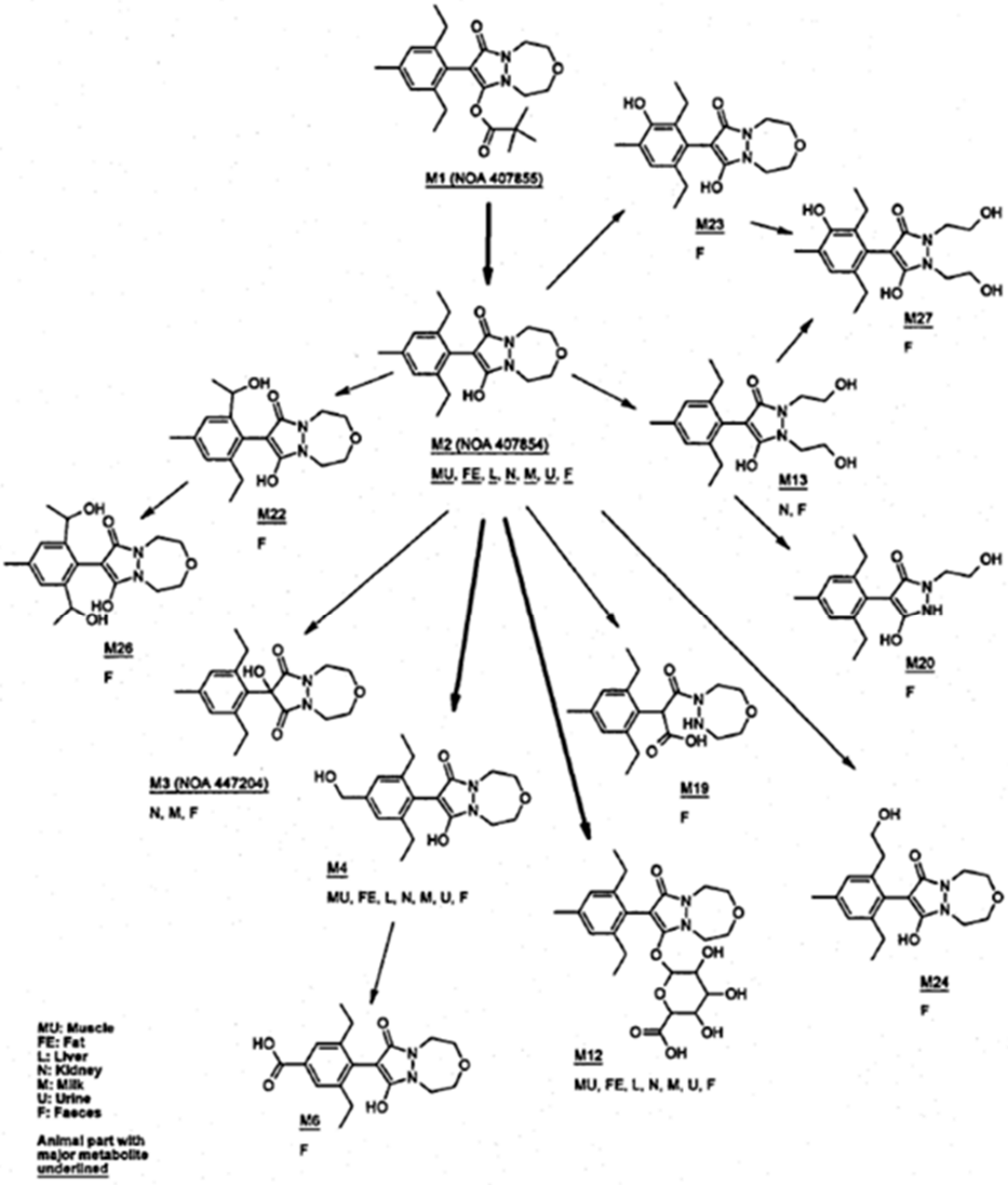


Figure 2 Metabolic pathway of pinoxaden in the lactating goat

The metabolism of the major plant metabolite M4 was investigated in two lactating goats (*Capra hircus*), weighing on average 57 kg, dosed orally once daily for 4 consecutive days, by a balling gun, with [pyrazole-5-^{14}C]-labelled M4 (specific activity: 10.3 µCi/mg) at a dose level of approximately 15 mg/day equivalent to 9 and 11 ppm in the diet (Close, 2003). Milk production ranged from 2.3–3 L/day. During the treatment period, milk was collected twice daily while urine and faeces were collected once daily after administration of the test substance. At sacrifice (within 6 hours after the final dose) samples of liver, kidney, muscle, fat, blood, bile and GI tract were collected.

The total radioactive residues (TRRs) were determined by liquid LSC for liquid samples and by combustion/LSC or tissue solubilisation/LSC for solid samples.

The major route of elimination of the radioactivity was via the faeces which accounted for 58–62% of the total administered radioactivity (AD), while urine accounted for 8.4–8.9% of the AD and milk accounted for ≤ 0.01% of the AD. The tissue burden was very low (< 0.1% of the AD). The overall recovery of administered radioactivity averaged 92%.

The total radioactive residues (TRRs) were highest in kidney (0.05 mg eq/kg) followed by liver (0.02–0.03 mg eq/kg). TRRs in milk were < 0.002 mg eq/kg while those in fat and muscle were each < 0.011 mg eq/kg, demonstrating very limited transfer of residues.

Table 13 Balance of radioactivity in goats following oral administration of [pyrazole-5-^{14}C]-M4 for 4 days

Sample	Goat 1		Goat 2	
	%AD	mg eq/kg	%AD	mg eq/kg
Milk	< 0.01	< 0.002	< 0.01	< 0.002
Liver	0.04	0.02	0.05	0.03
Kidney	0.01	0.05	0.01	0.05
Fat	< 0.01	< 0.011	< 0.01	< 0.011
Muscle	< 0.01	< 0.011	< 0.01	< 0.011
GI tract/Rumen	24.4	1.2	22.8	1.2
Blood	< 0.01	< 0.011	< 0.01	< 0.011
Bile	0.01	5.8	0.02	3.0
Urine	8.9	–	8.4	–
Faeces	57.7	–	61.6	–
Total Recovery	91.1		92.8	

While the nature of the residues in kidney and liver was investigated following at least two extractions using acetonitrile:water (80:20 v/v), the nature of the residue in milk, fat and muscle, was not further elucidated as TRRs were too low.

Identification of metabolites in liver and kidney was accomplished by co-chromatography with authentic reference standards using radio-TLC and HPLC with radio and UV-detection.

Table 14 Characterization and identification of radioactivity in composite samples of goat liver and kidney (9–11 ppm in the diet)

Fraction	Kidney (0.044 mg/kg)		Liver (0.025 mg/kg)	
	%TRR	mg eq/kg	%TRR	mg eq/kg
Extracted	91.6	0.040	87.9	0.022
M4	55.0	0.02	40.8	0.01
M10	9.1	0.004	8.1	0.002
Unextracted	1.5	< 0.001	6.5	0.002
Total	93.1	0.041	94.4	0.024

All homogenised liver and kidney samples were analysed within approximately 8 months of sampling. Re-extraction of samples 241 days (approximately 8 months) after sacrifice gave similar metabolic profiles by HPLC as the samples extracted 17 and 18 days post sacrifice. Therefore, the tissue residues were considered stable under frozen conditions.

The major component identified in kidney and liver was unchanged M4. Minor amounts of the hydroxylated metabolite M10 were also identified. Therefore, the only metabolic route was hydroxylation of M4 at the 8-position to form M10.

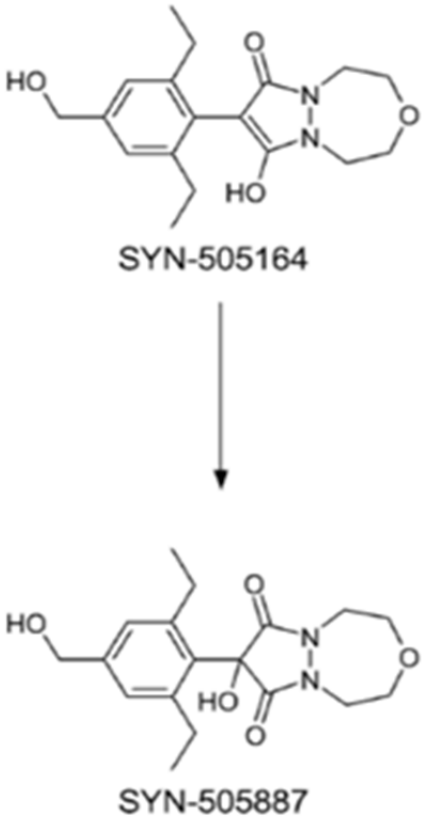


Figure 3 Metabolic pathway of the metabolite SYN 505164 (M4) in the lactating goat

Laying hen

Five Leghorn Hyline W-98 laying hens were dosed orally once daily for 4 consecutive days with [phenyl-1-^{14}C]-labelled pinoxaden (specific activity: 16.8 µCi/mg), at 12.38 mg/day, equivalent to 96.7 ppm in the feed (Rumbeli, 2002a). Eggs were collected twice daily, in the morning before and in the afternoon after administration, while excreta were collected once daily. The animals were sacrificed approximately 6 h after the last dose and the liver, kidney, lean meat, skin with attached fat and peritoneal fat were collected and pooled. The total radioactive residues (TRRs) were determined by LSC for liquid samples and by combustion/LSC or tissue solubilisation/LSC for solid samples.

Approximately 85% of the administered dose (AD) was recovered, most of which (75% of the AD) was excreta-related. Total radioactive residues (TRR) in egg white and egg yolk accounted for about 0.007% of AD (0.003% AD in egg white plus 0.004% AD in yolk). The TRRs in egg white reached a plateau by Day 3 of dosing; however, no plateau was observed in egg yolk. The tissue burden was very low (< 0.2% of the AD) with highest concentrations found in kidney (1.8 mg eq/kg) followed by liver (0.62 mg eq/kg), skin (0.12 mg eq/kg), lean meat (0.06 mg eq/kg) and peritoneal fat (0.04 mg eq/kg).

Table 15 Balance of radioactivity in hens following oral administration of [^{14}C]pinoxaden for 4 days

Sample	%AD	mg eq/kg
Egg white	0.003	0.01
Egg yolk	0.004	0.03
Liver	0.06	0.62
Kidney	0.04	1.8

Sample	%AD	mg eq/kg
Lean meat	0.04	0.06
Skin and attached fat	0.02	0.12
Peritoneal fat	0.002	0.04
Blood	0.008	0.30
Excreta	70.9	–
Cage wash	4.1	–
Gizzard	10.0	–
Total Recovery	85.3	

Table 16 TRRs in eggs following oral administration of [^{14}C]pinoxaden for 4 days

Day	Egg White		Egg Yolk	
	%AD	mg eq/kg	%AD	mg eq/kg
1	0.001	0.012	0.000	0.000
2	0.001	0.015	0.001	0.022
3	0.001	0.013	0.002	0.048
4	0.001	0.013	0.002	0.064
	0.003 (Total)	0.013 (Mean)	0.004 (Total)	0.031 (Mean)

Homogenised tissue samples (lean meat, fat and skin), egg white and egg yolk were extracted sequentially with acetonitrile, acetonitrile:water (80:20, v/v) and methanol:water (80:20, v/v), shaken, centrifuged and filtered until less than 5% of the initially extracted radioactivity remained. Extracts were concentrated, usually by rotary evaporation. Liver samples were extracted with methanol, followed by methanol:water (80:20, v/v). Where necessary, specific samples, for example egg yolks and liver samples, underwent further extraction and clean-up via partitioning against hexane and solid phase extraction (SPE). Tissue samples were also additionally extracted with mixtures of methanol and formic acid where required. Radioactivity in the extracts were either analysed directly by LSC, or combusted in a sample oxidiser, then analysed by LSC.

Unextracted residues in egg yolk were extracted with n-hexane and filtered. The remaining post-extraction solids were dried, re-extracted with methanol:water:formic acid 50:50:0.1 v/v/v and filtered to separate the extract from the solid residues. The latter were hydrolysed with 1 N HCl for 15 hours (temperature not provided) after which the solid samples were solubilised and analysed by LSC.

Isolation of metabolites was performed by fractionation using HPLC. The fractions were analysed using LC-MS, NMR or 2-D TLC. The nature of the residues in extracts was elucidated using LC-MS, ^{1}H-NMR or 2-D TLC or by co-chromatography against authentic reference standards.

Table 17 Characterization and identification of radioactivity in eggs, liver, skin and lean meat (97 ppm in the diet)

Fraction	Egg white		Egg yolk		Liver		Skin with attached fat		Lean Meat	
	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
Extracted	0.012	95.1	0.021	67.2	0.597	96.7	0.107	92.5	0.056	93.0
M2	0.006	45.5	0.0005	1.7	0.041	6.7	0.010	8.6	0.010	17.0
M4	0.0004	27.3	0.007	23.7	0.111	18.0	0.035	30.2	0.027	44.3
M6	n.d.	n.d.	0.004	13.0	0.279	45.2	0.026	22.4	0.008	13.9
M31	n.d.	n.d.	n.d.	n.d.	0.005	0.8	0.002	1.3	n.d.	n.d.
M33	0.0009	7.0	0.001	3.7	0.026	4.1	0.010	8.6	0.004	7.2
M34	0.0001	1.1	0.001	3.5	0.009	1.5	0.004	3.2	0.002	3.8
M35	0.0002	1.5	0.0005	1.7	0.003	0.5	0.003	2.7	n.d.	n.d.
Unknown	0.001	10.0	0.003	10.4	0.092	14.8	0.010	8.4	0.001	2.0
Others	0.0003	2.6	0.003	9.4	0.031	5.1	0.008	7.3	0.003	4.8
Unextracted	0.0006	4.9	0.010	32.8	0.020	3.2	0.009	7.5	0.004	6.9
Total	0.013	100.0	0.031	100.0	0.616	99.9	0.116	100.0	0.060	99.9

n.d. = Not detected

All homogenised samples were analysed within ca.9 months of sampling. Storage stability of liver and blood was investigated, where liver samples were homogenised, sequentially extracted with acetonitrile and methanol:water (80:20, v/v) and analysed. Blood samples were also extracted with acetonitrile and methanol:water (80:20 v/v) and analysed. These extracts were stored and subsequently re-analysed approximately 17 months later. Following 17 months of frozen (–18 °C) storage, the composition of the metabolites for both the liver samples and blood samples remained unchanged.

No parent compound was detected in any of the samples. In all samples ≥ 76% of the TRR was identified, with unextracted residues below 8%, except for egg yolks, where it was about 33% of the TRR, (0.01 mg/kg), of which 12% was released by hydrolysis with 1 N HCl.

The major metabolites in all tissues and eggs were M2 (1.7–46% of the TRR, 0.0005–0.041 mg eq/kg), M4 (18–44% of the TRR, 0.0004–0.111 mg eq/kg) and M6 (13–45% of the TRR, 0.004–0.279 mg eq/kg; only observed in egg yolks).

Along with the major metabolites listed above, additional metabolites were identified, namely M31 (aldehyde precursor of M6), M33 (ether cleavage of oxadiazepine moiety of M4), M34 (dealkylation product of M33) and M35 (hydroxylation at the 1-ethyl position of M4), none of which exceeded 10% of the TRR (0.01 mg eq/kg).

The metabolic pathway proceeded via hydrolysis of the parent compound to M2 followed by hydroxylation of the 4-methyl group of the phenyl moiety to form M4. This was followed by further oxidation of M4 via the intermediate product M31 to M6. A further metabolic route was ether cleavage of the oxadiazepine moiety of M4 to M33 followed by dealkylation to give M34. In some samples hydroxylation at the 1-ethyl position to give M35 was observed, see Figure 4.

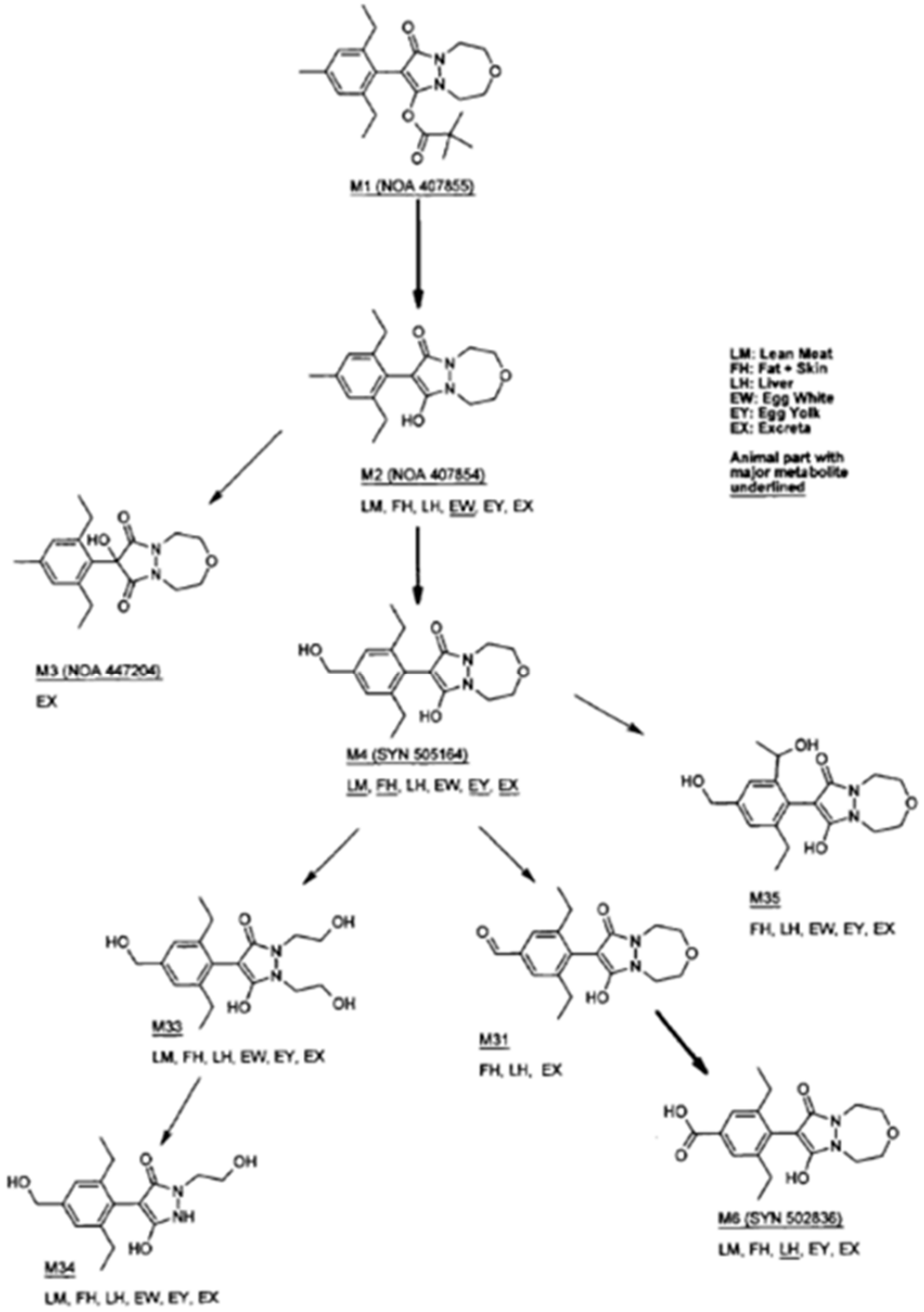


Figure 4 Metabolic pathway in the hen

Environmental fate in soil, water, water-sediment systems

The FAO Manual (FAO, 2016) explained the data requirements for studies of environmental fate. The focus should be on those aspects that are most relevant to MRL setting. For the herbicide pinoxaden, supervised residue trials data were received for foliar spray on annual crops. Therefore, per the FAO manual, only studies on aerobic degradation and hydrolysis were evaluated. For information on hydrolysis see also section "Physical and chemical properties",.

Rotational crop studies

Study 1

Pinoxaden, labelled in the [phenyl-1-^{14}C] ring (specific activity: 52.43 µCi/mg) and formulated as an emulsifiable concentrate formulation was applied once to bare clay loam soil (33.6% sand, 44.7% silt, 21.6% clay; pH 7.1; 1.8% organic matter; 24.2 meq/100 g CEC) at a rate of 60.3 g ai/ha, equivalent to the registered GAP (Sandmeier, 2002). Spring lettuce (variety Sunny) and autumn lettuce (variety Libusa), spring radish (variety Selma) and autumn radish (variety Wiela), spring wheat (variety Toronit) and winter wheat (variety Galaxie) were cultivated under outdoor conditions per procedures simulating normal agricultural practices. Crops were planted as follows: lettuce and radish 30 and 120 days, spring wheat 30, 120 and 365 days, and winter wheat 177 days after soil treatment. Lettuce was transplanted, and spring and winter wheat and radishes were sown after soil treatment.

Samples of lettuce heads, radish tops and roots, spring and winter wheat as whole tops at 50% maturity (forage), fodder (straw and husk) and grain were sampled at the appropriate intervals. In addition, soil samples were taken immediately after application and up to 496 days after treatment and analysed by combustion.

Fresh lettuce samples were homogenised in the presence of liquid nitrogen while radish samples were separated into roots and tops, then homogenised in the presence of liquid nitrogen. Whole winter and spring wheat samples harvested at the autumn cutting (25% maturity) and at 50% maturity were homogenised in the presence of liquid nitrogen. Mature wheat samples were dried at room temperature and separated manually into fodder (straw plus husk) and grain. Fodder and grain samples were homogenised by grinding in mills. After homogenisation, samples were combusted and the levels of radioactivity were measured by LSC.

The total radioactive residues (TRRs) were determined by combustion and LSC. The radioactive residues in all crop fractions were very low, with a maximum of 0.038 mg/kg in spring wheat fodder at the 120-day plant-back interval. Analysis was only conducted on crop fractions where residues were above 0.01 mg/kg.

Table 18 Distribution of total radioactive residues of pinoxaden in succeeding crops following bare ground application of [^{14}C]phenyl pinoxaden

Crop	Plantback Interval (Days)	Harvest (DAT)	Total Radioactive Residues (mg eq/kg)
Lettuce			
Heads	30	84	0.011
	120	170	0.001
Radish			
Tops	30	84	0.014
Roots	30	84	0.001
Radish			
Tops	120	170	0.001
Roots	120	170	< 0.001
Spring Wheat			
50% Maturity	30	84	0.024
Fodder [a]	30	141	0.035
Grain	30	141	0.004
Spring Wheat			
50% Maturity	120	170	0.008
Fodder	120	240	0.038
Grain	120	240	0.005

Crop	Plantback Interval (Days)	Harvest (DAT)	Total Radioactive Residues (mg eq/kg)
Spring Wheat			
50% Maturity	365	450	0.003
Fodder	365	496	0.005
Grain	365	496	0.001
Winter Wheat			
Fall Cutting	177	240	0.004
50% Maturity	177	430	0.001
Fodder	177	470	0.009
Grain	177	470	0.001

[a] Fodder = Straw + husk

For extraction of the radioactive residues, the homogenised plant material was suspended in a mixture of acetonitrile:water (80:20, v/v) using a mechanical shaker for 4–24 hours, and then centrifuged. This procedure was repeated until the radioactivity of the last extract was equal or less than 5% of the radioactivity contained in the first extract. The extracts were combined and analysed by radio-TLC. The unextracted radioactivity was determined by combustion.

Aliquots of extracts from lettuce and fodder were hydrolysed with 1 N HCl under reflux for 6 hours. The hydrolysates were fractionated using a cartridge which was washed with water and eluted with 50% acetonitrile/water. Polar conjugates were hydrolysed using either β-glucosidase (37 °C, overnight) or cellulase (37 °C, overnight) and the mixtures analysed by radio-TLC.

Identification of metabolites was achieved either by co-chromatographing metabolite fractions with reference standards, or with metabolite fractions isolated and identified from the wheat metabolism study (Sandmeier, 2001).

Table 19 Summary of characterization and identification of residues in rotational crop samples following bare ground application of [^{14}C]phenyl pinoxaden

Plant Back Interval (Days)	30	30	30	30	120
Plant Part	Lettuce Heads	Radish Tops	Spring Wheat Forage (50% Maturity)	Spring Wheat Fodder (husk & straw)	Spring Wheat Fodder (husk & straw)
TRR [mg/kg]	0.011	0.014	0.024	0.035	0.038
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted	86.1	100.9	93.6	65.7	73.3
M2	4.8 (0.0005)	n.d.	n.d.	n.d.	n.d.
M3	5.3 (0.0006)	6.3 (0.0009)	17.6 (0.0042)	9.0 (0.0032)	16.1 (0.0061)
M8	5.6 (0.0006)	n.d.	13.1 (0.0031)	3.3 (0.0012)	7.0 (0.0027)
M9	n.d. [c]	n.d. [c]	20.3 (0.0049)	3.9 (0.0014)	13.7 (0.0052)
M10	n.d.	n.d.	n.d.	5.8 (0.0020)	2.2 (0.0008)
M11	n.d.	n.d. [c]	n.d.	2.4 (0.0008)	0.3 (0.0001)
M32	n.d.	0.8 (0.0001)	n.d.	4.2 (0.0015)	3.6 (0.0014)
Unknowns (up to 15)	61.2 (0.0067) [b]	72.7 (0.0102)	28.6 (0.0069)	18.8 (0.0065)	20.9 (0.0079)
Unresolved	9.3 (0.0010)	21.0 (0.0029)	14.0 (0.0034)	18.3 (0.0064)	9.5 (0.0036)
Unextracted	17.1 (0.0019)	7.7 (0.0011)	14.4 (0.0035)	40.5 (0.0142)	27.3 (0.0104)
Total	103.2 (0.011)	108.6 (0.014)	108.0 (0.024)	106.2 (0.035)	100.6 (0.038)

n.d. = Not detected

[a] In % of the total radioactivity found in the plant part, determined by combustion

[b] Contains a metabolite fraction (43.3% and 0.0048 mg/kg) which after refluxing with 1 N HCl releases M3

[c] Trace amounts of the corresponding metabolite may be present but could not be identified with certainty due to the very low amount

Lettuce

Lettuce was transplanted 30 and 120 days after treatment of the soil. Due to the very low residue at 120 days (0.001 mg/kg), no lettuce was planted at 365 days. Furthermore, due to the very low residue at 120 days, no characterisation of the radioactivity was performed. In the 30-day sample, about 86% of the TRR was extracted. While no parent was observed, several metabolites were detected, none of which exceeded 10% of the TRR or 0.01 mg/kg. Metabolites identified were M2, M3 and M8. The unidentified fraction (I_{13a}) accounted for 43% of the TRR (0.005 mg/kg) and acid hydrolysis converted this fraction to M3.

Radish

Radish was sown into the soil 30 and 120 days after treatment. Like lettuce, as residues at 120 days in both roots and tops were very low (< 0.001 mg eq/kg), no radish seed was planted at 365 days. The TRRs in radish roots were 0.001 mg/kg and < 0.001 mg/kg at the 30 and 120-day plant-back intervals, respectively. The corresponding TRRs for radish tops were 0.014 and 0.001 mg/kg, respectively. Due to the very low residues, characterisation of the radioactivity was only performed on radish tops from the 30-day plant-back interval. Radio-TLC analysis of the extracts revealed a very complex metabolite pattern. All metabolite fractions were well below 0.01 mg/kg. Moreover, no parent compound was detected and M3 accounted for 6.3% of the TRR (0.0009 mg eq/kg). After partitioning the crude extract at pH 7 and pH 2, analysis of the organic and aqueous phases by radio-TLC further demonstrated a complex metabolite pattern.

Wheat

At the 30-day plant-back interval the residue in spring wheat grain was very low at 0.004 mg/kg and hence no further work was conducted on this sample. Residues in fodder amounted to 0.035 mg/kg with an extractability of about 66%. Metabolites identified were M3, M8, M9, M10, M11 and M32, none of which exceeded 10% of the TRR (0.01 mg eq/kg). Acid hydrolysis of the unextracted residue (41%) released about 15% of the TRR. Only 5.7% of the TRR partitioned into the organic phase, the major part of which was attributed to M10.

At the 120-day plant-back interval, the TRR in grain was 0.005 mg/kg. Due to the low TRRs no further work was conducted on this sample. The TRR in fodder amounted to 0.038 mg/kg, about 73% of which was extracted. Metabolites identified were M3, M8, M9, M10, M11 and M32, none of which exceeded 10% of the TRR (0.01 mg eq/kg). The metabolite M10 accounted for 23% of the TRR following acid hydrolysis and partitioning of the solvent extract. At the 365-day plant-back interval the residues in all spring wheat matrices were well below 0.01 mg/kg and hence no further work was conducted on samples from this interval.

Winter wheat seed was planted 177 days after treatment. The residues in all crop fractions were well below 0.01 mg/kg and hence no further work was conducted on samples from this interval.

Analysis of soil samples indicated that most the TRRs were in the 0–10 cm layer where the parent pinoxaden rapidly degraded within the first 6 days (88% of the TRR to non-detected) after soil application. Residues of M2 and M3 peaked to 20% of the TRR and 67% of the TRR, respectively, by Day 3; however, by Day 10, residues of M2 were no longer detectable, while M3 continued to decline gradually, reaching 6% of the TRR by Day 496. Traces of M11 were only observed starting on Day 6, peaked on Day 30 (3.9% of the TRR) and were no longer detectable by Day 265. Up to 11 unknown metabolites were observed throughout the study duration, none of which exceeded 10% of the TRR.

Study 2

Pinoxaden, labelled in the [oxadiazepin 3,6-^{14}C] position (specific activity: 105.68 µCi/mg) and formulated as an emulsifiable concentrate formulation was applied once to bare clay loam soil (22.2% sand, 44.0% silt, 33.8% clay; pH 7.2; 1.8% organic matter; 23.0 meq/100 g CEC) at a rate of 65.5 g ai/ha, equivalent to the registered GAP (Sandmeier, 2003b). Spring lettuce (variety Sunny) and autumn lettuce (variety Libusa), spring radish (variety Selma) and autumn radish (variety Wiela),

spring wheat (variety Toronit) and winter wheat (variety Galaxie) were cultivated under outdoor conditions per procedures simulating normal agricultural practices. Crops were planted as follows: lettuce and radish 29 and 120 days after soil treatment, spring wheat 29, 120 and 361 days after soil treatment, and winter wheat 168 days after soil treatment. Lettuce was transplanted, and spring and winter wheat and radishes were sown after soil treatment.

Samples of lettuce heads, radish tops and roots, spring and winter wheat as whole tops at 50% maturity (forage), fodder (straw and husk) and grain were sampled at the appropriate intervals following application. In addition, soil samples were taken immediately after application and at each sowing and the last sampling event.

Fresh lettuce samples were homogenised in the presence of liquid nitrogen. Radish samples were separated into roots and tops, then homogenised in the presence of liquid nitrogen. Whole spring and winter wheat samples harvested at the autumn cutting (25% maturity) and at 50% maturity were homogenised in the presence of liquid nitrogen. Mature wheat samples were dried at room temperature and separated manually into fodder (straw + husk) and grain. Fodder and grain samples were homogenised by grinding in mills.

The total radioactive residues (TRRs) were determined by combustion and LSC.

The total radioactive residues (TRR) in all crop fractions were very low, with a maximum of 0.077 mg/kg in spring wheat fodder at the 29-day plant-back interval. Further analysis was only conducted on crop fractions where residues were above 0.01 mg/kg.

Table 20 Distribution of total radioactive residues of pinoxaden in succeeding crops following bare ground application of [^{14}C]oxadiazepine pinoxaden

Crop	Plantback Interval (Days)	Harvest (DAT)	Total Radioactive Residues (mg eq/kg)
Lettuce			
Heads	29	70	0.014
	120	166	0.001
Radish			
Tops	29	70	0.022
Roots	29	70	0.002
Radish			
Tops	120	166	0.001
Roots	120	166	< 0.001
Spring Wheat			
50% Maturity	29	70	0.048
Fodder [a]	29	139	0.077
Grain	29	141	0.007
Spring Wheat			
50% Maturity	120	166	0.004
Fodder	120	249	0.032
Grain	120	249	0.004
Spring Wheat			
50% Maturity	361	433	0.001
Fodder	361	473	0.004
Grain	361	473	0.001
Winter Wheat			
Fall Cutting	168	249	0.002
50% Maturity	168	424	0.001
Fodder	168	447	0.005
Grain	168	447	0.001

[a] Fodder = straw + husks

All harvested samples were kept frozen at ≤ -18 °C. None of the samples were stored for greater than 6 months from the time of sampling until analysis; therefore, no storage stability data is required.

For extraction of the radioactive residues, the homogenised plant material was suspended in a mixture of acetonitrile:water (80:20; v/v) using a mechanical shaker for 4–24 hours, and then centrifuged. This procedure was repeated until the radioactivity of the last extract was equal or less than 5% of the radioactivity contained in the first extract. The extracts were combined and analysed by 2-dimensional radio-TLC. The unextracted radioactivity was determined by combustion.

Identification of metabolites was achieved either by co-chromatographing metabolite fractions with reference standards, or with metabolite fractions isolated and identified from the wheat metabolism studies (Sandmeier, 2001).

Table 21 Summary of characterization and identification of residues in rotational crop samples following bare ground application of [^{14}C]oxadiazepine pinoxaden

Plant Back Interval (Days)	29	29	29	29	120
Plant Part	Lettuce Heads	Radish Tops	Spring Wheat Forage (50% Maturity)	Spring Wheat Fodder (husk + straw)	Spring Wheat Fodder (husk + straw)
TRR [mg/kg]	0.014	0.022	0.048	0.077	0.032
Metabolite Fraction	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)	%TRR [a] (mg eq/kg)
Extracted	99.1	97.7	91.8	63.8	76.5
M2	4.1 (0.0006)	n.d.	1.2 (0.006)	n.d.	n.d.
M3	3.7 (0.0005)	7.3 (0.0016)	49.3 (0.0237)	9.9 (0.0077)	23.2 (0.0074)
M8	3.2 (0.0005)	n.d.[d]	3.9 (0.0019)	5.2 (0.0040)	7.0 (0.0022)
M9	n.d.[d]	n.d.[d]	8.0 (0.0038)	5.0 (0.0038)	15.6 (0.0050)
M10	n.d.	n.d.[d]	n.d.	3.5 (0.0027)	1.5 (0.0005)
M11	n.d.	n.d.[d]	n.d.	1.8 (0.0014)	0.4 (0.0001)
Unknowns (up to 15)	81.3 (0.0114) [b]	67.3 (0.0147)	21.6 (0.0104)	27.6 (0.0213)	21.9 (0.0069)
Unresolved	6.8 (0.001)	23.2 (0.0051)	7.9 (0.0038)	10.8 (0.0083)	7.0 (0.0022)
Unextracted	6.0 (0.0008)	7.0 (0.0015)	8.7 (0.0042)	37.7 (0.0290)	27.6 (0.0088)
Total	105.1 (0.014) [c]	104.7 (0.022)	100.5 (0.049)	101.5 (0.077)	104.1 (0.032)

n.d. = Not detected

[a] As % of the total radioactivity found in the plant part, determined by combustion

[b] The largest metabolite fraction accounted for 69.1% (0.0097 mg eq/kg)

[c] TRR determined by combustion.

[d] Trace amounts of the corresponding metabolite may be present but could not be identified due to low TRRs.

Lettuce

Lettuce was transplanted into soil 29 and 120 days after treatment. Due to the very low residue at 120 days (0.001 mg eq/kg) no lettuce was planted after 361 days. Furthermore, due to this very low residue at 120 days, no characterisation of the radioactivity was performed. In the 29-day sample about 99% of the TRR was extracted. While the parent, pinoxaden, was not detected, there were several metabolites observed, including M2, M3 and M8, all of which were less than 10% of the TRR (< 0.01 mg/kg).

Radish

Radish seed was planted 29 and 120 days after treatment. Due to the very low residues in both roots and tops at 120 days (≤ 0.001 mg eq/kg) no radish was sown at 361 days. The TRRs in radish roots were 0.002 mg/kg and < 0.001 mg eq/kg at the 29 and 120-day plant-back intervals, respectively. The corresponding TRRs for radish tops were 0.022 and 0.001 mg eq/kg, respectively. Due to the very low residues in radish roots, characterisation of the radioactivity was only performed on radish tops from the 29-day plant-back interval. Extractability was 98% of the TRR and radio-TLC analysis of the extract revealed a very complex metabolite pattern. No parent compound or M2 was detected and M3 accounted for 7.3% of the TRR (0.0016 mg eq/kg).

Wheat

At the 29-day plant-back interval, the residue in spring wheat grain was very low at 0.007 mg eq/kg and hence no further work was conducted on this sample. TRRs in fodder amounted for 0.077 mg eq/kg with an extractability of about 64% of the TRR and again all metabolite fractions were below 0.01 mg eq/kg. Minor metabolites identified were M3 (9.9% of the TRR, 0.008 mg eq/kg), M8 (5.2% of the TRR; 0.004 mg eq/kg), M9 (5.0% of the TRR; 0.004 mg eq/kg), M10 (3.5% of the TRR; 0.003 mg eq/kg) and M11 (1.8% of the TRR; 0.001 mg eq/kg).

At the 120-day plant-back interval the TRR in grain was 0.004 mg/kg. Due to the low TRRs, no further work was conducted on this sample. The TRR in fodder amounted to 0.032 mg eq/kg, about 77% of which was extracted. M2 was not detected, but all other identified metabolites M3, M8, M9, M10 and M11 accounted for 23% of the TRR (0.007 mg eq/kg), 7.0% of the TRR (0.002 mg eq/kg), 16% of the TRR (0.005 mg eq/kg), 1.5% of the TRR (0.0005 mg eq/kg) and 0.4% of the TRR (0.0001 mg eq/kg).

At the 361-day plant-back interval the residues in all spring wheat fractions were well below 0.01 mg/kg and hence no further work was conducted on samples from this interval.

Winter wheat seed was planted 168 days after treatment. The residues in all crop fractions were well below 0.01 mg/kg and hence no further work was conducted on these samples.

Total radioactive residues in soil in the 0–10 cm layer decreased from 0.063 mg eq/kg immediately after treatment to 0.01 mg eq/kg at the end of the study (473 days after treatment). Unchanged parent compound was not detected, however, M2 was detected in trace amounts (≤ 0.0001 mg eq/kg) up to Day 70, after which it was no longer detectable. M3 was found as a major fraction accounting for 52% of the TRRs (0.024 mg eq/kg) at Day 29 and then continuously declined to non-detectable levels (0.0005 mg eq/kg) by the end of the study.

Study 3

Pinoxaden, labelled in the [phenyl-1-^{14}C] ring (specific activity: 55.1 µCi/mg) and [oxadiazepin-3,6-^{14}C] (specific activity: 52.8 µCi/mg) and formulated as an emulsifiable concentrate formulation was applied once to bare soil as a spray at a rate of 70 g ai/ha, equivalent to the registered GAP (Brown, 2003, 174-01). Three rotational crops, spring wheat (Oxen), mustard (Southern Giant Curled) and turnip (Alamo) were cultivated under outdoor conditions per procedures simulating typical agricultural practices. All the crops were sown as seed 15 days after soil treatment and harvested at maturity except for spring wheat which was also sampled at 25% and 50% maturity.

Mustard greens were harvested 61 days after planting. Turnips were harvested 89 days after planting and tops were separated from tubers. Wheat was harvested 26 days after planting for the 25% mature stage (jointing, BBCH growth stage 20–30), 50 days after planting for the 50% mature stage (head emergence, BBCH growth stage 57–61), and at 89 days after planting at full wheat maturity.

Samples were homogenised in the presence of dry-ice. The total radioactive residues (TRRs) were determined by combustion and LSC. Only samples with TRRs greater than 0.01 mg eq/kg were subjected to further characterization/identification.

The TRRs in the rotational crops following soil application of phenyl-^{14}C-pinoxaden and oxadiazepine-^{14}C-pinoxaden were low. The highest residues were found in spring wheat mature fodder; 0.069 mg eq/kg for the phenyl label and 0.063 mg eq/kg for the oxadiazepine label, followed by spring wheat forage at 25% maturity and 50% maturity, accounting for 0.022 mg eq/kg and 0.027 mg eq/kg from the phenyl label and 0.023 mg eq/kg and 0.021 mg eq/kg from the oxadiazepine label, respectively. Spring wheat mature grain residues were 0.006 mg eq/kg for both labels. In mature mustard leaves, TRRs were 0.013 mg eq/kg and 0.007 mg eq/kg from the phenyl and oxadiazepine labels, respectively. The TRRs in mature turnip tubers and leaves were 0.005 mg eq/kg and 0.010 mg eq/kg from the phenyl label and 0.004 mg eq/kg and 0.006 mg eq/kg from the oxadiazepine label, respectively.

Table 22 Distribution of total radioactive residues of pinoxaden in succeeding crops following bare ground application of [^{14}C]pinoxaden

Sample	DAP (days)	TRR	Total Extracted		Aqueous Soluble		Organic Soluble		Post Extraction Solids	
		mg eq/kg	TRR %	mg eq/kg	TRR %	mg eq/kg	TRR %	mg eq/kg	TRR %	mg eq/kg
Phenyl										
25% Mature Forage	26	0.022	91.1	0.020	53.9	0.012	28.9	0.006	14.6	0.003
50% Mature Forage	50	0.027	80.3	0.022	47.5	0.013	26.3	0.007	21.4	0.006
Mature Fodder	89	0.069	65.7	0.045	34.0	0.024	27.2	0.019	32.8	0.023
Mature Turnip Leaves	89	0.010	81.4	0.008	54.8	0.006	20.4	0.002	13.1	0.001
Mature Mustard Leaves	61	0.013	83.1	0.011	73.0	0.010	21.1	0.003	9.8	0.001
Oxadiazepine										
25% Mature Forage	26	0.023	82.4	0.019	53.2	0.012	25.4	0.006	15.0	0.004
50% Nature Forage	50	0.021	83.9	0.018	48.0	0.010	27.8	0.006	27.1	0.006
Mature Fodder	89	0.063	62.4	0.039	25.5	0.016	39.7	0.025	41.0	0.026

DAP: Days after planting

Plant samples, except for mature fodder samples, were extracted three times with acetonitrile: water (9:1, v/v). The samples were extracted for ca. 10 minutes and filtered. Triplicate aliquots of the combined extracts were bleached, neutralized with L-ascorbic acid (5 g in 125 mL water), chilled at freezer temperatures and radio-assayed in triplicate. The extract was passed through a pre-conditioned solid phase extraction (SPE) column and the eluted solution was concentrated to an aqueous material and partitioned three times with chloroform. The organic fractions were combined, concentrated and radio-assayed. The remaining aqueous fraction was radio-assayed. The post-extracted solids (PES) were air-dried then combusted.

Mature fodder from both labels was soaked in water at refrigerator temperatures for 24 to 42 hours. Acetonitrile was then added to the pre-swollen samples. Fodder samples were subsequently extracted following the procedure described previously. After the first extraction, the solids were extracted two additional times with acetonitrile:water (8:2, v/v). The combined extracts were eluted through a SPE column and partitioned into organic and aqueous fractions. The PES were refluxed with acetonitrile:water (4:1, v/v) for *ca* 24 hours. The refluxed material was filtered and the filtrate was radio-assayed. The remaining solids were air-dried and combusted. Soil samples were extracted with acetonitrile:water (4:1, v/v) and the extracts were shaken on an orbital shaker for 1 hour. The samples were filtered and the filtrate radio-assayed while the solids were air-dried and combusted.

Liquid extracts were concentrated prior to partitioning three times with chloroform. The chloroform fractions were combined, concentrated and radio-assayed.

Thin layer chromatography (TLC, 1D and 2D) and HPLC were used to characterize and isolate metabolites of pinoxaden in rotational crops.

Isolated metabolites, aqueous fractions and whole extracts were treated with β-glucosidase and/or cellulase (*Aspergillus niger*). Samples were placed into appropriate containers and incubated with sodium acetate buffer solution, pH 4.6.

Elucidation of isolated metabolite fractions was by Electrospray (ESI) LC/MS in positive and/or negative mode.

Table 23 Summary of characterization and identification of residues in rotational crops planted 15-days following bare ground application of [^{14}C]phenyl pinoxaden

Plant Part	Spring Wheat 25% Mature Forage		Spring Wheat 50% Mature Forage		Spring Wheat Mature Fodder		Mature Turnip Leaves		Mature Mustard Leaves	
TRRs (mg eq/kg)	0.022		0.027		0.069		0.010		0.013	
Metabolite Fraction	TRR%	mg eq/kg	TRR%	mg eq/kg	TRR%	mg eq/kg	TRR%	mg eq/kg	TRR%	mg eq/kg

Plant Part	Spring Wheat 25% Mature Forage		Spring Wheat 50% Mature Forage		Spring Wheat Mature Fodder		Mature Turnip Leaves		Mature Mustard Leaves	
TRRs (mg eq/kg)	0.022		0.027		0.069		0.010		0.013	
Extracted	91.1	0.020	80.3	0.022	65.7	0.045	81.4	0.008	83.1	0.011
M3	28.9	0.006	16.8	0.005	16.9 [a]	0.012	20.4	0.002	21.1	0.003
M6	n.d.	n.d.	n.d.	n.d.	2.1 [b]	0.001	n.d.	n.d.	n.d.	n.d.
M10	n.d.	n.d.	9.5	0.003	12.0	0.008	n.d.	n.d.	n.d.	n.d.
M8 [d]	23.7	0.005	30.6	0.008	n.d.	n.d.	54.8	0.006	45.7	0.006
ME2 [c]	5.7	0.001	6.9	0.002	n.d.	n.d.	n.d.	n.d.	10.8	0.001
ME3 [c]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.8	< 0.001
ME5 [c]	24.6	0.005	10.0	0.003	n.d.	n.d.	n.d.	n.d.	13.6	0.002
M11 (ME7)	n.d.	n.d.	n.d.	n.d.	34.0	0.024	n.d.	n.d.	n.d.	n.d.
Total identified	82.9	0.018	73.8	0.020	61.2	0.042	75.2	0.008	94.0	0.012
Unknowns	8.2	0.002	6.5	0.002	4.5	0.003	–	–	–	–
Unextracted	14.6	0.003	21.4	0.006	32.8	0.023	13.1	0.001	9.8	0.001
Total	105.7	0.023	101.7	0.028	98.5	0.068	94.5	0.009	91.9	0.012

n.d. = Not detected

[a] 1.7%TRR released from PES

[b] Released from PES

[c] Conjugates of M10

[d] Glucose conjugate of M10

Table 24 Summary of characterization and identification of residues in spring wheat samples following bare ground application of [^{14}C]oxadiazepine pinoxaden

Plant Part	25% Mature Forage		50% Mature Forage		Mature Fodder	
TRRs (mg eq/kg)	0.023		0.021		0.063	
Metabolite Fraction	TRR%	mg eq/kg	TRR%	mg eq/kg	TRR%	mg eq/kg
Extracted	82.4	0.019	83.9	0.018	62.4	0.039
M3	25.4	0.006	12.6	0.003	26.1 [a]	0.016
M10	n.d.	n.d.	10.8	0.002	15.9	0.010
M8 [d]	22.6	0.005	31.0	0.007	n.d.	n.d.
ME2 [c]	6.7	0.002	5.3	0.001	n.d.	n.d.
ME5 [c]	23.9	0.006	11.8	0.003	n.d.	n.d.
M6	n.d.	n.d.	n.d.	n.d.	2.6 [b]	0.002
M11 (ME7)	n.d.	n.d.	n.d.	n.d.	25.5	0.016
Total Identified	78.6	0.018	71.5	0.015	65.2	0.041
Unknowns	n.d.	n.d.	4.4	< 0.001	n.d.	n.d.
Unextracted	15.0	0.004	27.1	0.006	41.0	0.026
Total	97.4	0.02	111.0	0.024	103.5	0.065

[a] 2.3%TRR released from PES

[b] Released from PES

[c] Conjugates of M10

[d] Glucose conjugates of M10

Metabolites identified and common to samples from both labels included M3 and M10. Concentrations of M3 ranged from 17–29% of the TRR (0.002–0.012 mg eq/kg) in phenyl labelled samples and 13–26% of the TRR (0.003–0.016 mg eq/kg) in oxadiazepine labelled samples. Values for M10 ranged from 10–12% of the TRR (0.003–0.008 mg eq/kg) for phenyl-labelled samples and 11–16% of the TRR (0.002–0.010 mg eq/kg) for oxadiazepine-labelled samples. M11 was observed only in mature fodder and accounted for 34% of the TRR (0.02 mg eq/kg) and 26% of the TRR (0.02 mg eq/kg) in the phenyl and oxadiazepine labels, respectively. Aqueous metabolites from 25% and 50% mature forage, mature mustard leaves and mature turnip leaves were M8 (24–55% of the TRR), ME2 (5–11% of the TRR), ME5 (10–25% of the TRR) and ME3 (3% of the TRR); these were

identified as conjugates of M10 by enzymatic hydrolysis of aqueous fractions. Metabolites M6 and M3 were released from mature fodder PES following acetonitrile:water refluxing. Less than 3% of the TRR was released as M6 and approximately 2% of the TRR as M3 for both the phenyl and oxadiazepine labels

Overall, the metabolic pathway of pinoxaden in confined rotational crops, after bare ground application, proceeds via hydrolysis to produce M2. M2 then undergoes oxidative hydroxylation at either the 8 position of the pyrazole, generating M3 or at the phenyl methyl group producing M4. Either of these compounds may hydroxylate further in the positions described above to yield M10. M10 undergoes conjugation to M8, ME2, ME3 and ME5. M8 has been identified as a glucose conjugate. Oxidation of the benzylic alcohol present in M4 leads to the related benzoic acid M6. Subsequent oxidative hydroxylation of the pyrazole ring provides M11. M11 may also be obtained by oxidation of the benzylic alcohol moiety present in M10 to the corresponding carboxylic acid (see Figure 5).

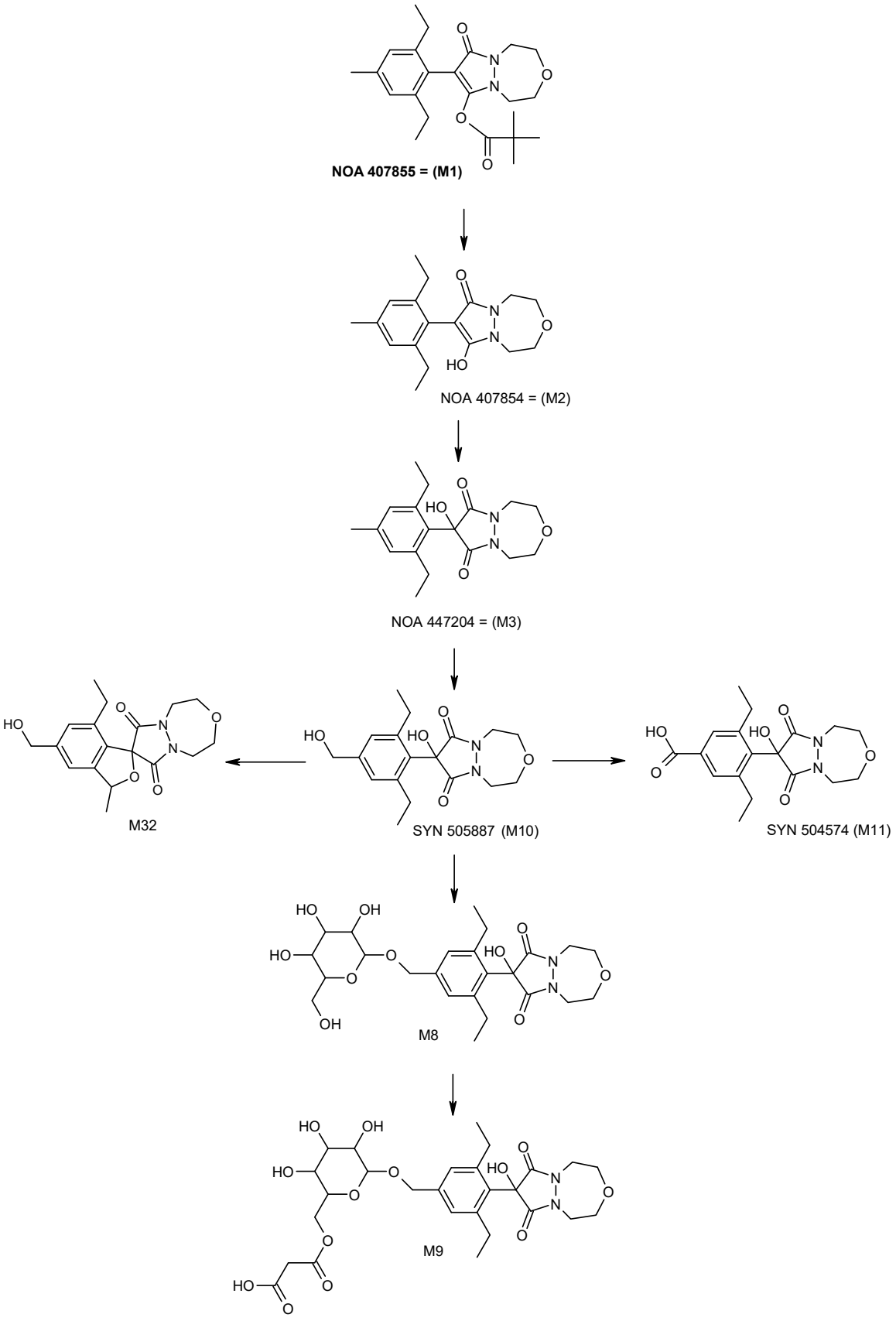


Figure 5 Metabolic pathway of pinoxaden in rotational crops

Field rotational crops

Pinoxaden was applied to the primary crop, wheat, as a single application at a rate of 69 g ai/ha, equivalent to the registered GAP (Lin, 2007c). Spinach, radish and oat crops were planted 60 and 90 days after the application (60- and 90-day plant-back intervals (PBI)).

Samples of spinach leaves, radish tops and roots and oat forage, hay, straw and grain were harvested at the appropriate intervals and analysed for residues of the metabolite M3 using a validated analytical method GRM017.02A (LOQ, 0.01 mg/kg).

At the 60-day PBI, no quantifiable residues (< 0.01 ppm) of the metabolite were found in any of the collected samples except for oat hay, where residues were found to be 0.01 mg/kg.

Based on this information, measurable residues of M3 are not expected in follow crops, when planted in rotation with wheat and barley treated in accordance with the registered GAP.

Aerobic degradation

Study 1

^{14}C-phenyl labelled pinoxaden (specific activity 78.4 µCi/mg) was applied to a loam-silt loam soil (Gartenacker) and incubated in the dark at 20 °C (Reischmann, 2001b). The concentration was 0.2 mg pinoxaden/kg soil. The study was run in a laboratory under three different conditions: aerobic, aerobic followed by anaerobic and aerobic/sterile. The samples of the aerobic sub-study were incubated over 155 days at a soil moisture content of 40% of the maximum water holding capacity. Those of the sterile-aerobic sub-study were incubated at the same soil moisture content for 120 days. In the aerobic-anaerobic sub-study, samples were incubated first aerobically for 3 hours and afterwards anaerobically for a maximum of 119 days.

Samples were analysed after pre-defined intervals during the entire incubation period. All soil samples were extracted three to four times with acetonitrile under agitation. After each extraction step, the suspensions were centrifuged and the radioactivity in the supernatants was determined by LSC. The soil samples remaining after extraction were refluxed (Soxhlet) with acetonitrile for 6 hours. The Soxhlet extracted soil samples were further subjected to neutral harsh extraction with acetonitrile:water (40:10, v:v) followed by hydrolysis with acetonitrile:0.1 N HCl (90:10, v:v). After hydrolysis, the unextracted soil residues were extracted with 0.5 N NaOH and centrifuged. Concentrated HCl was added to the supernatants while 0.5 N NaOH was added to the remaining solids after which all samples were radioassayed.

The distribution of the radioactivity showed that volatiles were exclusively carbon dioxide, demonstrating mineralization. The formation of carbon dioxide increased over the entire study period, reaching 33% of the applied radioactivity (AR) after 120 days. The unextracted residues reached a maximum of almost 60% of the AR after 2 months and decreased thereafter. Small amounts of M2 and M3 were found following the harsh extraction procedures. After 155 days, 30% of the applied material was found in the soluble fraction (fulvic acid), 4% in the humic acid fraction, and 31% was incorporated into the insoluble humin fraction. The radioactivity incorporated into the humin fraction increased over the entire study period.

HPLC with UV, RAM and mass spectrometric detectors and 2D-TLC analysis were among the analytical techniques used to elucidate the nature of the radioactivity in the soil.

Table 25 Summary of characterization and identification of residues in soil at 20 °C following application of [^{14}C]phenyl pinoxaden

Incubation Time	Percent Applied Radioactivity								
	Aerobic			Aerobic-Anaerobic			Sterile-Aerobic		
	Pinoxaden	M2	M3	Pinoxaden	M2	M3	Pinoxaden	M2	M3
0	90.3	3.1	–	n.a.	n.a.	n.a.	90.7	4.7	–
3 hours	41.8	45.6	0.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6 hours	34.7	50.6	0.4	26.0	62.7	1.7	n.a.	n.a.	n.a.
1 day	3.6	69.1	1.7	2.6	85.5	1.5	n.a.	n.a.	n.a.

Incubation Time	Percent Applied Radioactivity								
	Aerobic			Aerobic-Anaerobic			Sterile-Aerobic		
	Pinoxaden	M2	M3	Pinoxaden	M2	M3	Pinoxaden	M2	M3
3 days	0.3	62.8	2.6	0.8	88.7	1.2	n.a.	n.a.	n.a.
7 days	–	62.9	4.2	0.6	92.3	0.8	0.4	92.3	–
14 days	–	46.1	5.4	–	93.2	0.6	–	92.6	–
30 days	–	13.3	4.8	–	94.2	0.4	–	89.7	0.3
59 days	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	–	83.5	–
68 days	–	2.8	2.2	–	94.4	0.6	n.a.	n.a.	n.a.
90 days	–	3.1	3.3	–	94.2	0.7	n.a.	n.a.	n.a.
119 days	–	1	0.7	–	93.5	0.3	–	85.1	–
155 days	–	0.8	0.4	–	n.a.	n.a.	n.a.	n.a.	n.a.

Under aerobic conditions, pinoxaden was rapidly hydrolysed to M2 which was subsequently oxidized to M3 and further degraded. The maximum concentration observed for M2 was 69% of the AR (after 1 day) and the maximum concentration observed for M3 was 5% of the AR after 14 days. Several minor degradates were observed (each ≤ 1.7% of AR at any point of time) but could not be identified.

Similarly to aerobic conditions, under anaerobic conditions, pinoxaden was rapidly hydrolysed to M2 with very limited degradation of M2 thereafter. The concentration remained at 94% of the AR beyond Day 14. During the entire period, no volatiles or CO_2 was observed and the unextracted fraction decreased during the anaerobic phase.

Under sterile-aerobic conditions, pinoxaden was rapidly hydrolysed and decreased from 91% of the AR (at Day 0) to 0.4% of the AR (Day 7). The major metabolite M2 reached 93% of the AR on Day 14 and accounted for 85% of the AR on Day 120. Traces of M3 were observed (each ≤ 0.3% of the AR). Again, no volatiles were observed, but the level of unextracted increased to 8.6%.

Kinetic calculations were done assuming first order kinetics.

Table 26 Route and rate of degradation in soil at 20 °C (aerobic conditions) following application of [^{14}C]phenyl pinoxaden

Incubation Condition	Half-life (days)		
	Pinoxaden	M2	M3
Aerobic	0.2	16.4	6.6
Aerobic-anaerobic	0.2	Stable	Not formed
Sterile-aerobic	0.9	Stable	Not formed

Pinoxaden was degraded rapidly by hydrolysis of the ester bond to M2, with half-lives between 0.2 and 0.9 days under aerobic, aerobic-anaerobic, and sterile-aerobic conditions. M2 was degraded with a half-life of 16 days under aerobic conditions, forming M3 that was in turn degraded with a half-life of approximately 7 days under aerobic conditions. Under anaerobic and sterile-aerobic conditions, degradation of M2 was limited.

Study 2

^{14}C-phenyl-, ^{14}C-pyrazole- and ^{14}C-oxadiazepine labelled pinoxaden (specific activity: 52.4–55.1 µCi/mg) were each applied to a loamy sand soil (Plaza/ND, USA) and incubated at 25 °C in the dark under aerobic flow-through conditions (Clark, 2003a/2003b, McKillican, 2003). The concentrations were respectively 0.046/0.047/0.046 mg [^{14}C]pinoxaden per kg soil in the kinetic set, to determine degradation patterns, and 4.4/0.56/0.55 mg/kg in the bulk set used for identification. The samples were analysed after pre-defined intervals covering a period of up to 181 days (phenyl label) and 100 days (pyrazole and oxadiazepine labels).

Samples were analysed after pre-defined intervals during the entire incubation period. All soil samples were extracted twice with acetonitrile:water (80:20, v:v) under agitation. After each extraction step, the suspensions were centrifuged and the radioactivity in the supernatants was

determined by LSC. The remaining soil samples were extracted twice with acetonitrile:acidified water (0.5 N HCl, adjusted to pH 6) (75:25, v:v). After each extraction, the soil samples were centrifuged and the supernatants from both extractions were combined and radio-assayed. The pellets remaining from the centrifugation were further extracted using hot (60 °C) acetonitrile:acidified water (75:25, v:v) and extracts were radio-assayed. The remaining unextracted residues were hydrolysed with 0.5 N NaOH overnight to characterize the fulvic acid, humic acid and humin fractions.

Like Study 1, the volatiles were identified exclusively as carbon dioxide, demonstrating mineralization. The formation of carbon dioxide increased over the entire study period, reaching 45% after 181 days for the phenyl label and 44–48% after 100 days for the pyrazole and oxadiazepine labels.

For all three radiolabels, the percent applied radioactivity remaining unextracted reached a maximum of 25% after 1 month, and decreased thereafter. After 181 days, of the unextracted radioactivity in the phenyl-labelled soil samples, 2% were bound to humic acid, 13% to fulvic acid, and 25% was incorporated into the insoluble humin fraction. After 100 days, of the 34–36% unextracted radioactivity in the pyrazole- and oxadiazepine-labelled soil samples, 12–13% were found in the soluble fraction (fulvic acid), 2% in the humic acid fraction and 19–22% was incorporated into the insoluble humin fraction. The radioactivity incorporated into the humin fraction increased over the entire study period.

HPLC with UV, RAM and mass spectrometric detectors and 2D-TLC analysis were among the analytical techniques used to elucidate the nature of the radioactivity in the soil.

Table 27 Summary of characterization and identification of residues in soil at 25 °C (aerobic conditions) following application of [^{14}C]phenyl, [^{14}C]pyrazole and [^{14}C]oxadiazepine-labelled pinoxaden

Time	Percent Applied Radioactivity [a]								
	Phenyl			Pyrazole			Oxadiazepine		
	Pinoxaden	M2	M3	Pinoxaden	M2	M3	Pinoxaden	M2	M3
0	90.2	5.9	–	89.5	2.0	–	87.6	5.7	–
2 hours	61.8	37.6	0.8	66.1	25.4	–	67.8	23.8	0.3
4 hours	47.4	53.5	0.9	56.2	33.0	0.5	52.4	38.6	0.3
8 hours	21.7	72.8	1.2	35.4	55.0	0.2	27.2	56.3	4.0
1 days	4.7	88.8	1.5	6.3	74.9	3.9	6.7	67.3	6.5
3 days	2.4	65.3	8.5	–	41.5	12.3	–	47.0	10.0
5 days	2.0	65.5	7.4	1.2	19.7	13.9	–	25.2	15.3
7 days	1.6	45.0	12.6	–	13.7	15.2	–	19.4	17.4
14 days	0.7	13.7	16.5	0.5	5.0	15.6	1.0	6.4	15.4
30 days	–	5.9	16.3	–	1.8	12.9	–	2.4	12.3
62 days	–	4.1	6.7	–	0.6	10.1	–	1.0	7.8
100 days	n.a.	n.a.	n.a.	–	0.9	4.6	–	1.2	6.6
120 days	–	2.1	4.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
181 days	–	1.4	2.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[a] Values reported are from the kinetic set which did not differ noticeably from the bulk set

Pinoxaden was rapidly hydrolysed to M2 followed by oxidation of M2 to M3, which was further degraded. The maximum observed concentration of M2 was 67–88% of the applied material (after 1 d), and the maximum observed concentration of M3 was 17% (between 7 and 30 days). In addition, several minor degradates were observed (each ≤ 4% of the applied radioactivity at any point in time), see Figure 6.

Calculations were done assuming first order kinetics.

Table 28 Route and rate of degradation in soil at 25 °C (aerobic conditions) following application of [^{14}C]phenyl pinoxaden

Half-life (days)		
Phenyl	Pyrazole	Oxadiazepine

Half-life (days)								
Phenyl			Pyrazole			Oxadiazepine		
Pinoxaden	M2	M3	Pinoxaden	M2	M3	Pinoxaden	M2	M3
4.1 hours	6.7	15.4	6.0 hours	2.2	10.7	5.1 hours	3.1	11.2

Under aerobic conditions pinoxaden was degraded rapidly by hydrolysis of the ester bond to M2. M2 was then degraded with a half-life of 2–6 days, forming M3 that was in turn degraded with a half-life of 37–51 days.

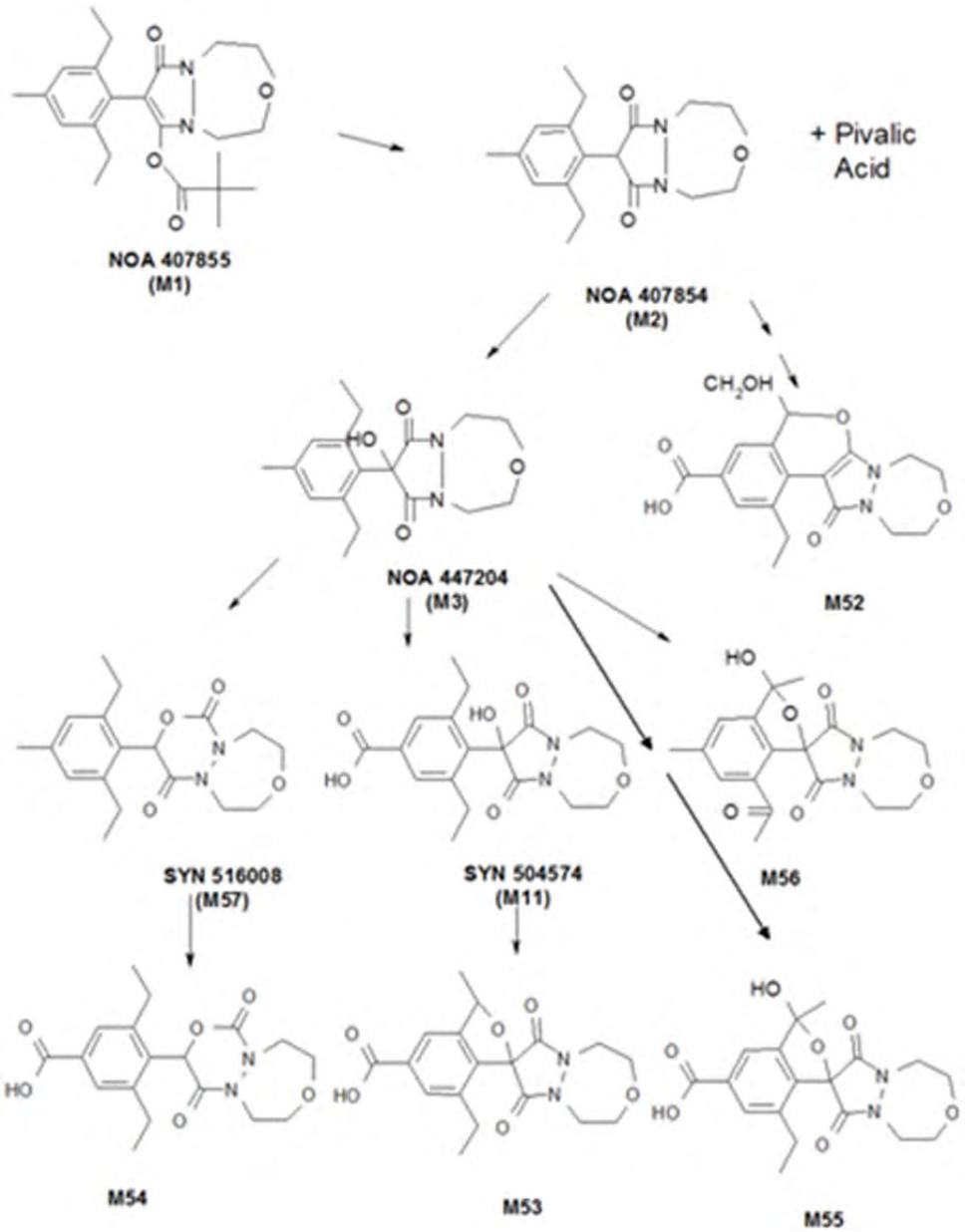


Figure 6 Aerobic degradation pathway in soil

Rate of degradation

The rate of degradation of [^{14}C]pyrazole ring-labelled M3 was investigated in three different soils: Krone (silt loam), 18 Acres (sandy clay loam) and Borstel (loamy sand) (Adam, 2012). ^{14}C-labelled M3 was applied at a dose rate of 0.08 mg/kg dry weight soil, equivalent to a single field application rate of 63 g ai/ha (assuming an incorporation depth of 5 cm and a bulk density of 1.5 g/cm^3). The soils were incubated under aerobic conditions in the laboratory and maintained at soil moisture of pF 2 under dark conditions at 20 °C ± 2 °C for up to 120 days. For each soil, duplicate samples were taken for analysis at 0, 7, 14, 28, 56, 91 and 120 days after treatment (DAT).

At each sampling time, samples were extracted with acetonitrile:water (4:1, v/v), analysed for parent compound, degradation products and unextracted residues. Any volatile radioactivity was continuously flushed from the vessels and collected in traps. A mass balance was determined for each sample.

The mean mass balance was 97%, 98% and 97% of the applied radioactivity (AR) for Krone, 18 Acres and Borstel, respectively (range 91 to 106% with one single value of 89%).

The amount of extracted radioactivity in Krone, 18 Acres and Borstel samples decreased with time from 96 to 101% at 0 DAT to 70 to 81% by 120 DAT. Correspondingly, unextracted residues increased slowly throughout the incubation period, reaching a maximum of 5%, 10% and 2% AR by the end of the incubation period for Krone, 18 Acres and Borstel, respectively.

Mineralization to carbon dioxide reached comparable levels in all soils with maximum levels ranging from 13–19% of the applied dose by the end of the incubation.

Table 29 Summary of characterization and identification of residues in soil at 20 °C (aerobic conditions following application of [^{14}C]pyrazolyl labelled M3

	Percent of Applied Radioactivity																				
	Krone							18 Acres							Borstel						
DAT	0	7	14	28	56	91	120	0	7	14	28	56	91	120	0	7	14	28	56	91	120
M3	96.5	89.6	77.5	69.4	64.3	61.8	58.7	99.2	91.2	87.7	79.2	68.5	66.6	47.0	100.5	98.2	88.6	81.6	72.6	75.5	59.9
Metabolite 1	–	1.3	1.5	0.7	5.1	3.4	3.3	–	1.8	1.8	–	4.7	2.8	4.8	–	–	–	–	–	–	–
Metabolite 2	–	–	0.5	0.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.6
Metabolite 3	–	–	0.8	1.0	0.6	1.2	1.5	–	–	–	–	2.0	1.3	1.0	–	–	–	–	–	–	0.6
Metabolite 4	–	4.2	4.6	4.4	1.7	1.2	2.3	–	0.9	3.4	3.8	1.8	1.8	1.7	–	1.5	6.6	5.0	12.1	8.5	10.2
Metabolite 5	–	–	1.2	1.6	0.8	2.6	1.4	–	–	–	1.8	1.0	2.0	1.0	–	–	1.8	1.6	1.6	2.6	4.7
Metabolite 6	–	0.5	1.4	2.6	8.9	7.5	5.8	–	2.4	0.4	1.9	9.5	7.9	14.3	–	–	–	0.7	–	1.9	2.9
Metabolite 7	–	–	–	–	–	0.4	–	–	–	–	1.1	–	–	–	–	–	–	–	3.2	1.7	1.9

The amount of unchanged M3 extracted from the soil decreased continuously throughout the study in all three soil types.

The half-lives (DT_{50}) and DT_{90} values were calculated for [^{14}C]pyrazolyl labelled M3 in the three soils, using single first-order (SFO) or hockey-stick (HS) kinetic models.

Table 30 Modelling endpoints

Soil	Degradation kinetics	
	DT_{50} [days]	DT_{90} [days]
Krone (HS)	220.4	1122.0
18 Acres (SFO)	129.7	430.8
Borstel (SFO)	179	594.6

The rate of degradation of the soil metabolite of pinoxaden, M11, was also investigated in three different soils: Gartenacker (Switzerland: silt loam), 18 Acres (UK: loam) and Marsillargues (France: silty clay loam). M11 was applied at a nominal rate of 0.08 mg/kg dry weight soil, equivalent

to a single field application rate of 60 g ai/ha (assuming an incorporation depth of 5 cm and a bulk density of 1.5 g/cm^3) (Robinson, 2012). The soils were incubated under aerobic conditions in the laboratory and maintained at a soil moisture content of pF 2 in the dark at 20 °C for up to 90 days. Duplicate treated soil samples were taken for analysis on days 0, 2, 5, 7, 14, 28, 61 and 90 for all three soils used in this study. The soil samples were extracted with acetonitrile:0.1M HCl (4:1, v:v) and analysed using LC-MS to determine the amount of M11 present.

M11 degraded rapidly in all three soils. The mean initial amounts of 103%, 102% and 96% of the applied radioactivity decreased to ≤ 6% for all three soil types by the end of the incubation period (i.e. 90 days).

The half-lives (DT_{50}), and DT_{90} values were calculated using single first order kinetics (SFO).

Table 31 DT_{50} and DT_{90} values for M11 in three European soils

Soil	Degradation kinetics	
	DT_{50} [days]	DT_{90} [days]
Gartenacker	7.6	25.2
18 Acres	13.0	43.3
Marsillargues	9.2	30.6

Hydrolytic degradation

Study 1

^{14}C-Phenyl-labelled pinoxaden was incubated in diluted aqueous buffer solution at a concentration of 5 mg/L at temperatures of 15 °C (pH 7 and pH 9), 25 °C and 50 °C (pH 4, 5, 7, and 9), and at 60 °C (pH 4 and pH 5), under sterile conditions in the dark (Phaff, 2003).

Identification and quantification of the parent compound and degradates was achieved using TLC and HPLC (radioactivity detector and UV/VIS detector).

Table 32 Hydrolytic half-lives (days) of pinoxaden at different pH and temperatures

Temperature	pH 4	pH 5	pH 7	pH 9
15 °C	n.p.	n.p.	23.3	0.6
20 °C (calculated)	24.1	25.3	14.9	0.3
25 °C	17.2	17.5	9.9	0.2
50 °C	3.9	3.5	1.2	< 0.2
60 °C	2.2	1.9	n.p.	n.p.

n.p. = Not performed

Pinoxaden was hydrolytically unstable at all four pH values. Under acidic conditions, hydrolysis was slower, while under alkaline conditions it was faster. M2 was the only product formed by hydrolysis which showed no further hydrolytic degradation at all test conditions.

Study 2

[^{14}C]Pyrazole labelled M3 was incubated in dilute aqueous buffer solution at a concentration of 5 mg/L under sterile conditions in the dark (Buckel, 2003). Pre-tests showed M3 to be stable at pH 4 and 5, therefore the final test was run under conditions as follows: pH 7 at 25 °C (30 days of incubation), 50 °C (72 hours), and 60 °C (20 hours), and at pH 9 at 25 °C (24 hours) and 15 °C (88.5 hours).

Table 33 Hydrolytic half-life times (days) of M3 at different pH and temperatures

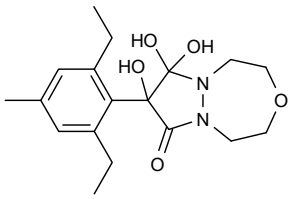
Temperature	pH 7	pH 9
15°C	Not performed	43.8 hours
20°C (calculated)	130.5 days	Not calculated
25°C	57.5 days	14.3 hours

Temperature	pH 7	pH 9
50°C	42.8 hours	Not performed
60°C	9.9 hours	Not performed

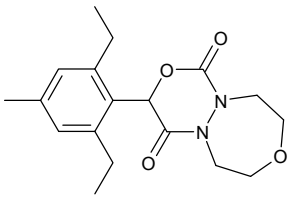
Under neutral conditions (pH 7) M3 hydrolysed with a DT_{50} of 58 days at 25 °C, 43 hours at 50 °C and 10 hours at 60 °C. Under alkaline conditions (pH 9), hydrolysis of M3 is more rapid, with DT_{50}s of 43.8 hours at 15 °C and 14.3 hours at 25 °C.

The main degradation product formed is M57 because of a rearrangement reaction of the transient precursor SYN516007. Rearrangement to M57, accounting for a maximum of 15% of the applied material (pH 7, 25 °C), was observed as well as the formation of CO_2, reaching 2.6% within the study period of 30 days, NOA 456301 and other products, none of which exceeded 3%. M57 degrades with a DT_{50} of 35.9 days at 25 °C, 25.1 hours at 50 °C, and 9.4 hours at 60 °C.

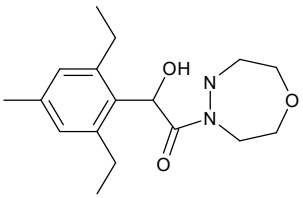
Structures of hydrolysis products of M3



SYN516007



M57



NOA456301

Analytical methods

The Meeting received descriptions and validation data for analytical methods for residues of pinoxaden and its metabolites M2, M4 (including its conjugates), M6 and M10 (including its conjugates) in plant commodities and M4 and M6 in animal commodities. All residue analytical methods rely on LC-MS/ MS. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.02 mg/kg/analyte. The methods described briefly below have been used for the analysis of the samples generated during the storage stability investigations, supervised field trials, processing studies and livestock feeding studies.

Table 34 Characterization of Enforcement Analytical Methods for Plant and Animal Commodities

Method ID	Method Type	Detector	Analytes	LOQ/analyte	Matrices	Report
Plant Commodities						
REM 199.02	Enforcement	LC-MS/MS	M2 M4 + conjugates M6 M10 + conjugates	0.01 mg/kg for cereal grains 0.02 mg/kg for cereal whole plants, ears, stalks and straw	Cereal grains, whole plants, ears, stalks and straw	0057/0058 (02-S302)
REM 199.03	Enforcement	LC-MS/MS	M2 M4 + conjugates M6 M10 + conjugates	0.01 mg/kg for cereal grain and processed fractions 0.02 mg/kg for cereal straw and whole plant	Cereal grains, whole plants, straw and processed fractions	0457
	ILV	LC-MS/MS	M2 M4 + conjugates M6 M10 + conjugates	0.01 mg/kg for wheat grain 0.02 mg/kg for whole plant	Wheat grain, barley whole plant	1983/060
117-01	Enforcement	LC-MS/MS	M2 M4 + conjugates M6	0.01 mg/kg for grain 0.02 mg/kg for forage, straw, hay, AGF	Cereal grains, forage, straw, hay and AGF	0505/117-01
	ILV	LC-MS/MS	M2 M4 + conjugates	0.01 mg/kg for grain 0.02 mg/kg for	Wheat (forage, straw, grain,	03-0019

Method ID	Method Type	Detector	Analytes	LOQ/analyte	Matrices	Report
			M6	forage, straw, hay, AGF	aspirated grain fractions (AGF)) and barley (hay, grain)	
QuEChERS	Enforcement	LC-MS/MS	M4 M6	0.01 mg/kg	Barley grain, lettuce, oilseed rape seed and orange	S12-04302
	ILV	LC-MS/MS	M4 M6	0.01 mg/kg	Lettuce, wheat grain	TK0171737
Animal Commodities						
1530-03	Enforcement	LC-MS/MS	M4 M6	0.01 mg/kg for milk 0.02 mg/kg for all tissues and eggs	Animal tissues, milk and eggs	0261
	ILV	LC-MS/MS	M4 M6	0.01 mg/kg for milk 0.02 mg/kg for beef tissues and eggs	Beef muscle and fat, milk, and eggs	0721

Plant Commodities

Method REM 199.02 (A. Gasser, 2002)

The homogenized samples are hydrolysed and extracted with 1 N HCl by boiling under reflux for two hours. After cooling to room temperature, an aliquot of the extract is centrifuged and filtered and the pH adjusted with a 3% ammonia solution. An aliquot of the extract is loaded onto an SPE cartridge which is subsequently eluted with water, hexane and dichloromethane:ethyl acetate:formic acid (80:20:0.5, v:v:v). The eluted fractions are acidified with 1 N HCl prior to evaporation and analysis using reversed phase HPLC with a column switching system connected to a pneumatically and thermally assisted electrospray ionization (ESI) to a tandem mass spectrometer (LC-LC-ESI/MS/MS; M2: m/z 317.3 →115.2, M4: m/z 333.1 → 303.1, M6 m/z 345.1 →172.7 and M10 m/z 349.1 → 146.9).

Method REM 199.03 (S.J. Crook, 2004)

This method is the same as 199.02 with the only modification being that the column switching procedure has changed to off-line SPE using single column determination. (LC-MS/MS; M2: *m/z* 317.3 → 171.15, M4: *m/z* 333.25 → 101.05, M6 *m/z* 345.16 → 173.15 and M10: *m/z* 349.3 → 147.15).

The method REM 199.03 underwent successful interlaboratory validation by Covance Laboratories Inc using samples of wheat grain and barley whole plant (M.H. Peatman *et al.,* 1983). Average recoveries of M2, M4, M6 and M10 ranged from 70–95% with RSD of ≤ 14%, when wheat grain and barley whole plant were fortified at the LOQ of 0.01 mg/kg/analyte and 0.02 mg/kg/analyte, respectively, and 10× the LOQ, demonstrating good reproducibility.

Method 117-01(K. Lin)

The extraction procedure of this method is based on Methods REM199.02 and REM199.03, in which a subsample is refluxed with a 1 N HCl:acetonitrile (90:10, v:v) solution for extraction of residues of pinoxaden, M2, M4 (+ conjugates) and M6 from wheat commodities. This acidic reflux serves to hydrolyse pinoxaden to M2 and to determine pinoxaden by analysis of M2 as a common moiety. For determination of M2, an aliquot is taken from the extract and separated by an HPLC system with RP18 to ODS-3 column-switching techniques. The analyte is detected by MS/MS with ion-spray atmospheric pressure ionization (API) to introduce the HPLC effluent into the mass spectrometer (M2: *m/z* 315 → 187). For determination of M4 and M6, a separate aliquot is taken from the extract

and purified with a SCX (2) SPE cartridge followed by a C_8 cartridge. The sample is analysed by a second HPLC-MS/MS with SCX to C_8 column-switching M4: *m/z* 333 → 303, M6: *m/z* 345 → 173).

The method underwent successful interlaboratory validation by EN-CAS laboratories (K. Faltinski, 2004). Average recoveries of M2 (expressed as pinoxaden equivalents), M4 and M6 ranged from 84–110% with RSD of ≤ 16% (except for wheat straw/ M4 where the RSD was 22%), when wheat forage, straw, aspirated grain fractions (AGF) and barley hay were fortified at the LOQ of 0.02 mg/kg/analyte and 10× LOQ and wheat and barley grain were fortified at the LOQ of 0.01 mg/kg/analyte and 10× LOQ, demonstrating overall good reproducibility.

To validate the extraction efficiency of methods REM 199.02/199.03 and 117-01 (J.M. Hamlet *et al.,* 2003), samples of grain, straw and husks from the winter wheat metabolism study were extracted by heating under reflux in 1 N HCl for 2 hours or by heating under reflux in 1 M HCl:acetonitrile (90:10, v:v). Following suitable SPE clean-up of the extracts, quantitative analysis of the metabolites present was performed by TLC in conjunction with a phosporimager and by LC-MS/MS. The overall extractabilities achieved with the analytical methods REM199.02/199.03 and 117-01 were comparable to those achieved using the procedure in the metabolism study (Sandmeier, 2003). Therefore, these analytical methods are capable of successfully extracting residues for quantitative analysis.

Table 35 Radiovalidation of methods REM 199.02/03 and 117-01

Commodity	Metabolite	Method 199.02/03 (1 N HCl—2 hr reflux)			117-01 (1N HCl:acetonitrile, 90:10 v/v—2 hr reflux)			Metabolism (following acetonitrile:water extraction) [a]		Metabolism (following 1 N Cl hydrolysis) [b]	
		LC/ MS-MS	2D-TLC		LC/MS-MS	2D-TLC		2D-TLC		2D-TLC	
		mg/kg	%TRR	mg/kg	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Grain	M2	< 0.01	ND	ND	< 0.01	ND	ND	ND	ND	ND	ND
	M4	0.22	74.4	0.22	0.14	51.6	0.17	29.1	0.07	79.3	0.20
	M6	0.06	12.9	0.04	0.06	12.7	0.04	9.6	0.02	10.6	0.03
	M10	< 0.01	ND	ND	< 0.01	ND	ND	0.7	< 0.01	ND	ND
Straw	M2	0.05	ND	ND	0.05	ND	ND	ND	ND	ND	ND
	M4	1.99	41.8	2.30	1.69	38.1	2.13	43.0	2.36	45.8	2.51
	M6	0.33	8.0	0.40	0.25	7.9	0.44	3.2	0.17	4.3	0.23
	M10	0.33	7.6	0.42	0.30	6.3	0.35	15.1	0.83	15.4	0.85

ND: Not detected

[a] Represents combined free and conjugated forms of M4 (M4+M5+M7) and M10 (M10+M8)

[b] Calculated from the figures within the metabolism study

QuEChERS Method (EN 15662:2009) (S.Amic, 2012)

QuEChERS analytical method involves extraction of free M4 and M6 from crop samples, by agitating for 2 minutes with acetonitrile:ultra pure water (80:20, v:v). The extract is subjected to SPE clean-up where the eluate is then centrifuged at room temperature. An aliquot of the supernatant is then diluted with acetonitrile:water (80:20, v:v) prior to analysis by LC-MS/MS (M4: *m/z* 333.2 → 303.2; M6: *m/z* 345.1 → 173.1).

The QuEChERS analytical method was successfully validated by Eurofins Agroscience Services Chem SAS for the determination of residues of M4 and M6 in lettuce and wheat grain. Average recoveries of the metabolites, when fortified at the LOQ (0.01 mg/kg/analyte) and 10× LOQ, ranged from 88–110% with RSD of ≤ 7%, which demonstrated good reproducibility.

Animal Commodities

Method 1530-03 (K. Lin, 2003)

Residues of M4 and M6 in animal tissues, milk and eggs are refluxed with 1 N HCl for two hours and filtered. The filtrates are injected into a SCX (2) SPE cartridge followed by a C_8 SPE cartridge for clean-up. The eluates are evaporated and brought to an appropriate final volume with 0.2% formic acid prior to being injected onto an HPLC equipped with a column-switching system consisting of an SCX separatory column followed by a C_8 analytical column. The analytes were separated with the HPLC system and detected with a mass spectrometer equipped with a triple stage quadrupole mass analyser. Ion-spray atmospheric pressure ionization (API) was used to introduce the HPLC effluent into the mass spectrometer (M4: *m/z* 333→303, M6: *m/z* 345→173).

The method underwent successful interlaboratory validation by EN-CAS laboratories (K. Faltinski, 2003) using beef muscle, beef fat, milk and eggs. Average recoveries of M4 and M6 ranged from 84–110% with RSD of ≤ 16%, which demonstrated overall good reproducibility.

Table 36 Method recovery data of pinoxaden and metabolites in plants and animal products

Matrix	Compound	Fortification level (mg/kg)	N	Recovery (%)			Method	Reference
				Range	Mean	RSD		
Barley								
Whole plant	M2	0.02	5	75–86	81	7	REM199.02 / REM 199.03	3030/01 - 0156
		2.0	5	79–90	83	6		
	M4	0.02	5	92–97	93	3		
		2.0	5	82–93	85	5		
	M6	0.02	5	99–104	101	2		
		2.0	5	83–92	87	4		
	M10	0.02	5	77–95	87	8		
		2.0	5	83–92	87	5		
Straw	M2	0.02	5	60–88	72	15		
		0.50	5	77–84	80	4		
	M4	0.02	5	77–91	87	7		
		0.50	5	79–88	84	5		
	M6	0.02	5	75–88	82	7		
		0.50	5	68–84	78	8		
	M10	0.02	5	76–88	82	5		
		0.50	5	68–80	76	6		
Grain	M2	0.01	5	83–103	93	9		
		0.50	5	75–86	81	5		
	M4	0.01	5	80–96	87	7		
		0.50	5	84–91	87	3		
	M6	0.01	5	88–107	93	9		
		0.50	5	74–89	84	8		
	M10	0.01	5	84–102	89	8		
		0.50	5	81–87	84	3		
Grain	M4	0.01	5	92–96	94	2	QuEChERS (EN 15662:2009)	
		0.1	5	91–92	92	0		
	M6	0.01	5	90–103	98	6		
		0.1	5	93–95	94	1		
Wheat								
Whole plant	M2	0.02	5	97–104	102	3	REM 199.02	0057, 0058/02 - S302
		0.20	5	96–104	101	3		
	M4	0.02	5	94–110	103	6		
		0.20	5	97–104	100	3		
	M6	0.02	5	93–105	100	5		
		0.20	5	92–105	98	5		
	M10	0.02	5	91–97	93	3		

Matrix	Compound	Fortification level (mg/kg)	N	Recovery (%)			Method	Reference
				Range	Mean	RSD		
		0.20	5	89–94	2			
Straw	M2	0.02	5	75–82	80	4		
		0.20	5	76–86	82	6		
	M4	0.02	5	92–105	99	6		
		0.20	5	96–101	99	2		
	M6	0.02	5	76–97	90	9		
		0.20	5	84–96	91	6		
	M10	0.02	5	81–90	85	4		
		0.20	5	82–87	84	3		
Grain	M2	0.01	5	91–111	104	7		
		0.10	5	94–98	96	2		
	M4	0.01	5	89–101	95	6		
		0.10	5	92–96	95	2		
	M6	0.01	5	90–116	103	9		
		0.10	5	101–117	107	7		
	M10	0.01	5	78–86	83	4		
		0.10	5	74–79	77	2		
Forage	M2 (expressed as pinoxaden equivalents)	0.02	6	89–98	94	4	117–01	RJ3408B
		0.1	2	91–106	99	11		
		1.0	2	88–108	98	14		
	M4	0.02	6	74–93	84	10		
		0.1	2	77–83	80	5		
		1.0	2	73–80	77	6		
	M6	0.02	6	93–99	96	3		
		0.1	2	92–98	95	4		
		1.0	2	94–98	96	3		
Hay	M2 (expressed as pinoxaden equivalents)	0.02	6	80–92	87	7		
		0.1	2	94	94	0		
		1.0	2	96–99	98	2		
	M4	0.02	6	80–87	82	3		
		0.1	2	76–95	86	16		
		1.0	2	80–85	83	4		
	M6	0.02	6	83–103	93	9		
		0.1	2	87–101	94	11		
		1.0	2	85–89	87	3		
Straw	M2 (expressed as pinoxaden equivalents)	0.02	6	74–88	81	7		
		0.1	2	74–94	84	17		
		1.0	2	80–96	88	13		
	M4	0.02	6	70–86	79	8		
		0.1	2	83–94	89	9		
		1.0	2	80–89	85	8		
	M6	0.02	6	87–106	96	8		
		0.1	2	87–88	88	1		
		1.0	2	79–86	83	6		
Grain	M2 (expressed as pinoxaden equivalents)	0.01	6	83–105	92	9		
		0.1	1	102	102	n/a		
		1.0	2	94–96	95	1		
	M4	0.01	6	72–102	83	14		
		0.1	1	75	75	n/a		

Matrix	Compound	Fortification level (mg/kg)	N	Recovery (%)			Method	Reference
				Range	Mean	RSD		
		1.0	2	76–79	78	3		
	M6	0.01	6	74–111	88	15		
		0.1	1	89	89	n/a		
		1.0	2	81–88	85	6		
Other food crops								
Lettuce	M4	0.01	5	92–96	94	2	QuEChERS (EN 15662:2009)	S12-04302/1000
		0.1	5	100–107	104	3		
	M6	0.01	5	90–97	93	3		
		0.1	5	98–105	102	3		
Rapeseed	M4	0.01	5	86–117	101	13		
		0.1	5	91–99	95	4		
	M6	0.01	5	93–117	103	10		
		0.1	5	94–98	95	2		
Orange fruit	M4	0.01	5	100–101	101	1		
		0.1	5	96–104	100	3		
	M6	0.01	5	79–102	89	12		
		0.1	5	94–95	95	1		
Animal Commodities								
Cows' milk	M4	0.01	6	87–110	99	12	1530-03	T001530-03/0261
		0.1	6	96–110	102	5		
		0.5	1		79	n/a		
		1.0	1		98	n/a		
	M6	0.01	6	98–108	103	5		
		0.1	6	93–93	93	n/a		
		0.5	1		94	n/a		
		1.0	1		94	n/a		
Beef liver	M4	0.02	6	82–100	96	7		
		0.1	2	88–95	92	5		
		1.0	2	87–96	92	7		
	M6	0.02	6	93–104	99	4		
		0.1	2	76–99	88	19		
		1.0	2	95–99	97	3		
Beef muscle	M4	0.02	6	100–104	103	1		
		0.1	2	98–101	100	2		
		0.2	5	86–101	95	6		
		1.0	2	93–95	94	2		
	M6	0.02	6	98–104	101	2		
		0.1	2	99–106	103	5		
		0.2	5	85–95	91	4		
		1.0	2	91–97	94	5		
Beef fat	M4	0.02	6	93–97	95	2		
		0.1	2	100–101	101	1		
		0.2	5	93–104	98	4		
		1.0	2	96–100	98	3		
	M6	0.02	6	95–101	98	2		
		0.1	2	96–100	98	3		
		0.2	5	85–101	94	6		
		1.0	2	96–99	98	2		
Beef kidney	M4	0.02	6	81–98	90	7		
		0.1	2	87–99	93	9		
		1.0	2	88–96	92	6		
	M6	0.02	6	80–99	93	7		
		0.1	2	98–101	100	2		
		1.0	2	97–104	101	5		
Chicken	M4	0.02	6	81–97	88	8		

Matrix	Compound	Fortification level (mg/kg)	N	Recovery (%)			Method	Reference
				Range	Mean	RSD		
liver								
		0.1	2	69–84	77	14		
		1.0	2	88–90	89	2		
	M6	0.02	6	96–100	97	2		
		0.1	2	83–99	91	12		
		1.0	2	92–104	98	9		
Chicken muscle	M4	0.02	6	87–104	97	7		
		0.1	2	94–99	97	4		
		0.2	5	89–95	92	2		
		1.0	2	96–101	99	4		
	M6	0.02	6	100–105	103	2		
		0.1	2	95–101	98	4		
		0.2	5	78–92	86	7		
		1.0	2	98–102	100	3		
Chicken eggs	M4	0.02	6	86–100	95	6		
		0.1	2	99–103	101	3		
		0.2	5	81–95	89	8		
		1.0	2	99–102	101	2		
	M6	0.02	6	97–104	101	3		
		0.1	2	99–105	102	4		
		0.2	5	84–98	92	7		
		1.0	2	96–100	98	3		
Chicken fat	M4	0.02	5	88–93	91	2		
		0.2	5	72–85	80	8		
	M6	0.02	5	98–100	99	1		
		0.2	5	89–93	90	2		

Stability of residues in stored analytical samples

Information was received on the freezer storage stability of pinoxaden and its metabolites in plant and animal commodities. The storage stability of pinoxaden and its metabolites M2, M4, M6, M10 are described as follows. The results are shown in Table 37.

Plant commodities

Wheat (whole plant, straw and grain)

Report No.: 02-S305 (Kwiatkowski, 2004)

Methods: REM199.02 (for analyses carried out up to and including 9 month intervals)

REM199.03 (for analyses of the 15, 19, 24 and 28 month intervals)

Description: Untreated control samples were individually fortified with each of the pinoxaden metabolites M2, M4, M6 and M10 at a concentration of 0.2 mg/kg/analyte for whole plant and straw and 0.1 mg/kg/analyte for grain and then frozen at –18 °C or lower. Samples were analysed immediately after fortification (0 Day) and after storage intervals up to 28 months. At each interval, three stored samples were analysed, with one or more procedural recovery samples (control samples fortified just before analysis).

Table 37 Freezer storage stability of pinoxaden metabolites in wheat

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
M2					
Wheat whole plant					

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
0	0.20, 0.18, 0.19	0.19	100	98, 100	99
1	0.21, 0.20, 0.21	0.21	110	99, 102	100
4	0.20, 0.19, 0.19	0.20	105	97, 96	96
6	0.19, 0.19, 0.19	0.19	100	98, 95	96
9	0.18, 0.20, 0.19	0.19	100	100, 99	100
15	0.20, 0.21, 0.22	0.21	110	78, 78	78
19	0.19, 0.19, 0.21	0.20	105	86, 81	94
24	0.19, 0.19, 0.21	0.20	105	89, 86	88
28	0.22, 0.22, 0.20	0.21	110	92, 95	94
Wheat straw					
0	0.17, 0.16, 0.16	0.16	100	83, 81	82
1	0.14, 0.16, 0.16	0.15	94	84, 78	81
4	0.16, 0.16, 0.16	0.16	100	80, 85	82
6	0.15, 0.15, 0.14	0.15	94	81, 78	80
9	0.16, 0.16, 0.15	0.16	100	84, 79	82
15	0.17, 0.17, 0.16	0.17	106	72, 78	75
19	0.17, 0.17, 0.18	0.17	106	84, 87	86
24	0.15, 0.15, 0.14	0.15	94	78, 75	76
28	0.16, 0.16, 0.15	0.16	100	78, 76	77
Wheat grain					
0	0.09, 0.10, 0.10	0.10	100	92, 82	87
1	0.09, 0.09, 0.09	0.09	90	93, 95	94
4	0.09, 0.09, 0.08	0.09	90	94, 86	90
6	0.09, 0.09, 0.08	0.09	90	96, 85	90
9	0.08, 0.08, 0.08	0.08	80	88, 85	86
15	0.09, 0.09, 0.09	0.09	90	81, 83	82
19	0.06, 0.08, 0.07	0.07	70	68, 72	70
26	0.07, 0.08, 0.08	0.08	80	86, 85	86
28	0.09, 0.08, 0.08	0.08	80	94, 89	92
M4					
Wheat whole plant					
0	0.22, 0.21, 0.21	0.21	100	113, 111	112
1	0.20, 0.19, 0.21	0.20	95	100, 102	101
4	0.21, 0.21, 0.20	0.21	100	100, 101	100
6	0.19, 0.19, 0.19	0.19	90	100, 98	99
9	0.20, 0.20, 0.20	0.20	95	101, 98	100
15	0.21, 0.24, 0.24	0.23	110	101, 99	100
19	0.21, 0.22, 0.23	0.22	105	98, 100	99
24	0.23, 0.25, 0.25	0.24	114	95, 94	94
28	0.23, 0.22, 0.23	0.23	110	94, 99	96
Wheat straw					
0	0.19, 0.19, 0.20	0.19	100	99, 100	100
1	0.17, 0.17, 0.19	0.18	95	96, 95	96
4	0.18, 0.18, 0.17	0.18	95	95, 94	94
6	0.17, 0.16, 0.16	0.16	84	95, 92	94
9	0.18, 0.18, 0.18	0.18	95	94, 94	94
15	0.21, 0.21, 0.20	0.21	110	95, 98	96
19	0.16, 0.16, 0.17	0.16	84	87, 95	91
24	0.16, 0.16, 0.15	0.16	84	90, 85	88
28	0.16, 0.17, 0.18	0.17	89	90, 83	86
Wheat grain					
0	0.09, 0.11, 0.11	0.10	100	101, 96	98
1	0.08, 0.09, 0.09	0.09	90	93, 91	92
4	0.09, 0.08, 0.07	0.08	80	94, 77	86
6	0.08, 0.08, 0.08	0.08	80	93, 75	84
9	0.08, 0.08, 0.08	0.08	80	88, 87	88
15	0.09, 0.10, 0.09	0.09	90	86, 83	84
19	0.08, 0.08, 0.07	0.08	80	76, 77	75
24	0.09, 0.10, 0.09	0.09	90	77, 88	82

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
28	0.09, 0.09, 0.08	0.09	90	94, 97	96
M6					
Wheat whole plant					
0	0.20, 0.21, 0.22	0.21	100	111, 108	110
1	0.21, 0.21, 0.22	0.21	100	103, 109	106
4	0.20, 0.21, 0.22	0.21	100	103, 103	103
6	0.19, 0.19, 0.16	0.18	86	105, 93	99
9	0.17, 0.19, 0.19	0.18	86	98, 98	98
15	0.20, 0.26, 0.27	0.24	114	93, 87	90
19	0.23, 0.22, 0.22	0.22	105	100, 98	99
24	0.20, 0.20, 0.20	0.20	95	98, 93	96
28	0.21, 0.20, 0.22	0.21	100	96, 95	96
Wheat straw					
0	0.20, 0.20, 0.19	0.20	100	97, 108	102
1	0.21, 0.21, 0.19	0.20	100	96, 107	101
4	0.19, 0.20, 0.21	0.20	100	94, 113	103
6	0.18, 0.18, 0.20	0.19	95	103, 94	98
9	0.16, 0.17, 0.17	0.17	85	87, 86	86
15	0.17, 0.17, 0.16	0.17	85	90, 73	81
19	0.15, 0.15, 0.16	0.15	75	86, 102	94
24	0.16, 0.17, 0.19	0.17	85	89, 83	86
28	0.17, 0.18, 0.19	0.18	90	88, 86	87
Wheat grain					
0	0.09, 0.10, 0.10	0.10	100	89, 86	88
1	0.10, 0.10, 0.10	0.10	100	101, 101	101
4	0.10, 0.10, 0.09	0.10	100	93, 101	97
6	0.08, 0.11, 0.11	0.10	100	93, 98	96
9	0.08, 0.08, 0.08	0.08	80	90, 89	90
15	0.09, 0.10, 0.10	0.10	100	93, 94	94
19	0.09, 0.10, 0.10	0.10	100	95, 125	110
24	0.09, 0.09, 0.08	0.09	90	76, 81	78
28	0.10, 0.10, 0.09	0.10	100	98, 106	102
M10					
Wheat whole plant					
0	0.18, 0.18, 0.18	0.18	100	87, 90	88
1	0.17, 0.19, 0.20	0.19	105	96, 92	94
4	0.19, 0.18, 0.18	0.18	100	90, 87	88
6	0.18, 0.18, 0.18	0.18	100	93, 94	94
9	0.17, 0.18, 0.18	0.18	100	92, 90	91
15	0.22, 0.24, 0.26	0.24	133	101, 102	102
19	0.22, 0.24, 0.24	0.23	128	95, 96	96
24	0.22, 0.22, 0.22	0.22	122	92, 94	93
28	0.24, 0.24, 0.23	0.24	133	90, 94	92
Wheat straw					
0	0.16, 0.16, 0.16	0.16	100	83, 89	86
1	0.15, 0.15, 0.13	0.14	88	83, 84	84
4	0.14, 0.15, 0.15	0.15	94	81, 78	80
6	0.13, 0.13, 0.13	0.13	81	82, 82	82
9	0.14, 0.14, 0.14	0.14	88	87, 82	84
15	0.17, 0.17, 0.17	0.17	106	93, 97	95
19	0.13, 0.13, 0.12	0.13	81	80, 89	84
24	0.12, 0.12, 0.12	0.12	75	86, 82	84
28	0.12, 0.12, 0.12	0.12	75	90, 87	88
Wheat grain					
0	0.08, 0.09, 0.09	0.09	100	84, 80	82
1	0.08, 0.08, 0.08	0.08	88	83, 79	81
4	0.08, 0.07, 0.06	0.07	77	79, 71	75
6	0.08, 0.07, 0.07	0.07	77	82, 71	76
9	0.07, 0.07, 0.06	0.07	77	71, 71	71

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
15	0.09, 0.10, 0.08	0.08	88	92, 80	86
19	0.07, 0.09, 0.07	0.08	88	70, 70	70
24	0.10, 0.10, 0.10	0.10	111	75, 91	83
28	0.10, 0.09, 0.09	0.10	111	101, 107	104

Wheat processed fractions

Project No.: T022294-04 (Lin, 2006)

Method: 117-01

Description: Untreated control samples of wheat processed fractions (flour, bran, shorts, germ, middlings and aspirated grain fractions) were individually fortified with pinoxaden reported as M2 and its metabolites M4 and M6 at a concentration of 1.0 mg/kg/analyte and then frozen at–20 °C or lower. Samples were analysed immediately after fortification (0 Day) and after storage intervals up to 16 months. At each interval, two stored samples were analysed with two procedural recovery samples (control samples fortified just before analysis).

Table 38 Freezer storage stability of pinoxaden, M4 and M6 in wheat processed commodities

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
Pinoxaden (reported as M2)					
Flour					
0	0.89, 0.86	0.88	100	112, 109	110
3	0.73, 0.73	0.73	83	97, 91	94
7	0.85, 0.80	0.82	93	109, 109	109
16	0.70, 0.80	0.75	85	102, 98	100
Bran					
0	0.79, 0.80	0.80	100	101, 107	104
3	0.82, 0.67	0.75	94	94, 93	94
7	0.90, 0.82	0.86	108	110, 109	110
16	0.75, 0.75	0.75	94	90, 97	94
Germ					
0	0.73, 0.76	0.74	100	98, 99	98
3	0.73, 0.75	0.74	100	92, 94	93
7	0.81, 0.82	0.82	110	104, 105	104
16	0.77, 0.76	0.76	103	97, 102	100
Shorts					
0	0.81, 0.79	0.80	100	103, 101	102
3	0.78, 0.75	0.76	95	100, 93	96
7	0.80, 0.81	0.80	100	106, 107	106
16	0.80, 0.84	0.82	102	111, 110	110
Middlings					
0	0.82, 0.79	0.80	100	103, 104	104
3	0.76, 0.80	0.78	98	99, 99	99
7	0.80, 0.83	0.82	102	110, 108	109
16	0.72, 0.69	0.70	88	87, 102	94
Aspirated grain fraction					
0	0.70, 0.68	0.69	100	80, 86	83
3	0.58, 0.53	0.56	81	74, 73	74
7	0.75, 0.67	0.71	103	91, 86	88
16	0.75, 0.69	0.72	104	83, 98	90
M4					
Flour					
0	0.91, 1.1	0.10	100	104, 107	106
3	0.78, 0.83	0.80	80	90, 98	94
7	0.89, 0.88	0.88	88	93, 95	94

Storage time (months)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining (%)	Individual procedural recoveries (%)	Mean procedural recovery (%)
16	0.92, 0.94	0.93	93	97, 89	93
Bran					
0	1.1, 1.1	1.1	100	116, 105	110
3	0.96, 0.97	0.96	87	92, 94	93
7	0.93, 0.92	0.92	84	93, 96	94
16	0.89, 0.80	0.84	76	95, 91	93
Germ					
0	1.1, 1.0	1.05	100	113, 100	106
3	0.95, 0.88	0.92	88	105, 95	100
7	0.98, 0.90	0.94	90	98, 102	100
16	0.96, 0.90	0.93	89	97, 91	94
Shorts					
0	1.1, 1.1	1.1	100	106, 101	104
3	1.0, 1.0	1.0	90	99, 116	108
7	0.89, 0.85	0.87	79	94, 95	94
16	0.86, 0.95	0.90	82	96, 99	98
Middlings					
0	1.1, 1.1	1.1	100	104, 99	102
3	0.94, 0.94	0.94	85	104, 97	100
7	0.92, 0.94	0.93	84	101, 94	98
16	0.91, 0.94	0.92	84	92, 93	92
Aspirated grain fraction					
0	1.0, 0.87	0.94	100	103, 98	100
3	1.0, 1.0	1.0	106	87, 96	92
7	0.76, 0.70	0.73	77	73, 81	77
16	0.92, 0.78	0.85	90	75, 70	72
M6					
Flour					
0	0.91, 0.77	0.84	100	80, 92	86
3	0.94, 0.88	0.91	108	86, 94	90
7	0.75, 0.79	0.77	92	80, 84	82
16	0.87, 0.91	0.89	106	92, 89	90
Bran					
0	0.86, 0.83	0.84	100	75, 90	82
3	0.80, 0.88	0.84	100	81, 89	85
7	0.81, 0.72	0.76	90	76, 74	75
16	0.88, 0.87	0.88	105	90, 84	87
Germ					
0	0.67, 0.76	0.72	100	80, 78	79
3	0.89, 0.88	0.88	82	91, 95	93
7	0.69, 0.57	0.63	88	69, 70	70
16	0.79, 0.82	0.80	111	83, 77	80
Shorts					
0	0.89, 0.91	0.90	100	84, 88	86
3	0.89, 0.90	0.90	100	82, 101	92
7	0.72, 0.72	0.72	125	76, 92	84
16	0.87, 0.82	0.84	107	91, 90	90
Middlings					
0	0.83, 0.87	0.85	100	70, 78	74
3	0.87, 0.96	0.92	108	86, 91	88
7	0.75, 0.75	0.75	88	79, 80	80
16	0.76, 0.75	0.76	89	84, 88	86
Aspirated grain fraction					
0	0.82, 0.78	0.80	100	78, 83	80
3	0.78, 0.85	0.82	102	80, 87	84
7	0.76, 0.70	0.73	91	75, 84	80
16	0.92, 0.78	0.85	106	87, 85	86

Animal commodities

Chicken muscle, beef liver, milk and eggs

Project No.: T001241-03 (Lin, 2003)

Method: 1530-03

Description: Untreated control samples of milk, egg, chicken muscle, and beef liver were individually fortified with the metabolites M4 and M6 at a concentration of 0.5 mg/kg/analyte and then frozen at –20 °C or lower. Samples were analysed immediately after fortification (0 day) and after storage intervals up to 3 months. At each interval, two stored samples were analysed with two procedural recovery samples (control samples fortified just before analysis).

Table 39 Freezer storage stability of M4 and M6 in chicken muscle, beef liver, milk and eggs

Storage time (days)	Individual stored sample residues (mg/kg)	Mean stored sample residue (mg/kg)	Remaining	Individual procedural recoveries (%)	Mean procedural recovery (%)
M4					
Chicken Muscle					
0	0.41, 0.42	0.42	100	84, 85	84
34	0.46, 0.46	0.46	110	93, 91	92
90	0.36, 0.41	0.38	90	82, 81	82
Beef liver					
0	0.45, 0.45	0.45	100	89, 90	90
34	0.39, 0.46	0.42	93	92, 93	92
90	0.47, 0.48	0.48	106	96, 100	98
Milk					
0	0.47, 0.48	0.48	100	96, 97	96
34	0.47, 0.48	0.48	100	91, 95	93
90	0.47, 0.49	0.48	100	94, 95	94
Eggs					
0	0.44, 0.45	0.44	100	88, 89	88
34	0.45, 0.46	0.46	104	90, 91	90
90	0.47, 0.49	0.48	109	94, 95	94
M6					
Chicken Muscle					
0	0.41, 0.42	0.42	100	99, 100	100
34	0.46, 0.46	0.46	110	93, 93	93
90	0.36, 0.41	0.38	90	83, 85	84
Beef liver					
0	0.45, 0.45	0.45	100	94, 95	94
34	0.39, 0.46	0.42	93	95, 95	95
90	0.47, 0.48	0.48	106	96, 97	96
Milk					
0	0.47, 0.48	0.48	100	94, 94	94
34	0.47, 0.48	0.48	100	98, 99	98
90	0.47, 0.49	0.48	100	99, 100	100
Eggs					
0	0.44, 0.45	0.44	100	92, 93	92
34	0.45, 0.46	0.46	104	91, 94	92
90	0.46, 0.48	0.47	107	92, 97	94

USE PATTERN

Pinoxaden is a post-emergence herbicide, registered in Canada, the United States and Europe, for control of annual grass and broadleaf weeds in wheat and barley. The products from Canada and the United States are co-formulated with florasulam and must be applied with an adjuvant while the product from EU is co-formulated with cloquintocet mexyl. The information available to the Meeting on registered uses on wheat and barley is summarized in Table 40. Labels were submitted for both uses.

Table 40 Registered uses of pinoxaden

Country / Trade Name	Form. (guarantee)	Application					PHI, days
		Growth Stage (BBCH)	Rate, kg ai/ha	Spray Volumes, L/ha	Maximum Spray conc., kg ai/hL	No.	
Spring Wheat							
Canada	Emulsifiable Concentrate (92.7 g/L)	up to 37	0.06	50–100	0.12	1	60
United States	Emulsifiable Concentrate (9%)	up to 39	0.06	20–40	0.30	1	60
Slovenia	Emulsion Concentrate (50 g/L)	13–39	0.06	200–400	0.03	1	NS
Barley							
Canada	Emulsifiable Concentrate (92.7 g/L)	up to 37	0.06	50–100	0.12	1	60
United States	Emulsifiable Concentrate (9%)	up to 39	0.06	20–40	0.30	1	60
Slovenia	Emulsion Concentrate (50 g/L)	13–39	0.06	200–400	0.03	1	NS

NS: Not specified

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for pinoxaden uses that produced residues on the following commodities:

Classification	Group	Commodity	Table No.
GC 0080	Cereal Grains	Wheat	41
		Barley	42
AF 0161 and AS 0161	Straw, fodder and forage of cereal grains, forage, straw and fodder, dry	Wheat forage/whole plant, hay/ears/stalks and hay	43, 44, 45
		Barley forage, hay/ears/stalks and straw	46, 47, 48

In the supervised residue trials tables, where two samples were taken from a single plot, the average value is reported (individual sample results in parentheses). Where results from separate plots with similar characteristics, such as location, year of trials and treatment schedules (dependent trials) were reported, results are listed for each plot and separated with a dashed line. However, in these cases, the higher residue has been used for calculation purposes. Dates of duration of residue sample storage before analysis were provided and are all covered by the demonstrated storage intervals.

Residue values from the trials conducted per the maximum GAP have been used for the estimation of maximum residue levels. Those results, included in the calculations using the OECD MRL-calculator, are underlined.

Wheat

A total of ninety-two trials were conducted in Canada, the USA, Germany, Netherlands, United Kingdom, France, Italy, Spain, Switzerland and Greece between 2001 and 2014. In most trials, a

single foliar spray application of an EC formulation was made either in accordance with the regional GAP or at exaggerated rates. Grain was harvested 55–132 DALA.

The analytical methods REM 199-03 and 117-01 were used to analyse the grain samples collected from Canadian and USA trials, respectively. For all trials conducted in Europe, samples were analysed using the REM 199.02/REM 199.03 LC-MS/MS methods. However, for the 2013 European trials, grain samples treated at the lower rate (60 g ai/ha) were analysed using the QuEChERS method only while those treated at the higher rate (180 g ai/ha) were analysed using both, the QuEChERS method and the REM 199.03 method. For the latter samples, only the residues resulting from method REM 199.03 are reported in the tables below. For all methods, the LOQs were determined to be 0.01 mg/kg/analyte for grain and 0.02 mg/kg/analyte for forage/whole plant, hay/ears/stalks and straw. While only the grain samples collected from the European trials and analysed using the REM 199.03 method reported residues of the metabolite M10, residues of this analyte were non-quantifiable (< 0.01 mg/kg) and therefore are not reported herein.

The maximum period of sample storage at -20 °C was 36–489 days (1–16 months) for all trials. Storage stability data on high starch content commodities show that the residues are stable for up to 28 months. The residues in wheat grain are summarized in Table 41, while those in wheat forage/whole plant, hay/ears/stalks and straw are reported in Tables 43, 44 and 45, respectively.

Table 41 Residues of pinoxaden in wheat grain following foliar spray with pinoxaden in North American and European regions

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
Canada GAP	0.06	0.12	up to 37	60			
Canada Portage la Prairie, MB, 2009 (AC Domain) T647 CER 07024/09	0.06	0.07	10–12 (2-leaf stage)	102	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Taber, AB, 2009 (Superb) T648 CER 07024/09	0.06	0.07	16–18 (leaves unfolding)	91	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	< 0.01 (< 0.01, < 0.01)
Canada Rosthern, SK, 2009 (Lillian) T649 CER 07024/09	0.06	0.06	12–13 (2–3-leaf stage)	91	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Elm Creek, MB, 2003 (AC Barrie) T566 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Elm Creek, MB, 2003 (Majestic) T567 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Delisle, SK, 2003 (Eatonia) T568 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	60	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)	0.01 (< 0.01, < 0.01, 0.01, 0.02, < 0.01, 0.02)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)
Canada Vanscoy, SK, 2003 (Prodigy)	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
T569 CER 0708/03				69	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Vanscoy, SK, 2003 (Eatonia) T570 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	59	< 0.01	0.01	< 0.01
				66	< 0.01 (< 0.01, < 0.01)	0.02 (0.01, 0.02)	< 0.01 (< 0.01, < 0.01)
				74	< 0.01	< 0.01	< 0.01
				80	< 0.01	0.02	< 0.01
Canada Wrentham, AB, 2003 (McKenzie) T571 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	69	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Wrentham, AB, 2003 (Prodigy) T573 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	71	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Taber, AB, 2003 (Prodigy) T572 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	75	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Taber, AB, 2003 (McKenzie) T574 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	76	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Taber, AB, 2003 (McKenzie) T575 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	85	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Rosthern, SK, 2003 (AC Barrie) T576 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	79	< 0.01 (< 0.01, < 0.01)	0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Rosthern, SK, 2003 (AC Eatonia) T581 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	79	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Lacombe, AB, 2003 (AC Crystal) T577 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	98	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Lacombe, AB, 2003 (AC Intrepid) T580 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	81	< 0.01	< 0.01	< 0.01
				88	< 0.01 (< 0.01, < 0.01)	0.01 (< 0.01, 0.01)	< 0.01 (< 0.01, < 0.01)
				94	< 0.01	0.01	< 0.01
				101	< 0.01	< 0.01	< 0.01
Canada Penhold, AB, 2003 (Intrepid) T578 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	90	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada Penhold, AB, 2003	0.07	0.06–0.09	23 (3–6 leaf stage)	90	< 0.01 (< 0.01,	< 0.01 (< 0.01,	< 0.01 (< 0.01,

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
(AC Crystal) T579 CER 0708/03					< 0.01)	< 0.01)	< 0.01)
Canada Hepburn, SK, 2003 (AC Barrie) T582 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	58	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.01 (0.01, < 0.01)
Canada Minto, MB, 2003 (Super B) T583 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	58	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01,< 0.01, < 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)
Canada Minto, MB, 2003 (Avonlea) T584 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	66	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)	0.02 (0.02, 0.03, 0.01, 0.01, 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)
Canada Boissevain, MB, 2003 (AC Barrie) T585 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	61	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
USA GAP	0.06	0.30	up to 39	60			
USA Champaign, IL, 2003 (Kaskaskia) NAHR00702 824-02	0.07	0.06	51 (start of earing)	60	< 0.01 (< 0.01, < 0.01)	0.24 (0.25, 0.23)	0.03 (0.03, 0.02)
USA Nickerson, KS 2002 (Heyne) NAHR01102 824-02	0.07	0.06	45 (flag leaf sheath swollen (late boot))	60	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.12)	0.01 (0.01, 0.01)
USA Larned, KS 2002 (Jagger) NAHR01202 824-02	0.07	0.05	33 (nodes detectable)	60	< 0.01 (< 0.01, < 0.01)	0.11 (0.12, 0.10)	0.01 (0.01, 0.01)
USA Belpre, KS, 2002 (Jagger) NAHR01302 824-02	0.07	0.38	47 (flag leaf sheath opening)	60	< 0.01 (< 0.01, < 0.01)	0.09 (0.09, 0.09)	0.01 (0.01, 0.01)
USA Grand Island, NE, 2003 (Nuplains) NBHR01102 824-02	0.07	0.04	32 (2-node stage)	60	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.03)	< 0.01 (< 0.01, < 0.01)
USA Lake Andes, SD, 2002 (Forge HRS) NCHR00702 824-02	0.07	0.05	31 (1-node stage)	60	< 0.01 (< 0.01, < 0.01)	0.07 (0.05, 0.08)	< 0.01 (< 0.01, < 0.01)
USA St. Joseph, MO, 2003 (Karl) NDHR00702	0.07	0.06	39 (ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.15 (0.16, 0.13)	0.01 (0.01, 0.01)

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
824-02							
USA Geneva, MN, 2002 (Oxen) NFHR00902 824-02	0.07	0.05	up to 49 (opening of leaf sheath)	60	< 0.01 (< 0.01, < 0.01)	0.13 (0.13, 0.12)	0.01 (0.01, < 0.01)
USA Stillwater, OK, 2002-2003 (Jaggar PVPA) SCHR01202 824-02	0.07	0.05	39 (ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.24 (0.22, 0.25)	0.03 (0.03, 0.04)
USA Colony, OK, 2003 (Coker 9663) SCHR01302 824-02	0.07	0.06	47 (flag leaf sheath opening)	60	< 0.01 (< 0.01, < 0.01)	0.12 (0.10, 0.13)	0.03 (0.02, 0.03)
	0.36	0.31	47 (flag leaf sheath opening)	60	< 0.01 (< 0.01, < 0.01)	0.48 (0.45, 0.51)	0.14 (0.14, 0.14)
USA Levelland, TX, 2003 (TAM 105) SCHR01402 824-02	0.07	0.04	41–45 (boot stage)	60	< 0.01 (< 0.01, < 0.01)	0.19 (0.19, 0.19)	0.03 (0.03, 0.03)
USA Rincon, NM, 2003 (TAM 200) SCHR01502 824-02	0.07	0.07	20–30 (jointing)	60	< 0.01 (< 0.01, < 0.01)	0.09 (0.10, 0.07)	0.01 (0.01, < 0.01)
USA Shoffner, AR, 2003 (DK7900) SEHR00602 824-02	0.07	0.04	51 (start of earing)	60	< 0.01 (< 0.01, < 0.01)	0.31 (0.28, 0.33)	0.05 (0.04, 0.05)
USA Rose Hill, NC, 2003 (Coker 9803) SJHR02202 824-02	0.07	0.04	11 (1-leaf stage)	60	< 0.01 (< 0.01, < 0.01)	0.55 (0.64, 0.45)	0.06 (0.07, 0.04)
USA Visalia, CA, 2003 (Yecoro, Rojo) W2HR00202 824-02	0.07	0.06	57 (between middle point of earing and end of earing)	60	< 0.01 (< 0.01, < 0.01)	0.42 (0.26, 0.57)	0.08 (0.05, 0.10)
USA Ephrata, WA, 2003 (Stephens) WFHR01102 824-02	0.07	0.04	59 (end of earing)	60	< 0.01 (< 0.01, < 0.01)	0.26 (0.26, 0.25)	0.03 (0.02, 0.03)
USA Ault, CO, 2003 (Platte) WHHR00702 824-02	0.07	0.05	49 (opening of leaf sheath)	60	< 0.01 (< 0.01, < 0.01)	0.06 (0.07, 0.06)	< 0.01 (< 0.01, < 0.01)
USA Gardner, ND, 2002 (Alsen) WIHR00902 824-02	0.07	0.06	23 (tillering)	60	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	< 0.01 (< 0.01, < 0.01)
	0.22	0.19	23 (tillering)	60	< 0.01 (< 0.01, < 0.01)	0.05 (0.06, 0.05)	0.01 (0.01, 0.01)
USA Eldridge, ND, 2002 (Belzer)	0.07	0.06	45 (late boot stage)	60	< 0.01 (< 0.01, < 0.01)	0.26 (0.18, 0.33)	0.04 (0.03, 0.05)

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
WIHR01002 824-02							
USA Dagmar, MT, 2002 (Challis) WIHR01102 824-02	0.07	0.38	33 (3-node stage)	60	< 0.01 (< 0.01, < 0.01)	0.19 (0.19, 0.18)	0.02 (0.02, 0.02)
USA Dagmar, MT, 2002 (Pristine) WIHR01202 824-02	0.07	0.05	33 (3-node stage)	60	< 0.01 (< 0.01, < 0.01)	0.29 (0.28, 0.30)	0.04 (0.04, 0.04)
Slovenia GAP	0.06	0.03	13–39	Not specified			
Greece Polidendri Domokou, 2004 (Simeto) GRHR040024 04-7004	0.03	0.01	25 (main stage of tillering)	90	< 0.01	< 0.01	< 0.01
			31–32 (1- to 2-node stage)	77	< 0.01	0.03	< 0.01
			39 (ligule stage)	69	< 0.01	0.04	0.01
	0.04	0.02	25 (main stage of tillering)	90	< 0.01	0.01	< 0.01
			31–32 (1- to 2-node stage)	77	< 0.01	0.05	0.01
			39 (ligule stage)	69	< 0.01	0.04	< 0.01
Germany Frechen, Rhein-Nordrhein-Westfalen, 2013 (Julius) 13-00434-01 TK0179719	0.06	0.02	33–37 (2-node stage- appearance of last leaf)	75	n.a.	< 0.01	< 0.01
	0.18	0.06	33–37 (2-node stage- appearance of last leaf)	75	n.a.	0.05	< 0.01
Germany Bakum, Niedersachsen, 2013 (KWS Chamsin) 13-00434-02 TK0179719	0.06	0.03	37–39 (appearance of last leaf- ligule stage)	61	n.a.	< 0.01	0.01
	0.18	0.09	37–39 (appearance of last leaf- ligule stage)	61	n.a.	0.21	0.06
Germany 2001 (Flair) gwh40601	0.06	0.02	31 (1-node stage)	98	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			39 (ligule stage)	66	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	< 0.01 (< 0.01, < 0.01)
Germany Zschäschütz, Saxony, 2004 (Terrier) gwh013004	0.03	0.01	25 (main stage of tillering)	126	< 0.01	< 0.01	< 0.01
			31 (1-node stage)	107	< 0.01	< 0.01	< 0.01
			39 (ligule stage)	78	< 0.01	< 0.01	< 0.01
	0.05	0.02	25 (main stage of tillering)	126	< 0.01	< 0.01	< 0.01
			31 (1-node stage)	107	< 0.01	< 0.01	< 0.01

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
			39 (ligule stage)	78	< 0.01	0.01	< 0.01
France La Bruère sur Loir, Pays de la Loire, 2013 (Altigo) 13-00434-07 TK0179719	0.06	0.02	37 (appearance of last leaf)	78	n.a.	< 0.01	< 0.01
	0.18	0.07	37 (appearance of last leaf)	78	n.a.	0.14	0.02
France Juniville, Champagne Ardenne, 2013 (Orcas) 13-00434-08 TK0179719	0.06	0.03	38–39 (up to ligule stage)	62	n.a.	< 0.01	< 0.01
	0.18	0.09	38–39 (up to ligule stage)	62	n.a.	0.08	0.02
France Brannens, Aquitaine, 2013 (Solario) 13-00435-05 TK0179720	0.06	0.02	39 (ligule stage)	71	n.a.	< 0.01	< 0.01
	0.18	0.07	39 (ligule stage)	71	n.a.	0.20	0.02
France Saint Restitut, Rhones-Alpes, 2013 (Karur) 13-00435-06 TK0179720	0.06	0.02	39 (ligule stage)	77	n.a.	< 0.01	< 0.01
	0.17	0.06	39 (ligule stage)	77	n.a.	0.12	0.01
France Monferran Savès, Midi-Pyrénées, 2012 (Pescadou) SRFR12-001-37HR CEMR-5447	0.06	0.02	39 (ligule stage)	69	< 0.01	0.02	< 0.01
France Tourtenay, Poitou-Charentes, 2011 (Miradoux) CEMR-4983	0.06	0.02	35–37 (up to appearance of last leaf)	73	< 0.01	0.04	0.01
France Realville, Midi-Pyrénées, 2001 (Aztec) 3023/01	0.06	0.02	32 (2-node stage)	97	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			39 (ligule stage)	69	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.06)	0.01 (0.01, 0.01)
France Izy, Loiret, 2001 (Cezanne) 3021-01	0.06	0.02	31–32 (1-node stage)	103	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			39 (ligule stage)	74	< 0.01 (< 0.01, < 0.01)	0.07 (0.07, 0.06)	< 0.01 (< 0.01, < 0.01)
France Tiercé, Maine-et-Loire, 2001 (Vivant) 3020-01	0.06	0.02	31–32 (1 to 2-node stages)	100	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			39–41 (starting at ligule stage)	67	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.01 (0.01, 0.01)
France La Paluzette, Hérault, 2001 (Eureka) 3022-01	0.06	0.02	31–32 (1 to 2-node stages)	92	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			39 (ligule stage)	66	< 0.01 (< 0.01, < 0.01)	0.05 (0.06, 0.04)	0.02 (0.02, 0.01)
France	0.06	0.02	39	60	< 0.01	0.09	0.02

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
Ansonville, Loiret, 2005 (Nirvana) AF/8656/SY/3 05-7006			(ligule stage)		(< 0.01, < 0.01)	(0.09, 0.08)	(0.02, 0.02)
France Douzonville, Loiret, 2005 (Runal) AF/8656/SY/4 05-7006	0.06	0.02	39 (ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.05 (0.05, 0.04)	0.01 (0.01, 0.01)
France Montauban, Midi-Pyrénées, 2005 (Karur) AF/8657/SY/1 05-7007	0.06	0.02	39 (ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.11 (0.12, 0.10)	0.02 (0.02, 0.02)
France Castelnau, Haute-Garonne, 2005 (Anosys) AF/8657/SY/2 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	63	< 0.01 (< 0.01, < 0.01)	0.16 (0.16, 0.15)	0.02 (0.02, 0.02)
Italy Caleppio di Settala, Lombardia, 2013 (Genesi) 13-00435-01 TK0179720	0.06	0.02	33–35 (between 2-node stage and appearance of last leaf)	67	n.a.	< 0.01	< 0.01
	0.18	0.05	33–35 (between 2-node stage and appearance of last leaf)	67	n.a.	0.37	0.08
Italy Cassano D'adda, Lombardia, 2013 (Pharaon) 13-00435-02 TK0179720	0.06	0.02	33–34 (between 2-node stage and appearance of last leaf)	61	n.a.	0.02	0.02
	0.18	0.05	33–34 (between 2-node stage and appearance of last leaf)	61	n.a.	0.35	0.07
Italy Lajatico, Toscana, 2013 (Bologna) 13-00435-07 TK0179720	0.06	0.02	33–35 (between 2-node stage and appearance of last leaf)	58	n.a.	< 0.01	< 0.01
	0.18	0.05	33–35 (between 2-node stage and appearance of last leaf)	58	n.a.	0.28	0.04
Italy Castellaneta, Taranto, 2012 (Pietrafitta) SRIT12-1025-37HR CEMR-5447	0.06	0.02	33 (between 2-node stage and appearance of last leaf)	68	< 0.01	0.13	0.02
Italy Altamura, Bari, 2012 (Duilio) SRIT12-1026-37HR CEMR-5447	0.06	0.02	33 (between 2-node stage and appearance of last leaf)	69	< 0.01	0.04	< 0.01
Italy Marsciano, Umbria, 2011 (Dylan) CEMR-4983	0.06	0.02	31–32 (1-2-node stage)	83	< 0.01	0.01	< 0.01

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
Italy Bellinzago, Lombardo, 2011 (Accor) CEMR-4983	0.06	0.02	39 (ligule stage)	55	< 0.01	0.03	< 0.01
Italy Rignano Scalo-Foggia, 2001 (Simeto) 3014-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	First: 21–23 (starting at start of tillering) Second: 39 (ligule stage)	68	< 0.01 (< 0.01, < 0.01)	0.11 (0.10, 0.11)	0.01 (0.01, 0.01)
	0.06	0.03	39 (ligule stage)	68	< 0.01 (< 0.01, < 0.01)	0.09 (0.09, 0.09)	0.01 (0.01, 0.01)
Italy Rignano Scalo-Foggia, 2001 (Svevo) 3015-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	First: 21–23 (starting at start of tillering) Second: 39 (ligule stage)	68	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.12)	0.02 (0.02, 0.02)
	0.06	0.03	39 (ligule stage)	68	< 0.01 (< 0.01, < 0.01)	0.09 (0.09, 0.09)	0.01 (0.01, 0.01)
Italy Rignano Scalo-Foggia, 2002 (Svevo) 02-3007	0.04 (1st) + 0.06 (2nd) RTI = 41 days	0.02 (1st) + 0.03 (2nd)	First:23 (tillering) Second: 39	66	< 0.01 (< 0.01, < 0.01)	0.27 (0.27, 0.27)	0.05 (0.05, 0.05)
	0.06	0.03	39 (ligule stage)	66	< 0.01 (< 0.01, < 0.01)	0.32 (0.34, 0.30)	0.05 (0.05, 0.05)
Italy Manfredonia, Foggia, 2002 (Vitron) 02-3006	0.05 (1st) + 0.06 (2nd) RTI = 47 days	0.02(1st) + 0.03 (2nd)	First:22 (tillering stage), Second: 39 (ligule stage)	64	< 0.01 (< 0.01, < 0.01)	0.20 (0.19, 0.20)	0.03 (0.03, 0.03)
	0.06	0.03	39 (ligule stage)	64	< 0.01 (< 0.01, < 0.01)	0.18 (0.17, 0.18)	0.03 (0.03, 0.03)
Italy Rignano Scalo-Foggia, 2004 (Svevo) ITHR040015 04-7002	0.03	0.01	22 (2 tillers)	108	< 0.01	< 0.01	< 0.01
			30–31 (start of shooting to 1-node stage)	84	< 0.01	0.03	< 0.01
			39 (ligule stage)	68	< 0.01	0.09	0.02
	0.04	0.02	22 (2 tillers)	108	< 0.01	< 0.01	< 0.01
			30–31 (start of shooting to 1-node stage)	84	< 0.01	0.04	< 0.01
			39 (ligule stage)	68	< 0.01	0.11	0.02
Italy	0.03	0.01	23	104	< 0.01	< 0.01	< 0.01

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
Manfredonia, Foggia, 2004 (Kronos) ITHR040016 04-7002			(3 tillers)				
			31 (1-node stage)	91	< 0.01	0.03	< 0.01
			39 (ligule stage)	72	< 0.01	0.10	0.01
	0.04	0.02	23 (3 tillers)	104	< 0.01	0.01	< 0.01
			31 (1-node stage)	91	< 0.01	0.05	< 0.01
			39 (ligule stage)	72	< 0.01	0.13	0.01
Italy Poggio Piccolo, Bologna, 2005 (San Carlo) AF/8657/SY/3 05-7007	0.06	0.02	37–38 (appearance of last leaf)	60	< 0.01 (< 0.01, < 0.01)	0.11 (0.11, 0.11)	0.02 (0.02, 0.01)
Italy Idice, 2005 (Neolatino) AF/8657/SY/4 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.14 (0.16, 0.11)	0.02 (0.02, 0.02)
Netherlands Vlagtwedde, Groningen, 2013 (Tybalt) 13-00434-03 TK0179719	0.06	0.03	37–39 (appearance of last leaf- ligule stage)	65	n.a.	< 0.01	< 0.01
	0.18	0.09	37–39 (appearance of last leaf- ligule stage)	65	n.a.	0.23	0.05
Netherlands Nieuwolda, Groningen, 2013 (Tataros) 13-00434-04 TK0179719	0.06	0.03	34–39 (up to ligule stage)	83	n.a.	< 0.01	< 0.01
	0.17	0.09	34–39 (up to ligule stage)	83	n.a.	0.15	0.02
Spain Zafaraya, Andalucia, 2013 (Mario) 13-00435-03 TK0179720	0.06	0.02	35–39 (up to ligule stage)	84	n.a.	< 0.01	< 0.01
	0.18	0.06	35–39 (up to ligule stage)	84	n.a.	0.14	0.03
Spain Maro-Nerja, Andalucia, 2014 (Marius) 13-00435-04 TK0179720	0.06	0.02	34–39 (up to ligule stage)	186	n.a.	< 0.01	< 0.01
	0.19	0.06	34–39 (up to ligule stage)	186	n.a.	< 0.01	< 0.01
Spain Almayate, Andalucia, 2014 (Marius) 13-00435-08 TK0179720	0.06	0.02	35–39 (up to ligule stage)	126	n.a.	< 0.01	< 0.01
	0.18	0.06	35–39 (up to ligule stage)	126	n.a.	< 0.01	< 0.01
Spain Albacete, Albacete, 2012 (Kalifa) SRES12-161-37HR CEMR-5447	0.06	0.02	32–33 (starting at 2-node stage)	56	< 0.01	0.04	< 0.01
Spain Dehesa de los Llanos, Albacetes, 2011 (Berdun)	0.07	0.02	31–32 (1–2-node stage)	77	< 0.01	< 0.01	< 0.01

Location, Year (Variety) Trial no, Study code	Application				Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application	DALA	M2 [a]	M4	M6
CEMR-4983							
Spain Renedo de Esgueva, Valladolid, 2002 (Soisson) 02-3003	0.04 (1st) + 0.06 (2nd) RTI = 38 days	0.02 (1st) + 0.03 (2nd)	First:22–24 (tillering stage) Second: 47–51 (flag leaf sheath opening-start of earing)	56	< 0.01 (< 0.01, < 0.01)	0.10 (0.10, 0.10)	0.03 (0.03, 0.03)
	0.06	0.03	31–39 (1-node stage- ligule stage)	56	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.01 (0.01, 0.01)
	0.06	0.03	47–51 (flag leaf sheath opening-start of earing)	56	< 0.01 (< 0.01, < 0.01)	0.09 (0.09, 0.09)	0.03 (0.03, 0.02)
Spain Las Cabezas, Sevilla, 2002 (Claudio 63) 02-3002	0.04 (1st) + 0.06 (2nd) RTI = 53 days	0.02 (1st) + 0.02 (2nd)	First:13–25 (3-leaf stage-main stage of tillering), Second: 39 (ligule stage)	73	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.11)	0.03 (0.03, 0.03)
	0.06	0.02	39 (ligule stage)	73	< 0.01 (< 0.01, < 0.01)	0.11 (0.10, 0.11)	0.03 (0.03, 0.03)
Switzerland Vouvry, Valais, 2004 (Arina) CHHR040029 04-7008	0.03	0.01	25 (main stage of tillering)	132	< 0.01	< 0.01	< 0.01
			31 (1-node stage)	111	< 0.01	< 0.01	< 0.01
			39 (ligule stage)	78	< 0.01	< 0.01	< 0.01
	0.04	0.01	25 (main stage of tillering)	132	< 0.01	< 0.01	< 0.01
			39 (ligule stage)	78	< 0.01	< 0.01	< 0.01
	0.05	0.01	31 (1-node stage)	111	< 0.01	< 0.01	< 0.01
United Kingdom Banbury, Oxfordshire, 2013 (JB Diego) 13-00434-05 TK0179719	0.06	0.02	34–39 (up to ligule stage)	70	n.a.	< 0.01	< 0.01
	0.18	0.07	34–39 (up to ligule stage)	70	n.a.	0.09	0.01
United Kingdom Tattingstone, Suffolk, 2013 (Cordiale) 13-00434-06 TK0179719	0.06	0.02	39–41 (up to ligule stage)	67	n.a.	< 0.01	< 0.01
	0.18	0.06	39–41 (up to ligule stage)	67	n.a.	0.42	0.06
United Kingdom Pendock, Gloucestershire, 2005 (Nijinsky) AF/8656/SY/1 05-7006	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	< 0.01 (< 0.01, < 0.01)
United Kingdom Ashby-de-la-Zouch, Leicestershire, 2005 (Soisson) AF/8656/SY/2 05-7006	0.06	0.02	39 (ligule stage)	60	< 0.01 (< 0.01, < 0.01)	0.08 (0.07, 0.09)	0.02 (0.02, 0.02)

[a] Only for the 2009 trials conducted in Canada are the residues measured as M2 and reported as pinoxaden equivalents. For all other trials, residues are measured as M2 and reported as M2

Barley

Fifty trials were conducted on barley in Canada, USA, Finland, Germany, United Kingdom, France, Italy and Spain between 2001 and 2009. In most trials, a single foliar spray application of an EC formulation was made either in accordance with GAP or at exaggerated rates. Grain was harvested 42–90 DALA. In three of the trials (one in Canada and two in the USA), additional barley grain samples were collected to assess residue decline.

The analytical methods REM 199.02 (EU trials), REM 199-03 (Canada and EU trials) and 117-01 (USA trials) were used to analyse the grain samples collected from all trials. The LOQs were determined to be 0.01 mg/kg/analyte for grain and 0.02 mg/kg/analyte for forage/whole plant, hay/ears/stalks and straw. In contrast with the wheat trials, none of the barley samples were analysed for the metabolite M10.

The maximum period of sample storage at –20 °C was 41–768 days (1–26 months) for all trials. Storage stability data on high starch content commodities show that the residues are stable for up to 28 months. The residues in barley grain are summarized in Table 42 while residues in forage/whole plant, hay/ears/stalks and straw are captured in Tables 46, 47 and 48, respectively.

Table 42 Residues of pinoxaden in barley grain following foliar spray with pinoxaden in North American and European Regions

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
Canada GAP	0.06	0.12	up to 37	60			
Canada, Branchton, ON, 2009 (HY 481-6R) T650 CER 07025/09	0.06	0.07	33–37 (flag leaf still visible)	70	< 0.01 (< 0.01, < 0.01)	0.14 (0.15, 0.12)	0.05 (0.05, 0.04)
Canada Woodlands, MB, 2009 (Trey) T651 CER 07025/09	0.06	0.07	12–13 (2–3 leaf stage)	80	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada, St-Pie-de Bagot, QC, 2003 (Grant) T 550 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	57	< 0.01 (< 0.01, < 0.01)	0.08 (0.08, 0.09)	0.05 (0.05, 0.05)
Canada, Elm Creek, MB, 2003 (Conlon) T 551 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	63	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.02 (0.02, 0.03)
Canada, Wrentham, AB, 2003 (Stein) T552 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	78	< 0.01 (< 0.01, < 0.01,< 0.01, < 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, 0.01, 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)
Canada, Vanscoy, SK, 2003 (CDC Dolly) T 553 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	62	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.06)	0.04 (0.04, 0.04)
				69	< 0.01 (< 0.01, < 0.01)	0.08 (0.07, 0.08)	0.05 (0.05, 0.05)

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
Canada, Lacombe, AB, 2003 (Metcalfe) T554 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	84	< 0.01 (< 0.01, < 0.01,< 0.01, < 0.01)	0.02 (0.02, 0.03, 0.02, 0.03)	0.02 (0.01, 0.02,0.03, 0.03)
Canada, Lacombe, AB, 2003 (Bold) T 555 CER0707/03	0.07	0.06	23 (up to the 4th tiller/3–6 leaf stage)	84	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.02 (0.02, 0.02)
Canada, Penhold, AB, 2003 (Metcalfe) T 556 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	89	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.01)	< 0.01 (< 0.01, < 0.01)
Canada, Penhold, AB, 2003 (Bold) T 564 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	89	< 0.01 (< 0.01, < 0.01)	0.01 (0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada, Rosthern, SK, 2003 (Kendall) T 557 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	59	< 0.01	0.01	< 0.01
				66	< 0.01 (< 0.01, < 0.01)	<u>0.02</u> (< 0.01, 0.02)	< 0.01 (< 0.01, < 0.01)
				73	< 0.01	< 0.01	< 0.01
				80	< 0.01	0.02	< 0.01
Canada, Rosthern, SK, 2003 (AC Dolly) T 558 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	66	< 0.01 (< 0.01, < 0.01)	0.01 (0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada, Rosthern, SK, 2009 (Copeland) T652 CER 07025/09	0.06	0.06	13–15 (3–5 leaf stage)	85	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
Canada, Hepburn, SK, 2003 (CDC Dolly) T559 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	58	< 0.01 (< 0.01, < 0.01)	<u>0.08</u> (0.08, 0.08)	0.06 (0.04, 0.07)
Canada, Minto, MB, 2003 (Lacey) T 563 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	57	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)	0.02 (0.02, 0.01, 0.01, 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01)
Canada, Minto, MB, 2003 (Conlon) T 560 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	46	< 0.01	0.01	0.01
				54	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	0.02 (0.01, 0.02)
				60	< 0.01	0.03	0.02
				70	< 0.01	0.02	0.02
Canada, Boissevain, MB, 2003 (Metcalfe) T 561 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	60	< 0.01 (< 0.01, < 0.01)	<u>0.04</u> (0.04, 0.04)	0.04 (0.03, 0.04)
Canada, Boissevain,	0.07	0.07	23 (up to	60	< 0.01	0.03	0.02 (0.02,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
MB, 2003 (Robust) T 562 CER0707/03			the 4th tiller/3–6 leaf stage)		(< 0.01, < 0.01)	(0.03, 0.03)	0.03)
Canada, Kipp, AB, 2003 (Stein) T 565 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	74	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	0.01 (0.01, < 0.01)
USA GAP	0.06	0.30	up to 39	60			
USA, Tule Lake, CA, 2002 (Legacy) WD-HR-008-02, 825-02	0.07	0.04	post foliar	60	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.02 (0.02, 0.02)
USA, Wellington, CO, 2002 (Moravian) WH-HR-008-02, 825-02	0.07	0.05	47 (flag leaf visible)	60	< 0.01 (< 0.01, < 0.01)	0.10 (0.09, 0.11)	0.02 (0.02, 0.03)
USA, Geneva, MN, 2002 (Royal) NF-HR-010-02, 825-02	0.07	0.04	51 (heads showing)	60	< 0.01 (< 0.01, < 0.01)	0.16 (0.15, 0.16)	0.08 (0.08, 0.08)
USA, Lake Andes, SD, 2002 (Robust) NC-HR-008-02, 825-02	0.07	0.37	32	60	< 0.01 (< 0.01, < 0.01)	0.15 (0.14, 0.16)	0.04 (0.04, 0.05)
USA, Dagmar, MT, 2002 (Robust) WI-HR-015-02, 825-02	0.07	0.05	33	60	< 0.01 (< 0.01, < 0.01)	0.18 (0.18, 0.18)	0.06 (0.05, 0.06)
USA, Dagmar, MT, 2002 (Conlin) WI-HR-016-02, 825-02	0.07	0.05	33	46	< 0.01 (< 0.01, < 0.01)	0.25 (0.23, 0.27)	0.12 (0.12, 0.12)
				53	< 0.01 (< 0.01, < 0.01)	0.31 (0.32, 0.30)	0.15 (0.15, 0.15)
				60	< 0.01 (< 0.01, < 0.01)	0.30 (0.29, 0.31)	0.16 (0.15, 0.16)
				67	< 0.01 (< 0.01, < 0.01)	0.17 (0.26, 0.08)	0.10 (0.13, 0.07)
USA, Windsor, VA, 2002 (Nomini) EB-HR-009-02, 825-02	0.07	0.05	35	60	< 0.01 (< 0.01, < 0.01)	0.08 (0.06, 0.10)	0.05 (0.04, 0.06)
USA, Ephrata, WA, 2002 (Baronesse) WF-HR-012-02, 825-02	0.07	0.04	51 (beginning of heading)	60	< 0.01 (< 0.01, < 0.01)	0.11 (0.15, 0.07)	0.04 (0.03, 0.05)
USA, Richmond Township, WI, 2002 (Robust) NI-HR-010-02, 825-02	0.07	0.04	30	60	< 0.01 (< 0.01, < 0.01)	0.47 (0.45, 0.49)	0.18 (0.17, 0.19)
USA, Eldridge, ND, 2002 (Robust) WI-HR-014-02, 825-02	0.07	0.04	41	46	< 0.01 (< 0.01, < 0.01)	0.18 (0.20, 0.16)	0.08 (0.10, 0.07)
				53	< 0.01	0.33	0.14 (0.10,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
					(< 0.01, < 0.01)	(0.45, 0.21)	0.18)
				60	< 0.01 (< 0.01, < 0.01)	0.28 (0.20, 0.35)	0.14 (0.18, 0.08)
				67	< 0.01 (< 0.01, < 0.01)	0.25 (0.32, 0.18)	0.14 (0.10, 0.18)
USA, Gardner, ND, 2002 (Robust) WI-HR-013-02, 825-02	0.07	0.06	23	60	< 0.01 (< 0.01, < 0.01)	0.07 (0.07, 0.07)	0.04 (0.04, 0.04)
	0.22	0.19	23	60	< 0.01 (< 0.01, < 0.01)	0.22 (0.21, 0.23)	0.10 (0.10, 0.10)
USA, Jerome, ID, 2002 (Baronesse) WG-HR-016-02, 825-02	0.07	0.05	57	60	< 0.01 (< 0.01, < 0.01, < 0.01)	0.27 (0.28, 0.33, 0.20)	0.08 (0.08, 0.09, 0.07)
	0.36	0.25	57	60	< 0.01 (< 0.01, < 0.01, < 0.01)	1.3 (1.3, 1.3, 1.3)	0.35 (0.34, 0.36, 0.35)
Slovenia GAP	0.06	0.03	13–39	Not specified			
England, Suffolk, 2001 (Regina) 3048/01	0.06	0.03	39–49	61	< 0.01 (< 0.01, < 0.01)	0.16 (0.13, 0.19)	0.06 (0.05, 0.07)
			31–32	82	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.03 (0.03, 0.03)
England, Wokingham, 2001 (Chariot) 3049/01	0.06	0.03	37–42	71	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01)	0.06 (0.05, 0.05, 0.06, 0.06)	0.02 (0.01, 0.02, 0.02, 0.02)
			31	90	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01, < 0.01)
England, Wokingham, 2001 (Chariot) 3050/01	0.06	0.03	37–42	71	< 0.01 (< 0.01, < 0.01)	0.04 (0.04, 0.05)	0.02 (0.02, 0.02)
			31	71	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
France, Les Petites Loges, 2001 (Esterel) 3024/01	0.06	0.02	39	71	< 0.01 (< 0.01, < 0.01)	0.04 (0.03, 0.05)	0.02 (0.01, 0.02)
			32	82	< 0.01 (< 0.01, < 0.01)	0.04 (0.03, 0.06)	0.02 (0.01, 0.02)
France, Marsillargues, 2001 (Baraka) 3026/01	0.06	0.02	39	76	< 0.01 (< 0.01, < 0.01)	0.04 (0.04, 0.05)	0.02 (0.01, 0.02)
			32	90	< 0.01 (< 0.01, < 0.01)	0.07 (0.07, 0.07)	0.03 (0.03, 0.03)
France, Le Puiset,	0.06	0.02	39	59	< 0.01	0.12	0.04 (0.04,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
2001 (Prisma) 3029/01					(< 0.01, < 0.01)	(0.11, 0.13)	0.04)
			32	69	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.06)	0.02 (0.02, 0.02)
France, St Porquier, 2001 (Volga) 3030/01	0.06	0.02	39	49	< 0.01 (< 0.01, < 0.01)	<u>0.06</u> (0.06, 0.05)	0.01 (0.01, 0.01)
			31–32	68	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	< 0.01 (< 0.01, < 0.01)
France, Rueil-Malmaison, 2001 (Cork) 3031/01	0.06	0.02	39	53	< 0.01 (< 0.01, < 0.01)	<u>0.14</u> (0.14, 0.15)	0.05 (0.05, 0.05)
			31–32	67	< 0.01 (< 0.01, < 0.01)	0.05 (0.04, 0.05)	0.02 (0.02, 0.02)
Finland, Jokioinen, 2006 (Saana) T000722-06	0.06	0.03	41–43	42	< 0.01	0.14	0.04
Germany, Dabrun, 2001 (Barke) gba 30401	0.06	0.02	39	69	< 0.01 (< 0.01, < 0.01)	<u>0.05</u> (0.05, 0.05)	0.02 (0.02, 0.02)
			31–32	78	< 0.01 (< 0.01, < 0.01)	0.05 (0.05, 0.05)	0.02 (0.02, 0.02)
Germany, Rohlstorf, 2001 (Barke) gba 10401	0.06	0.02	31–32	74	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)
			37–39	74	< 0.01 (< 0.01, < 0.01)	<u>0.02</u> (0.03, 0.02)	< 0.01 (< 0.01, < 0.01)
Italy, Bassano, 2002 (Baraka) 02-3004	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 41 days	0.02 (1^{st}) + 0.03 (2^{nd})	First: 23–25 Second: 39	55	< 0.01 (< 0.01, < 0.01)	0.08 (0.07, 0.09)	0.04 (0.03, 0.04)
	0.06	0.03	39	55	< 0.01 (< 0.01, < 0.01)	<u>0.07</u> (0.07, 0.08)	0.03 (0.03, 0.03)
Italy, Lungavilla, 2002 (Amillis) 02-3005	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 37 days	0.02 (1^{st}) + 0.030 (2^{nd})	First: 23–25 Second: 39	61	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.06)	0.02 (0.02, 0.02)
	0.06	0.03	39	61	< 0.01 (< 0.01, < 0.01)	<u>0.04</u> (0.04, 0.05)	0.01 (0.01, 0.01)
Italy, Voghera, 2001 (Amillis) 3012/01	0.06 (1^{st}) + 0.04 (2^{nd}) RTI = 29 days	0.02 (1^{st}) + 0.01 (2^{nd})	First: 23–25 Second: 39	62	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	< 0.01 (< 0.01, < 0.01)
	0.06	0.02	39	62	< 0.01 (< 0.01, < 0.01)	<u>0.03</u> (0.02, 0.04)	0.02 (0.01, 0.02)
Italy, Cascina, 2001 (Kelibia) 3013/01	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 29 days	0.01 (1^{st}) + 0.02 (2^{nd})	First: 23–25 Second: 39	62	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.06)	0.02 (0.02, 0.02)

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
	0.06	0.02	39	62	< 0.01 (< 0.01, < 0.01)	0.08 (0.06, 0.09)	0.02 (0.02, 0.03)
Spain, Valladolid, 2002 (Blanche) 02-3000	0.04 (1st) + 0.06 (2nd) RTI = 38 days	0.02 (1st) + 0.03 (2nd)	First: 22–24 Second: 47–51	53	< 0.01 (< 0.01, < 0.01)	0.62 (0.61, 0.64)	0.18 (0.18, 0.18)
	0.06	0.03	47–51	53	< 0.01 (< 0.01, < 0.01)	0.47 (0.46, 0.48)	0.14 (0.14, 0.14)
			31–39	69	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.12)	0.04 (0.03, 0.04)
Spain, Huesca, 2002 (Graphic) 02-3001	0.04 (1st) + 0.06 (2nd) RTI = 33 days	0.02 (1st) + 0.03 (2nd)	First: 13–21 Second: 37–39	65	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.01 (0.01, 0.01)
	0.06	0.03	37–39	65	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.01 (0.01, 0.01)
Spain, Grisalena-Burgos, 2001 (Cezzane) 3043/01	0.06	0.03	39–41	48	< 0.01 (< 0.01, < 0.01)	0.32 (0.31, 0.33)	0.11 (0.11, 0.11)
	0.06	0.03	31–32	61	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.13)	0.05 (0.05, 0.05)
Spain, Valladolid, 2001 (Garbo) 3044/01	0.06	0.03	39	54	< 0.01 (< 0.01, < 0.01)	0.14 (0.14, 0.15)	0.06 (0.06, 0.06)
	0.06	0.03	31–32	58	< 0.01 (< 0.01, < 0.01)	0.12 (0.13, 0.11)	0.06 (0.05, 0.06)

[a] Only for the 2009 trials conducted in Canada are the residues measured as M2 and reported as pinoxaden equivalents. For all other trials, residues are measured as M2 and reported as M2

Animal feeds

Wheat Forage/Whole Plant, Hay/Ears/Stalks and Straw

Table 43 Residues of pinoxaden in wheat forage and whole plant in North American and European Regions

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
Canada GAP	0.06	0.12	up to 37	7	Grazing				
Canada Portage la Prairie, MB, 2009 (AC Domain) T647 CER 07024/09	0.06	0.07	10–12 (emergence-2-leaf stage)	28	forage	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.
Canada Taber, AB,	0.06	0.07	16–18 (leaves	12	forage	< 0.01 (< 0.01,	0.40 (0.44,	0.03 (0.03,	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
2009 (Superb) T648 CER 07024/09			unfolding)			< 0.01)	0.36)	0.03)	
Canada Rosthern, SK, 2009 (Lillian) T649 CER 07024/09	0.06	0.06	12–13 (2 to 3-leaf stage)	16	forage	< 0.01 (< 0.01, < 0.01)	0.03 (0.04, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.
Canada Elm Creek, MB, 2003 (AC Barrie) T566 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	25	forage	< 0.02 (< 0.02, < 0.02)	0.02 (< 0.02, 0.03)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Elm Creek, MB, 2003 (Majestic) T567 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	25	forage	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Delisle, SK, 2003 (Eatonia) T568 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	7	forage	0.04 (0.04, 0.03, 0.03, 0.05, 0.03, 0.03)	1.39 (1.05, 0.86, 1.58, 1.80, 1.51, 1.56)	0.06 (0.07, 0.05, 0.04, 0.08, 0.05, 0.07)	n.a.
Canada Vanscoy, SK, 2003 (Prodigy) T569 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	7	forage	0.58 (0.10, 1.06)	1.73 (1.92, 1.55)	0.10 (0.09, 0.10)	n.a.
Canada Vanscoy, SK, 2003 (Eatonia) T570 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	8 15 22 29	forage	0.04 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	1.43 0.34 (0.48, 0.19) 0.21 0.10	0.10 0.03 (0.03, < 0.02) 0.03 < 0.02	n.a.
Canada Wrentham, AB, 2003 (McKenzie) T571 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	5	forage	0.09 (0.07, 0.10)	1.71 (1.53, 1.89)	0.15 (0.14, 0.15)	n.a.
Canada Wrentham, AB, 2003 (Prodigy) T573 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	5	forage	0.10 (0.07, 0.13)	1.98 (2.18, 1.80)	0.61 (0.10, 1.12)	n.a.
Canada Taber, AB, 2003 (Prodigy) T572 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	6	forage	0.03 (0.03, 0.04)	1.08 (1.39, 0.77)	0.07 (0.08, 0.05)	n.a.
Canada Taber, AB, 2003	0.07	0.07–0.14	23 (3–6 leaf stage)	6	forage	0.05 (0.04, 0.06)	1.11 (0.99, 1.25)	0.07 (0.06, 0.07)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
(McKenzie) T574 CER 0708/03									
Canada Taber, AB, 2003 (McKenzie) T575 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	7	forage	< 0.02 (< 0.02, < 0.02)	0.67 (0.60, 0.74)	0.04 (0.04, 0.05)	n.a.
Canada Rosthern, SK, 2003 (AC Barrie) T576 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	7	forage	0.04 (0.03, 0.05)	1.87 (2.01, 1.73)	0.09 (0.09, 0.09)	n.a.
Canada Rosthern, SK, 2003 (AC Eatonia) T581 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	7	forage	0.04 (0.03, 0.05)	1.74 (1.63, 1.85)	0.07 (0.07, 0.07)	n.a.
Canada Lacombe, AB, 2003 (AC Crystal) T577 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	15	forage	< 0.02 (< 0.02, < 0.02)	0.22 (0.22, 0.21)	0.02 (< 0.02, 0.03)	n.a.
Canada Lacombe, AB, 2003 (AC Intrepid) T580 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	10	forage	< 0.02	0.20	< 0.02	n.a.
				17		< 0.02 (< 0.02, < 0.02)	0.09 (0.09, 0.09)	< 0.02 (< 0.02, < 0.02)	
				24		< 0.02	0.04	< 0.02	
				31		< 0.02	< 0.02	< 0.02	
Canada Penhold, AB, 2003 (Intrepid) T578 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	7	forage	0.03 (0.03, 0.04)	1.06 (1.01, 1.11)	0.05 (0.05, 0.06)	n.a.
Canada Penhold, AB, 2003 (AC Crystal) T579 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	7	forage	0.03 (0.03, 0.03)	1.05 (1.11, 0.98)	0.33 (0.07, 0.59)	n.a.
Canada Hepburn, SK, 2003 (AC Barrie) T582 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	6	forage	0.03 (0.03, 0.02)	2.95 (2.42, 3.49)	0.23 (0.22, 0.24)	n.a.
Canada Minto, MB, 2003 (Super B) T583 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	5	forage	0.08 (0.03, 0.32, 0.04, 0.03, 0.03, 0.03)	2.46 (2.48, 2.50, 2.76, 2.12, 2.14, 2.12)	0.17 (0.18, 0.20, 0.17, 0.13, 0.12, 0.13)	n.a.
Canada Minto, MB,	0.07	0.04–0.07	23 (3–6 leaf	7	forage	0.02 (0.02,	1.23 (1.26,	0.06 (0.08,	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
2003 (Avonlea) T584 CER 0708/03			stage)			0.02, 0.02, 0.03, < 0.02, < 0.02)	1.21, 1.05, 1.41,1.19, 0.99)	0.06, 0.06, 0.06, 0.06, 0.05)	
Canada Boissevain, MB, 2003 (AC Barrie) T585 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	4	forage	< 0.02 (< 0.02, < 0.02)	1.48 (1.50, 1.47)	0.08 (0.07, 0.08)	n.a.
USA GAP	0.06	0.30	up to 39	30	Forage for hay				
USA Champaign, IL, 2003 (Kaskaskia) NAHR00702 824-02	0.08	0.06	23 (3 tillers)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.12 (0.09, 0.15)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Nickerson, KS 2002 (Heyne) NAHR01102 824-02	0.07	0.06	21 (start of tillering)	30	fall forage	0.05 (0.06, 0.04)	0.74 (0.69, 0.78)	0.05 (0.04, 0.05)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.34 (0.30, 0.38)	0.03 (0.03, 0.03)	
USA Larned, KS 2002 (Jagger) NAHR01202 824-02	0.07	0.05	21 (start of tillering)	30	fall forage	0.03 (0.02, 0.04)	1.70 (1.50, 1.80)	0.09 (0.09, 0.09)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.23 (0.29, 0.17)	0.03 (0.03, 0.02)	
USA Belpre, KS, 2002 (Jagger) NAHR01302 824-02	0.07	0.38	21 (start of tillering)	30	fall forage	0.12 (0.10, 0.15)	1.50 (1.30, 1.60)	0.09 (0.09, 0.09)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.29 (0.27, 0.31)	0.02 (0.02, 0.02)	
USA Grand Island, NE, 2003 (Nuplains) NBHR01102 824-02	0.07	0.04	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.19 (0.25, 0.13)	0.02 (0.02, < 0.02)	n.a.
USA Lake Andes, SD, 2002 (Forge HRS) NCHR00702 824-02	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
USA St. Joseph, MO, 2003 (Karl) NDHR00702 824-02	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.06 (0.05, 0.07)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Geneva, MN, 2002 (Oxen)	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
NFHR00902 824-02									
USA Stillwater, OK, 2002-2003 (Jaggar PVPA) SCHR01202 824-02	0.07	0.05	22 (2 tillers)	30	fall forage	< 0.02 (< 0.02, < 0.02)	0.51 (0.56, 0.46)	0.05 (0.06, 0.04)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.44 (0.46, 0.42)	0.05 (0.05, 0.04)	
USA Colony, OK, 2003 (Coker 9663) SCHR01302 824-02	0.07	0.06	21 (start of tillering)	30	fall forage	0.04 (0.03, 0.04)	2.70 (2.80, 2.60)	0.25 (0.24, 0.26)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.87 (0.86, 0.87)	0.06 (0.05, 0.06)	
USA Levelland, TX, 2003 (TAM 105) SCHR01402 824-02	0.07	0.05	23 (3 tillers)	30	fall forage	< 0.02 (< 0.02, < 0.02)	1.40 (1.50, 1.30)	0.16 (0.18, 0.13)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.56 (0.55, 0.57)	0.05 (0.05, 0.05)	
USA Rincon, NM, 2003 (TAM 200) SCHR01502 824-02	0.07	0.08	21 (start of tillering)	30	fall forage	< 0.02 (< 0.02, < 0.02)	0.19 (0.02, 0.35)	0.04 (< 0.02, 0.04)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.26 (0.26, 0.26)	0.02 (0.02, 0.03)	
USA Shoffner, AR, 2003 (DK7900) SEHR00602 824-02	0.07	0.04	21 (start of tillering)	30	fall forage	< 0.02 (< 0.02, < 0.02)	0.59 (0.51, 0.66)	0.04 (0.03, 0.05)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.05 (0.07, 0.04)	< 0.02 (< 0.02, < 0.02)	
USA Rose Hill, NC, 2003 (Coker 9803) SJHR02202 824-02	0.07	0.04	21 (start of tillering)	30	fall forage	0.04 (0.03, 0.04)	1.45 (1.50, 1.40)	0.15 (0.15, 0.15)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.11 (0.10, 0.12)	< 0.02 (< 0.02, < 0.02)	
USA Visalia, CA, 2003 (Yecoro, Rojo) W2HR00202 824-02	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.10 (0.10, 0.10)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Ephrata, WA, 2003 (Stephens) WFHR01102 824-02	0.07	0.04	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.10 (0.10, 0.10)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Ault, CO, 2003 (Platte) WHHR00702 824-02	0.07	0.05	22 (2 tillers)	30	fall forage	< 0.02 (< 0.02, < 0.02)	1.95 (1.90, 2.00)	0.19 (0.20, 0.17)	n.a.
				30	spring forage	< 0.02 (< 0.02, < 0.02)	0.16 (0.11, 0.21)	< 0.02 (< 0.02, < 0.02)	
USA Gardner, ND, 2002	0.07	0.04	21–29 (start of tillering-end	30	spring forage	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
(Alsen) WIHR00902 824-02			of tillering)						
USA Eldridge, ND, 2002 (Belzer) WIHR01002 824-02	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.07 (0.08, 0.06)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Dagmar, MT, 2002 (Challis) WIHR01102 824-02	0.07	0.38	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	0.02 (< 0.02, 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Dagmar, MT, 2002 (Pristine) WIHR01202 824-02	0.07	0.05	21 (start of tillering)	30	spring forage	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Slovenia GAP	0.060	0.03	13–39	Not Specified					
Germany Frechen, Rhein-Nordrhein-Westfalen, 2013 (Julius) 13-00434-01 TK0179719	0.06	0.02	34–39	47	whole plant	n.a.	0.01	< 0.01	n.a.
	0.18	0.06	33–37 (2-node stage-appearance of last leaf)	47	whole plant	n.a.	0.65	0.07	n.a.
Germany Bakum, Niedersachsen, 2013 (KWS Chamsin) 13-00434-02 TK0179719	0.06	0.03	34–39	47	whole plant	n.a.	0.13	0.02	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	48	whole plant	n.a.	0.94	0.18	n.a.
Germany 2001 (Flair) gwh40601	0.06	0.02	31 (1-node stage)	0	whole plant	2.9	0.02	< 0.02	< 0.02
	0.06	0.02	39 (ligule stage)	0	whole plant	1.5	0.15	< 0.02	< 0.02
France La Bruère sur Loir, Pays de la Loire, 2013 (Altigo) 13-00434-07 TK0179719	0.06	0.02	34–39	47	whole plant	n.a.	0.05	0.01	n.a.
	0.18	0.07	37 (appearance of last leaf)	58	whole plant	n.a.	0.48	0.06	n.a.
France Juniville, Champagne Ardenne, 2013 (Orcas) 13-00434-08 TK0179719	0.06	0.03	34–39	47	whole plant	n.a.	0.02	< 0.01	n.a.
	0.18	0.09	38–39 (up to ligule stage)	28	whole plant	n.a.	0.38	0.05	n.a.
France Brannens, Aquitaine, 2013	0.06	0.02	39 (ligule stage)	57	whole plant	n.a.	0.02	< 0.01	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
(Solario) 13-00435-05 TK0179720	0.18	0.07	39 (ligule stage)	57	whole plant	n.a.	0.21	0.05	n.a.
France Saint Restitut, Rhones-Alpes, 2013 (Karur) 13-00435-06 TK0179720	0.06	0.02	39 (ligule stage)	54	whole plant	n.a.	0.05	< 0.01	n.a.
	0.18	0.06	39 (ligule stage)	54	whole plant	n.a.	0.68	0.04	n.a.
France Tiercé, Maine-et-Loire, 2001 (Vivant) 3020-01	0.06	0.02	31–32 (1 to 2-node stage)	0	whole plant	1.1	0.09	< 0.02	< 0.02
				7	whole plant	0.05	0.19	< 0.02	< 0.02
				14	whole plant	0.02	0.13	< 0.02	< 0.02
				35	whole plant	< 0.02	0.05	< 0.02	< 0.02
	0.06	0.02	39–41 (ligule stage-early boot stage)	0	whole plant	0.46	0.08	< 0.02	< 0.02
				7	whole plant	0.09	0.29	0.04	< 0.02
				14	whole plant	0.06	0.26	0.04	< 0.02
France La Paluzette, Hérault, 2001 (Eureka) 3022-01	0.06	0.02	31–32 (1 to 2-node stage)	0	whole plant	1.0	0.33	< 0.02	< 0.02
				7	whole plant	0.15	0.61	0.04	0.04
				14	whole plant	0.06	0.53	0.05	0.05
				28	whole plant	< 0.02	0.26	0.03	0.03
	0.06	0.02	39 (ligule stage)	0	whole plant	0.48	0.41	< 0.02	< 0.02
				7	whole plant	0.10	0.30	0.02	< 0.02
				14	whole plant	0.03 (0.03, 0.03, 0.02, 0.03)	0.280.32, 0.25, 0.27, 0.26)	0.03 (0.03, 0.03, 0.03, 0.03)	0.03 (0.03, 0.03, 0.03, 0.03)
France Ansonville, Loiret, 2005 (Nirvana) AF/8656/SY/3 05-7006	0.06	0.02	39 (ligule stage)	0	whole plant	0.75 (0.77, 0.72)	0.08 (0.06, 0.09)	< 0.02 (< 0.02, < 0.02)	n.a.
France Douzonville, Loiret, 2005 (Runal) AF/8656/SY/4 05-7006	0.06	0.02	39 (ligule stage)	0	whole plant	0.57 (0.60, 0.53)	0.21 (0.26, 0.15)	< 0.02 (< 0.02, < 0.02)	n.a.
France Montauban, Midi-Pyrénées, 2005 (Karur) AF/8657/SY/1 05-7007	0.06	0.02	39 (ligule stage)	0	whole plant	0.62 (0.56, 0.67)	0.49 (0.47, 0.51)	< 0.02 (< 0.02, < 0.02)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
France Castelnau, Haute-Garonne, 2005 (Anosys) AF/8657/SY/2 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	0	whole plant	0.64 (0.54, 0.74)	0.66 (0.62, 0.69)	< 0.02 (< 0.02, < 0.02)	n.a.
Italy Caleppio di Settala, Lombardia, 2013 (Genesi) 13-00435-01 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	53	whole plant	n.a.	0.02	< 0.01	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	53	whole plant	n.a.	0.14	0.02	n.a.
Italy Cassano D'adda, Lombardia, 2013 (Pharaon) 13-00435-02 TK0179720	0.06	0.02	33–34 (starting at 3-node stage)	41	whole plant	n.a.	0.02	< 0.01	n.a.
	0.18	0.05	33–34 (starting at 3-node stage)	41	whole plant	n.a.	2.12	0.68	n.a.
Italy Lajatico, Toscana, 2013 (Bologna) 13-00435-07 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	35	whole plant	n.a.	0.08	0.02	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	35	whole plant	n.a.	0.45	0.05	n.a.
Italy Rignano Scalo-Foggia, 2001 (Simeto) 3014-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	21–23 (start of tillering-3 tillers),	0	whole plant	1.4	0.05	< 0.02	< 0.02
				7	whole plant	0.04	0.30	< 0.02	< 0.02
				14	whole plant	< 0.02	0.25	0.02	0.02
	0.06	0.03	39 (ligule stage)	0	whole plant	1.9	0.03	< 0.02	< 0.02
				7	whole plant	0.06	0.33	< 0.02	0.02
				14	whole plant	< 0.02	0.25	< 0.02	< 0.02
Italy Rignano Scalo-Foggia, 2002 (Svevo) 02-3007	0.04 (1st) + 0.06 (2nd) RTI = 41 days	0.02 (1st) + 0.03 (2nd)	23 (3 tillers),	0	whole plant	0.95	0.03	< 0.02	< 0.02
				14	whole plant	< 0.02	0.43	0.03	< 0.02
	0.06	0.03	39 (ligule stage)	0	whole plant	1.1	< 0.02	< 0.02	< 0.02
				14	whole plant	< 0.02	0.39	0.03	< 0.02
Italy Manfredonia, Foggia, 2002 (Vitron) 02-3006	0.05 (1st) + 0.06 (2nd)	0.02 (1st) + 0.03 (2nd)	22 (2 tillers), 39 (ligule	0	whole plant	1.4	0.12	< 0.02	< 0.02

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
	RTI = 47 days		stage)						
	0.06	0.03	39 (ligule stage)	0	whole plant	1.1	0.08	< 0.02	< 0.02
Italy Poggio Piccolo, Bologna, 2005 (San Carlo) AF/8657/SY/3 05-7007	0.06	0.02	37–38 (starting at appearance of last leaf)	0	whole plant	1.8 (1.7, 1.8)	0.26 (0.25, 0.26)	< 0.02 (< 0.02, < 0.02)	n.a.
Italy Idice, 2005 (Neolatino) AF/8657/SY/4 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	0	whole plant	1.3 (1.5, 1.1)	0.45 (0.65, 0.24)	< 0.02 (< 0.02, < 0.02)	n.a.
Netherlands Vlagtwedde, Groningen, 2013 (Tybalt) 13-00434-03 TK0179719	0.06	0.02	37–39 (2-node stage-ligule stage)	49	whole plant	n.a.	0.05	0.01	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	49	whole plant	n.a.	0.67	0.10	n.a.
Netherlands Nieuwolda, Groningen, 2013 (Tataros) 13-00434-04 TK0179719	0.06	0.09	34–39 (up to ligule stage)	67	whole plant	n.a.	0.03	< 0.01	n.a.
	0.17	0.09	34–39 (up to ligule stage)	67	whole plant	n.a.	0.31	0.07	n.a.
Spain Zafaraya, Andalucia, 2013 (Mario) 13-00435-03 TK0179720	0.06	0.02	35–39 (up to ligule stage)	59	whole plant	n.a.	0.05	0.02	n.a.
	0.18	0.06	35–39 (up to ligule stage)	59	whole plant	n.a.	0.71	0.15	n.a.
Spain Maro-Nerja, Andalucia, 2014 (Marius) 13-00435-04 TK0179720	0.06	0.03	34–39 (up to ligule stage)	159	whole plant	n.a.	< 0.01	< 0.01	n.a.
	0.18	0.09	34–39 (up to ligule stage)	159	whole plant	n.a.	< 0.02	< 0.02	n.a.
Spain Almayate, Andalucia, 2014 (Marius) 13-00435-08 TK0179720	0.06	0.02	35–39 (up to ligule stage)	97	whole plant	n.a.	< 0.01	< 0.01	n.a.
	0.18	0.06	35–39 (up to ligule stage)	97	whole plant	n.a.	< 0.02	< 0.02	n.a.
Spain Renedo de Esgueva, Valladolid, 2002 (Soisson) 02-3003	0.04 (1st) + 0.06 (2nd) RTI = 38 days	0.02 (1st) + 0.03 (2nd)	22–24 (starting at 2 tillers), 47–51 (flag leaf sheath opening-start of	0	whole plant	1.3	0.58	0.03	< 0.02
				15	whole plant	0.02	0.64	0.09	0.03

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6	M10
			earing)						
	0.06	0.03	31–39 (1-node stage-ligule stage)	0	whole plant	2.5	0.02	< 0.02	< 0.02
				14	whole plant	< 0.02	0.41	0.05	0.04
Spain Las Cabezas, Sevilla, 2002 (Claudio 63) 02-3002	0.04 (1st) + 0.06 (2nd) RTI = 53 days	0.01 (1st) + 0.02 (2nd)	13–25 (3-leaf stage-main stage of tillering), 39 (ligule stage)	0	whole plant	1.3	0.23	< 0.02	< 0.02
	0.06	0.02	39 (ligule stage)	0	whole plant	1.4	0.12	< 0.02	< 0.02
United Kingdom Banbury, Oxfordshire, 2013 (JB Diego) 13-00434-05 TK0179719	0.06	0.02	34–39 (up to ligule stage)	49	whole plant	n.a.	0.11	0.01	n.a.
	0.18	0.07	34–39 (up to ligule stage)	49	whole plant	n.a.	0.62	0.08	n.a.
United Kingdom Tattingstone, Suffolk, 2013 (Cordiale) 13-00434-06 TK0179719	0.06	0.02	39–41 (ligule stage-early boot stage)	42	whole plant	n.a.	0.18	0.02	n.a.
	0.18	0.06	39–41 (ligule stage-early boot stage)	42	whole plant	n.a.	1.71	0.16	n.a.
United Kingdom Pendock, Gloucestershire, 2005 (Nijinsky) AF/8656/SY/1 05-7006	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	0	whole plant	0.87 (0.89, 0.84)	0.15 (0.16, 0.14)	< 0.02 (< 0.02, < 0.02)	n.a.
United Kingdom Ashby-de-la-Zouch, Leicestershire, 2005 (Soisson) AF/8656/SY/2 05-7006	0.06	0.02	39 (ligule stage)	0	whole plant	0.94 (0.99, 0.88)	0.05 (0.06, 0.03)	< 0.02 (< 0.02, < 0.02)	n.a.

n.a. = Not analysed

[a] Only for the 2009 trials conducted in Canada are the residues measured as M2 and reported as pinoxaden equivalents. For all other trials, residues are measured as M2 and reported as M2

Table 44 Residues of pinoxaden in wheat hay, ears and stalks in North American and European Regions

Location, Year	Application	DALA	Portion	Residues, mg/kg

(Variety) Trial no, Study code	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		Analysed	M2	M4	M6	M10
Canada GAP	0.06	0.12	up to 37	30	Hay				
Canada Elm Creek, MB, 2003 (AC Barrie) T566 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	39	hay	< 0.02 (< 0.02, < 0.02)	0.05 (0.05, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Elm Creek, MB, 2003 (Majestic) T567 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	39	hay	< 0.02 (< 0.02, < 0.02)	0.05 (0.05, 0.05)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Delisle, SK, 2003 (Eatonia) T568 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	35	hay	< 0.02 (< 0.02, < 0.02, < 0.02,< 0.02, < 0.02)	0.07 (0.05, 0.07, 0.07, 0.08, 0.05, 0.11)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	n.a.
Canada Vanscoy, SK, 2003 (Prodigy) T569 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	28	hay	< 0.02 (< 0.02, < 0.02)	0.14 (0.13, 0.15)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Vanscoy, SK, 2003 (Eatonia) T570 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	22 29 36 43 50	hay	< 0.02 < 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	0.81 0.44 0.08 (0.08, 0.07) 0.04 0.04	0.03 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	n.a.
Canada Wrentham, AB, 2003 (McKenzie) T571 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	38	hay	< 0.02 (< 0.02, < 0.02)	0.02 (0.03, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Wrentham, AB, 2003 (Prodigy) T573 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	38	hay	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Taber, AB, 2003 (Prodigy) T572 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	28	hay	< 0.02 (< 0.02, < 0.02)	0.11 (0.13, 0.10)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Taber, AB, 2003 (McKenzie) T574 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	33	hay	< 0.02 (< 0.02, < 0.02)	0.09 (0.09, 0.08)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Taber, AB, 2003 (McKenzie)	0.07	0.07–0.14	23 (3–6 leaf stage)	36	hay	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
T575 CER 0708/03									
Canada Rosthern, SK, 2003 (AC Barrie) T576 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	35	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Rosthern, SK, 2003 (AC Eatonia) T581 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	35	hay	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Lacombe, AB, 2003 (AC Crystal) T577 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	29	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.06, 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Lacombe, AB, 2003 (AC Intrepid) T580 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	36	hay	< 0.02	0.03	< 0.02	n.a.
				43		< 0.02	0.02	< 0.02	
				50		< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	
				57		< 0.02	< 0.02	< 0.02	
				64		< 0.02	< 0.02	< 0.02	
Canada Penhold, AB, 2003 (Intrepid) T578 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	46	hay	< 0.02 (< 0.02, < 0.02)	0.05 (0.06, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Penhold, AB, 2003 (AC Crystal) T579 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	50	hay	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Hepburn, SK, 2003 (AC Barrie) T582 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	34	hay	< 0.02 (< 0.02, < 0.02)	0.72 (0.58, 0.87)	0.04 (0.04, 0.04)	n.a.
Canada Minto, MB, 2003 (Super B) T583 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	30	hay	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.09 (0.10, 0.09, 0.07, 0.12, 0.08, 0.08)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	n.a.
Canada Minto, MB, 2003 (Avonlea) T584	0.07	0.04–0.07	23 (3–6 leaf stage)	37	hay	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.08 (0.10, 0.09, 0.09, 0.08,	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02,	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
CER 0708/03							0.05, 0.05)	< 0.02, < 0.02)	
Canada Boissevain, MB, 2003 (AC Barrie) T585 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	28	hay	< 0.02 (< 0.02, < 0.02)	0.16 (0.15, 0.16)	< 0.02 (< 0.02, < 0.02)	n.a.
USA GAP [a]	0.06	0.30	up to 39	30	Hay				
USA Champaign, IL, 2003 (Kaskaskia) NAHR00702 824-02	0.08	0.06	23 (3 tillers)	30	hay	< 0.02 (< 0.02, < 0.02)	0.62 (0.29, 0.94)	0.06 (0.04, 0.07)	n.a.
USA Nickerson, KS 2002 (Heyne) NAHR01102 824-02	0.07	0.06	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.52 (0.51, 0.52)	0.05 (0.05, 0.05)	n.a.
USA Larned, KS 2002 (Jagger) NAHR01202 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02,< 0.02)	0.61 (0.76, 0.45)	0.06 (0.08, 0.04)	n.a.
USA Belpre, KS, 2002 (Jagger) NAHR01302 824-02	0.07	0.38	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.55 (0.44, 0.66)	0.03 (0.03, 0.03)	n.a.
USA Grand Island, NE, 2003 (Nuplains) NBHR01102 824-02	0.07	0.04	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.72 (0.56, 0.87)	0.05 (0.04, 0.06)	n.a.
USA Lake Andes, SD, 2002 (Forge HRS) NCHR00702 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.02 (0.02, 0.03)	< 0.02 (< 0.02, < 0.02)	n.a.
USA St. Joseph, MO, 2003 (Karl) NDHR00702 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.11 (0.11, 0.10)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Geneva, MN, 2002 (Oxen) NFHR00902 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.02 (0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Stillwater, OK, 2002-2003	0.07	0.05	22 (2 tillers)	30	hay	< 0.02 (< 0.02, < 0.02)	1.13 (0.66, 1.60)	0.08 (0.06, 0.09)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
(Jaggar PVPA) SCHR01202 824-02									
USA Colony, OK, 2003 (Coker 9663) SCHR01302 824-02	0.07	0.06	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	1.20 (1.20, 1.20)	0.08 (0.08, 0.08)	n.a.
USA Levelland, TX, 2003 (TAM 105) SCHR01402 824-02	0.07	0.05	23 (3 tillers)	30	hay	0.03 (< 0.02, 0.03)	1.02 (0.93, 1.10)	0.07 (0.06, 0.08)	n.a.
USA Rincon, NM, 2003 (TAM 200) SCHR01502 824-02	0.07	0.08	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.74 (0.75, 0.73)	0.10 (0.12, 0.09)	n.a.
USA Shoffner, AR, 2003 (DK7900) SEHR00602 824-02	0.07	0.04	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.16 (0.15, 0.16)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Rose Hill, NC, 2003 (Coker 9803) SJHR02202 824-02	0.07	0.04	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.22 (0.19, 0.25)	0.02 (< 0.02, 0.02)	n.a.
USA Visalia, CA, 2003 (Yecoro, Rojo) W2HR00202 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.68 (0.71, 0.64)	0.13 (0.15, 0.11)	n.a.
USA Ephrata, WA, 2003 (Stephens) WFHR01102 824-02	0.07	0.04	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.17 (0.18, 0.16)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Ault, CO, 2003 (Platte) WHHR00702 824-02	0.07	0.05	22 (2 tillers)	30	hay	< 0.02 (< 0.02, < 0.02)	0.20 (0.18, 0.22)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Gardner, ND, 2002 (Alsen) WIHR00902 824-02	0.07	0.04	21–29 (start of tillering-end of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Eldridge, ND, 2002	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.13 (0.11, 0.14)	0.02 (0.02, 0.03)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
(Belzer) WIHR01002 824-02									
USA Dagmar, MT, 2002 (Challis) WIHR01102 824-02	0.07	0.38	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Dagmar, MT, 2002 (Pristine) WIHR01202 824-02	0.07	0.05	21 (start of tillering)	30	hay	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Slovenia GAP	0.060	0.03	13–39	Not Specified					
Germany Frechen, Rhein-Nordrhein-Westfalen, 2013 (Julius) 13-00434-01 TK0179719	0.06	0.02	34–39	47	hay	n.a.	0.02	0.02	n.a.
	0.18	0.06	33–37 (2-node stage-appearance of last leaf)	47	hay	n.a.	1.84	0.19	n.a.
Germany Bakum, Niedersachsen, 2013 (KWS Chamsin) 13-00434-02 TK0179719	0.06	0.03	34–39	47	hay	n.a.	0.07	0.05	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	48	hay	n.a.	1.25	0.82	n.a.
France La Bruère sur Loir, Pays de la Loire, 2013 (Altigo) 13-00434-07 TK0179719	0.06	0.02	34–39	47	hay	n.a.	0.17	< 0.01	n.a.
	0.18	0.07	37 (appearance of last leaf)	58	hay	n.a.	0.98	0.15	n.a.
France Juniville, Champagne Ardenne, 2013 (Orcas) 13-00434-08 TK0179719	0.06	0.03	34–39	47	hay	n.a.	0.06	0.02	n.a.
	0.18	0.09	38–39 (up to ligule stage)	28	hay	n.a.	1.04	0.18	n.a.
France Brannens, Aquitaine, 2013 (Solario) 13-00435-05 TK0179720	0.06	0.02	39 (ligule stage)	57	hay	n.a.	0.04	0.02	n.a.
	0.18	0.07	39 (ligule stage)	57	hay	n.a.	0.34	0.06	n.a.
France Saint Restitut, Rhones-Alpes, 2013 (Karur) 13-00435-06	0.06	0.02	39 (ligule stage)	54	hay	n.a.	0.11	0.01	n.a.
	0.18	0.06	39 (ligule stage)	54	hay	n.a.	1.13	0.06	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
TK0179720									
France Tiercé, Maine-et-Loire, 2001 (Vivant) 3020-01	0.06	0.02	39–41 (ligule stage-early boot stage)	28	ears	< 0.02	0.07	< 0.02	< 0.02
				35	ears	< 0.02	0.07	< 0.02	< 0.02
				28	stalks	< 0.02	0.25	0.04	0.02
				35	stalks	< 0.02	0.27	0.04	0.02
France La Paluzette, Hérault, 2001 (Eureka) 3022-01	0.06	0.02	31–32 (1 to 2-node stage)	35	ears	< 0.02	< 0.02	< 0.02	< 0.02
				35	stalks	0.03	0.33	0.04	0.05
	0.06	0.02	39 (ligule stage)	28	ears	< 0.02	0.11	0.02	< 0.02
				35	ears	< 0.02	0.10	< 0.02	< 0.02
				28	stalks	0.03	0.28	0.04	0.03
				35	stalks	< 0.02	0.26	0.03	0.03
Italy Caleppio di Settala, Lombardia, 2013 (Genesi) 13-00435-01 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	53	hay	n.a.	0.50	0.10	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	53	hay	n.a.	1.98	0.45	n.a.
Italy Cassano D'adda, Lombardia, 2013 (Pharaon) 13-00435-02 TK0179720	0.06	0.02	33–34 (starting at 3-node stage)	41	hay	n.a.	0.50	0.10	n.a.
	0.18	0.05	33–34 (starting at 3-node stage)	41	hay	n.a.	2.12	0.46	n.a.
Italy Lajatico, Toscana, 2013 (Bologna) 13-00435-07 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	35	hay	n.a.	0.07	0.02	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	35	hay	n.a.	0.67	0.11	n.a.
Italy Rignano Scalo-Foggia, 2001 (Simeto) 3014-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	21–23 (start of tillering-3 tillers), 39 (ligule stage)	28	ears	< 0.02	0.11	< 0.02	< 0.02
				35	ears	< 0.02	0.11	< 0.02	< 0.02
				28	stalks	< 0.02	0.22	0.02	0.02
				35	stalks	< 0.02	0.18	0.02	0.02
	0.06	0.03	39 (ligule stage)	28	ears	< 0.02	0.11	< 0.02	< 0.02
				35	ears	< 0.02	0.08	< 0.02	< 0.02
				28	stalks	< 0.02	0.17	< 0.02	0.02
				35	stalks	< 0.02	0.19	0.02	0.02
Italy Rignano Scalo-Foggia, 2002 (Svevo) 02-3007	0.04 (1st) + 0.06 (2nd) RTI = 41 days	0.02 (1st) + 0.03 (2nd)	23 (3 tillers), 39 (ligule stage)	35	ears	< 0.02	0.20	0.02	< 0.02
				35	stalks	< 0.02	0.29	0.05	0.02

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
	0.06	0.03	39 (ligule stage)	35 35	ears stalks	< 0.02 < 0.02	0.21 0.27	0.03 0.04	< 0.02 < 0.02
Netherlands Vlagtwedde, Groningen, 2013 (Tybalt) 13-00434-03 TK0179719	0.06	0.02	37–39 (2-node stage-ligule stage)	49	hay	n.a.	0.11	0.13	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	49	hay	n.a.	0.56	0.59	n.a.
Netherlands Nieuwolda, Groningen, 2013 (Tataros) 13-00434-04 TK0179719	0.06	0.09	34–39 (up to ligule stage)	67	hay	n.a.	0.01	0.09	n.a.
	0.17	0.09	34–39 (up to ligule stage)	67	hay	n.a.	0.22	0.33	n.a.
Spain Zafaraya, Andalucia, 2013 (Mario) 13-00435-03 TK0179720	0.06	0.02	35–39 (up to ligule stage)	59	hay	n.a.	0.18	0.04	n.a.
	0.18	0.06	35–39 (up to ligule stage)	59	hay	n.a.	1.06	0.24	n.a.
Spain Maro-Nerja, Andalucia, 2014 (Marius) 13-00435-04 TK0179720	0.06	0.03	34–39 (up to ligule stage)	159	hay	n.a.	< 0.01	< 0.01	n.a.
	0.18	0.09	34–39 (up to ligule stage)	159	hay	n.a.	< 0.02	< 0.02	n.a.
Spain Almayate, Andalucia, 2014 (Marius) 13-00435-08 TK0179720	0.06	0.02	35–39 (up to ligule stage)	97	hay	n.a.	< 0.01	< 0.01	n.a.
	0.18	0.06	35–39 (up to ligule stage)	97	hay	n.a.	0.02	< 0.02	n.a.
Spain Renedo de Esgueva, Valladolid, 2002 (Soisson) 02-3003	0.04 (1st) + 0.06 (2nd) RTI = 38 days	0.02 (1st) + 0.03 (2nd)	22–24 (starting at 2 tillers), 47–51 (flag leaf sheath opening-start of earing)	38 38	ears stalks	< 0.02 < 0.02	0.30 0.74	0.04 0.09	0.02 0.06
	0.06	0.03	31–39 (1-node stage-ligule stage)	37 37	ears stalks	< 0.02 < 0.02	0.05 0.17	< 0.02 0.02	< 0.02 < 0.02
United Kingdom Banbury, Oxfordshire, 2013 (JB Diego) 13-00434-05	0.06	0.02	34–39 (up to ligule stage)	49	hay	n.a.	0.18	< 0.01	n.a.
	0.18	0.07	34–39 (up to ligule stage)	49	hay	n.a.	1.31	0.17	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Portion Analysed	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2	M4	M6	M10
TK0179719									
United Kingdom Tattingstone, Suffolk, 2013 (Cordiale) 13-00434-06 TK0179719	0.06	0.02	39–41 (ligule stage-early boot stage)	42	hay	n.a.	0.20	0.01	n.a.
	0.18	0.06	39–41 (ligule stage-early boot stage)	42	hay	n.a.	3.31	0.28	n.a.

[a] For the trials conducted in the USA, spring forage samples were cut for hay 30 DALA and left in the field to dry for 3–10 days (% dry matter was not reported).

Table 45 Residues of Pinoxaden in wheat straw in North American and European Regions

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
Canada GAP	0.06	0.12	up to 37	60				
Canada Elm Creek, MB, 2003 (AC Barrie) T566 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.02 (< 0.02, < 0.02)	0.02 (0.03, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Elm Creek, MB, 2003 (Majestic) T567 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Delisle, SK, 2003 (Eatonia) T568 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	60	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02,< 0.02, < 0.02)	0.04 (< 0.02, 0.03, 0.03, 0.05, < 0.02, 0.07)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	n.a.
Canada Vanscoy, SK, 2003 (Prodigy) T569 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	62	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
				69	< 0.02 (< 0.02, < 0.02)	0.06 (< 0.02, 0.04)	< 0.02 (< 0.02, < 0.02)	
Canada Vanscoy, SK, 2003 (Eatonia) T570 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	59 66 74 80	< 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	0.06 0.04 (0.05, 0.04) < 0.02 0.05	< 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	n.a.
Canada Wrentham, AB, 2003 (McKenzie) T571 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	69	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Wrentham, AB, 2003	0.07	0.07–0.14	23 (3–6 leaf	71	< 0.02 (< 0.02,	< 0.02 (< 0.02,	< 0.02 (< 0.02,	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
(Prodigy) T573 CER 0708/03			stage)		< 0.02)	< 0.02)	< 0.02)	
Canada Taber, AB, 2003 (Prodigy) T572 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	75	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.05)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Taber, AB, 2003 (McKenzie) T574 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	76	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.04)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Taber, AB, 2003 (McKenzie) T575 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	85	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Rosthern, SK, 2003 (AC Barrie) T576 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	79	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Rosthern, SK, 2003 (AC Eatonia) T581 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	79	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Lacombe, AB, 2003 (AC Crystal) T577 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	49	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.03)	< 0.02 (< 0.02, < 0.02)	n.a.
				98	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	
Canada Lacombe, AB, 2003 (AC Intrepid) T580 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	81 88 94 101	< 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	< 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	< 0.02 < 0.02 (< 0.02, < 0.02) < 0.02 < 0.02	n.a.
Canada Penhold, AB, 2003 (Intrepid) T578 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	90	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Penhold, AB, 2003 (AC Crystal) T579 CER 0708/03	0.07	0.06–0.09	23 (3–6 leaf stage)	90	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Hepburn, SK, 2003 (AC Barrie) T582 CER 0708/03	0.07	0.20–0.28	23 (3–6 leaf stage)	58	< 0.02 (< 0.02, < 0.02)	0.14 (0.15, 0.14)	< 0.02 (< 0.02, < 0.02)	n.a.
Canada Minto, MB, 2003 (Super B) T583 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	58	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.06 (0.10, 0.08, 0.06, < 0.02, 0.05, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
Canada Minto, MB, 2003 (Avonlea) T584 CER 0708/03	0.07	0.04–0.07	23 (3–6 leaf stage)	66	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.04 (0.06, 0.04, 0.03, 0.03, 0.03, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	n.a.
Canada Boissevain, MB, 2003 (AC Barrie) T585 CER 0708/03	0.07	0.07–0.14	23 (3–6 leaf stage)	61	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.05)	< 0.02 (< 0.02, < 0.02)	n.a.
USA GAP	0.06	0.30	up to 39	60				
USA Champaign, IL, 2003 (Kaskaskia) NAHR00702 824-02	0.07	0.06	51 (start of earing)	60	< 0.02 (< 0.02, < 0.02)	0.90 (0.99, 0.80)	0.11 (0.12, 0.10)	n.a.
USA Nickerson, KS 2002 (Heyne) NAHR01102 824-02	0.07	0.06	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.57 (0.55, 0.58)	0.08 (0.07, 0.08)	n.a.
USA Larned, KS 2002 (Jagger) NAHR01202 824-02	0.07	0.05	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.69 (0.76, 0.61)	0.03 (0.03, 0.03)	n.a.
USA Belpre, KS, 2002 (Jagger) NAHR01302 824-02	0.07	0.38	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.21 (0.21, 0.21)	0.04 (0.04, 0.04)	n.a.
USA Grand Island, NE, 2003 (Nuplains) NBHR01102 824-02	0.07	0.04	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.09 (0.12, 0.06)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Lake Andes, SD, 2002 (Forge HRS) NCHR00702 824-02	0.07	0.05	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.32 (0.27, 0.36)	0.05 (0.04, 0.06)	n.a.
USA St. Joseph, MO, 2003 (Karl) NDHR00702 824-02	0.07	0.06	39 (ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.35 (0.38, 0.31)	0.05 (0.05, 0.04)	n.a.
USA Geneva, MN, 2002 (Oxen) NFHR00902 824-02	0.07	0.05	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.14 (0.13, 0.15)	0.05 (0.05, 0.05)	n.a.
USA Stillwater, OK, 2002-2003 (Jaggar PVPA)	0.07	0.05	22 (2 tillers)	60	< 0.02 (< 0.02, < 0.02)	0.52 (0.47, 0.57)	0.08 (0.08, 0.08)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
SCHR01202 824-02								
USA Colony, OK, 2003 (Coker 9663) SCHR01302 824-02	0.07	0.06	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.20 (0.17, 0.22)	0.04 (0.03, 0.06)	n.a.
	0.36	0.31	47 (flag leaf sheath opening)	60	< 0.02 (< 0.02, < 0.02)	0.74 (0.70, 0.77)	0.19 (0.19, 0.19)	n.a.
USA Levelland, TX, 2003 (TAM 105) SCHR01402 824-02	0.07	0.04	Boot stage, few plants starting to head	60	0.02 (0.02, 0.03)	0.82 (0.73, 0.90)	0.05 (0.05, 0.05)	n.a.
USA Rincon, NM, 2003 (TAM 200) SCHR01502 824-02	0.07	0.07	20–30 (jointing)	60	< 0.02 (< 0.02, < 0.02)	1.09 (1.30, 0.87)	0.13 (0.17, 0.08)	n.a.
USA Shoffner, AR, 2003 (DK7900) SEHR00602 824-02	0.07	0.04	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.27 (0.28, 0.25)	0.08 (0.08, 0.08)	n.a.
USA Rose Hill, NC, 2003 (Coker 9803) SJHR02202 824-02	0.07	0.04	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.07 (0.07, 0.06)	< 0.02 (< 0.02, < 0.02)	n.a.
USA Visalia, CA, 2003 (Yecoro, Rojo) W2HR00202 824-02	0.07	0.06	57 (nearing end of earing)	60	< 0.02 (< 0.02, < 0.02)	0.09 (0.08, 0.10)	0.02 (0.03, 0.02)	n.a.
USA Ephrata, WA, 2003 (Stephens) WFHR01102 824-02	0.07	0.04	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.39 (0.36, 0.42)	0.05 (0.05, 0.05)	n.a.
USA Ault, CO, 2003 (Platte) WHHR00702 824-02	0.07	0.05	22 (2 tillers)	60	< 0.02 (< 0.02, < 0.02)	0.36 (0.35, 0.36)	0.03 (0.03, 0.03)	n.a.
USA Gardner, ND, 2002 (Alsen) WIHR00902 824-02	0.07	0.06	23 (3 tillers)	60	< 0.02 (< 0.02, < 0.02)	0.05 (0.05, 0.06)	< 0.02 (< 0.02, < 0.02)	n.a.
	0.22	0.19	23 (3 tillers)	60	< 0.02 (< 0.02, < 0.02)	0.15 (0.14, 0.15)	0.03 (0.03, 0.03)	n.a.
USA Eldridge, ND, 2002 (Belzer) WIHR01002 824-02	0.07	0.06	45 (late boot stage)	60	< 0.02 (< 0.02, < 0.02)	0.15 (0.11, 0.18)	0.03 (0.02, 0.04)	n.a.
USA Dagmar, MT, 2002 (Challis) WIHR01102 824-02	0.07	0.38	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.20 (0.17, 0.22)	0.03 (0.03, 0.04)	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
USA Dagmar, MT, 2002 (Pristine) WIHR01202 824-02	0.07	0.05	21 (start of tillering)	60	< 0.02 (< 0.02, < 0.02)	0.24 (0.25, 0.22)	0.06 (0.05, 0.06)	n.a.
Slovenia GAP	0.060	0.03	13–39	Not Specified				
Germany Frechen, Rhein-Nordrhein-Westfalen, 2013 (Julius) 13-00434-01 TK0179719	0.06	0.02	34–39	75	n.a.	0.02	< 0.01	n.a.
	0.18	0.06	33–37 (2-node stage-appearance of last leaf)	75	n.a.	1.09	0.14	n.a.
Germany Bakum, Niedersachsen, 2013 (KWS Chamsin) 13-00434-02 TK0179719	0.06	0.03	34–39	75	n.a.	0.10	0.03	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	61	n.a.	0.90	0.28	n.a.
Germany 2001 (Flair) gwh40601	0.06	0.02	31 (1-node stage)	98	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
	0.06	0.02	39 (ligule stage)	66	< 0.02 (< 0.02, < 0.02)	0.17 (0.17, 0.16)	0.02 (0.02, < 0.02)	0.03 (0.03, 0.03)
France La Bruère sur Loir, Pays de la Loire, 2013 (Altigo) 13-00434-07 TK0179719	0.06	0.02	34–39	78	n.a.	0.15	0.05	n.a.
	0.18	0.07	37 (appearance of last leaf)	78	n.a.	1.31	0.19	n.a.
France Juniville, Champagne Ardenne, 2013 (Orcas) 13-00434-08 TK0179719	0.06	0.03	34–39	62	n.a.	0.01	< 0.01	n.a.
	0.18	0.09	38–39 (up to ligule stage)	62	n.a.	0.16	0.04	n.a.
France Brannens, Aquitaine, 2013 (Solario) 13-00435-05 TK0179720	0.06	0.02	39 (ligule stage)	71	n.a.	0.06	0.02	n.a.
	0.18	0.07	39 (ligule stage)	71	n.a.	0.46	0.12	n.a.
France Saint Restitut, Rhones-Alpes, 2013 (Karur) 13-00435-06 TK0179720	0.06	0.02	39 (ligule stage)	77	n.a.	0.15	0.02	n.a.
	0.18	0.06	39 (ligule stage)	77	n.a.	1.33	0.08	n.a.
France Monferran Savès, Midi- Pyrénées, 2012 (Pescadou) SRFR12-001-37HR CEMR-5447	0.06	0.02	39 (ligule stage)	69	< 0.02	0.10	< 0.02	n.a.
France Tourtenay, Poitou-Charentes, 2011	0.06	0.02	35–37 (up to appearance of	73	< 0.02	0.74 (0.72, 0.74,	0.07 (0.06, 0.08,	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
(Miradoux) CEMR-4983			last leaf)			0.77, 0.73)	0.07, 0.08)	
France Realville, Midi-Pyrénées, 2001 (Aztec) 3023/01	0.06	0.02	32 (2-node stage)	97	< 0.02 (< 0.02, < 0.02)	0.02 (0.02, 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
	0.06	0.02	39 (ligule stage)	69	< 0.02 (< 0.02, < 0.02)	0.19 (0.18, 0.20)	0.04 (0.03, 0.04)	0.03 (0.03, 0.03)
France Izy, Loiret, 2001 (Cezanne) 3021-01	0.06	0.02	31–32 (1 to 2-node stage)	103	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.04)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
	0.06	0.02	39 (ligule stage)	74	< 0.02 (< 0.02, < 0.02)	0.20 (0.19, 0.20)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)
France Tiercé, Maine-et-Loire, 2001 (Vivant) 3020-01	0.06	0.02	31–32 (1 to 2-node stage)	100	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
	0.06	0.02	39–41 (ligule stage-early boot stage)	67	< 0.02 (< 0.02, < 0.02)	0.11 (0.10, 0.11)	0.02 (0.02, 0.02)	< 0.02 (< 0.02, < 0.02)
France La Paluzette, Hérault, 2001 (Eureka) 3022-01	0.06	0.02	31–32 (1 to 2-node stage)	92	< 0.02 (< 0.02, < 0.02)	0.10 (0.10, 0.09)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
	0.06	0.02	39 (ligule stage)	66	< 0.02 (< 0.02, < 0.02)	0.21 (0.20, 0.21)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)
France Ansonville, Loiret, 2005 (Nirvana) AF/8656/SY/3 05-7006	0.06	0.02	39 (ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.28 (0.27, 0.28)	0.05 (0.04, 0.05)	n.a.
France Douzonville, Loiret, 2005 (Runal) AF/8656/SY/4 05-7006	0.06	0.02	39 (ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.16 (0.18, 0.14)	0.04 (0.04, 0.03)	n.a.
France Montauban, Midi-Pyrénées, 2005 (Karur) AF/8657/SY/1 05-7007	0.06	0.02	39 (ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.35 (0.44, 0.25)	0.07 (0.09, 0.05)	n.a.
France Castelnau, Haute-Garonne, 2005 (Anosys) AF/8657/SY/2 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	63	< 0.02 (< 0.02, < 0.02)	0.35 (0.32, 0.37)	0.08 (0.08, 0.07)	n.a.
Italy Caleppio di Settala, Lombardia, 2013 (Genesi) 13-00435-01 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	67	n.a.	0.25	0.02	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	67	n.a.	1.32	0.31	n.a.
Italy Cassano D'adda, Lombardia, 2013 (Pharaon)	0.06	0.02	33–34 (starting at 3-node stage)	61	n.a.	0.25	0.07	n.a.
	0.18	0.05	33–34	61	n.a.	1.46	0.33	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
13-00435-02 TK0179720			(starting at 3-node stage)					
Italy Lajatico, Toscana, 2013 (Bologna) 13-00435-07 TK0179720	0.06	0.02	33–35 (starting at 3-node stage)	58	n.a.	0.09	0.03	n.a.
	0.18	0.05	33–35 (starting at 3-node stage)	58	n.a.	0.49	0.12	n.a.
Italy Castellaneta, Taranto, 2012 (Pietrafitta) SRIT12-1025-37HR CEMR-5447	0.06	0.02	33 (3-node stage)	68	< 0.02	0.17	0.03	n.a.
Italy Altamura, Bari, 2012 (Duilio) SRIT12-1026-37HR CEMR-5447	0.06	0.02	33 (3-node stage)	69	< 0.02	0.06	< 0.02	n.a.
Italy Marsciano, Umbria, 2011 (Dylan) CEMR-4983	0.06	0.02	31–32 (1 to 2-node stage)	83	< 0.02	0.16	< 0.02	n.a.
Italy Bellinzago, Lombardo, 2011 (Accor) CEMR-4983	0.06	0.02	39 (ligule stage)	55	< 0.02	0.09	0.06	n.a.
Italy Rignano Scalo-Foggia, 2001 (Simeto) 3014-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	21–23 (start of tillering-3 tillers), 39 (ligule stage)	68	< 0.02 (< 0.02, < 0.02)	0.24 (0.27, 0.20)	0.06 (0.07, 0.05)	0.04 (0.04, 0.04)
	0.06	0.03	39 (ligule stage)	68	< 0.02 (< 0.02, < 0.02)	0.17 (0.17, 0.16)	0.04 (0.04, 0.04)	0.03 (0.03, 0.02)
Italy Rignano Scalo-Foggia, 2001 (Svevo) 3015-01	0.05 (1st) + 0.06 (2nd) RTI = 34 days	0.02 (1st) + 0.03 (2nd)	21–23 (start of tillering-3 tillers), 39 (ligule stage)	68	< 0.02 (< 0.02, < 0.02)	0.24 (0.24, 0.23)	0.05 (0.05, 0.05)	0.07 (0.08, 0.06)
	0.06	0.03	39 (ligule stage)	68	< 0.02 (< 0.02, < 0.02)	0.17 (0.16, 0.18)	0.04 (0.04, 0.04)	0.04 (0.04, 0.04)
Italy Rignano Scalo-Foggia, 2002 (Svevo) 02-3007	0.04 (1st) + 0.06 (2nd) RTI = 41 days	0.02 (1st) + 0.03 (2nd)	23 (3 tillers), 39 (ligule stage)	66	< 0.02 (< 0.02, < 0.02)	0.29 (0.28, 0.30)	0.09 (0.09, 0.09)	0.03 (0.03, 0.03)
	0.06	0.03	39 (ligule stage)	66	< 0.02 (< 0.02, < 0.02)	0.31 (0.30, 0.31)	0.09 (0.08, 0.09)	0.02 (< 0.02, 0.02)

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
Italy Manfredonia, Foggia, 2002 (Vitron) 02-3006	0.05 (1st) + 0.06 (2nd) RTI = 47 days	0.02 (1st) + 0.03 (2nd)	22 (2 tillers), 39 (ligule stage)	64	< 0.02 (< 0.02, < 0.02)	0.35 (0.36, 0.34)	0.09 (0.09, 0.09)	0.06 (0.06, 0.06)
	0.06	0.03	39 (ligule stage)	64	< 0.02 (< 0.02, < 0.02)	0.28 (0.30, 0.25)	0.07 (0.07, 0.07)	0.05 (0.05, 0.04)
Italy Poggio Piccolo, Bologna, 2005 (San Carlo) AF/8657/SY/3 05-7007	0.06	0.02	37–38 (starting at appearance of last leaf)	60	< 0.02 (< 0.02, < 0.02)	0.16 (0.17, 0.15)	0.05 (0.06, 0.04)	n.a.
Italy Idice, 2005 (Neolatino) AF/8657/SY/4 05-7007	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.29 (0.33, 0.24)	0.06 (0.06, 0.06)	n.a.
Netherlands Vlagtwedde, Groningen, 2013 (Tybalt) 13-00434-03 TK0179719	0.06	0.02	37–39 (2-node stage-ligule stage)	65	n.a.	0.16	< 0.01	n.a.
	0.18	0.09	37–39 (2-node stage-ligule stage)	65	n.a.	0.99	0.24	n.a.
Netherlands Nieuwolda, Groningen, 2013 (Tataros) 13-00434-04 TK0179719	0.06	0.09	34–39 (up to ligule stage)	83	n.a.	0.04	< 0.01	n.a.
	0.17	0.09	34–39 (up to ligule stage)	83	n.a.	0.27	0.12	n.a.
Spain Zafaraya, Andalucia, 2013 (Mario) 13-00435-03 TK0179720	0.06	0.02	35–39 (up to ligule stage)	84	n.a.	0.16	0.05	n.a.
	0.18	0.06	35–39 (up to ligule stage)	84	n.a.	1.20	0.30	n.a.
Spain Maro-Nerja, Andalucia, 2014 (Marius) 13-00435-04 TK0179720	0.06	0.03	34–39 (up to ligule stage)	186	n.a.	< 0.01	0.01	n.a.
	0.18	0.09	34–39 (up to ligule stage)	186	n.a.	< 0.02	< 0.02	n.a.
Spain Almayate, Andalucia, 2014 (Marius) 13-00435-08 TK0179720	0.06	0.02	35–39 (up to ligule stage)	126	n.a.	< 0.01	< 0.01	n.a.
	0.18	0.06	35–39 (up to ligule stage)	126	n.a.	< 0.02	< 0.02	n.a.
Spain Albacete, Albacete, 2012 (Kalifa) SRES12-161-37HR CEMR-5447	0.06	0.02	32–33 (2 to 3-node stage)	56	< 0.02	0.08	< 0.02	n.a.
Spain	0.07	0.02	31–32	77	< 0.02	0.05	< 0.02	n.a.

Location, Year (Variety) Trial no, Study code	Application			DALA	Residues, mg/kg			
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6	M10
Dehesa de los Llanos, Albacetes, 2011 (Berdun) CEMR-4983			(1 to 2-node stage)					
Spain Renedo de Esgueva, Valladolid, 2002 (Soisson) 02-3003	0.04 (1st) + 0.06 (2nd) RTI = 38 days	0.02 (1st) + 0.03 (2nd)	22–24 (starting at 2 tillers), 47–51 (flag leaf sheath opening-start of earing)	56	0.02 (0.02, < 0.02)	0.64 (0.67, 0.60)	0.10 (0.10, 0.10)	0.10 (0.10, 0.09)
	0.06	0.03	31–39 (1-node stage-ligule stage)	72	< 0.02 (< 0.02, < 0.02)	0.29 (0.23, 0.34)	\0.04 (0.02, 0.06)	0.05 (0.04, 0.06)
Spain Las Cabezas, Sevilla, 2002 (Claudio 63) 02-3002	0.04 (1st) + 0.06 (2nd) RTI = 53 days	0.01 (1st) + 0.02 (2nd)	13–25 (3-leaf stage-main stage of tillering), 39 (ligule stage)	73	< 0.02 (< 0.02, < 0.02)	0.83 (0.90, 0.75)	0.07 (0.08, 0.06)	0.16 (0.17, 0.14)
	0.06	0.02	39 (ligule stage)	73	< 0.02 (< 0.02, < 0.02)	0.64 (0.61, 0.66)	0.05 (0.05, 0.05)	0.09 (0.09, 0.09)
United Kingdom Banbury, Oxfordshire, 2013 (JB Diego) 13-00434-05 TK0179719	0.06	0.02	34–39 (up to ligule stage)	70	n.a.	0.10	0.02	n.a.
	0.18	0.07	34–39 (up to ligule stage)	70	n.a.	0.27	0.12	n.a.
United Kingdom Tattingstone, Suffolk, 2013 (Cordiale) 13-00434-06 TK0179719	0.06	0.02	39–41 (ligule stage-early boot stage)	67	n.a.	0.38	0.03	n.a.
	0.18	0.06	39–41 (ligule stage-early boot stage)	67	n.a.	3.32	0.33	n.a.
United Kingdom Pendock, Gloucestershire, 2005 (Nijinsky) AF/8656/SY/1 05-7006	0.06	0.02	37–39 (appearance of last leaf-ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.25 (0.23, 0.26)	0.03 (0.03, 0.03)	n.a.
United Kingdom Ashby-de-la-Zouch, Leicestershire, 2005 (Soisson) AF/8656/SY/2 05-7006	0.06	0.02	39 (ligule stage)	60	< 0.02 (< 0.02, < 0.02)	0.32 (0.28, 0.35)	0.07 (0.06, 0.08)	n.a.

Barley Whole Plant, Hay/Ears/Stalks and Straw

Table 46 Residues of Pinoxaden in barley, whole plant, in European Regions

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6
Slovenia GAP	0.06	0.03	13–39	NS			
England, Suffolk, 2001 (Regina) 3048/01	0.06	0.03	39–49	0	0.66	0.17	< 0.02
				7	0.21	0.21	0.05
				14	0.13	0.15	0.05
			31–32	0	1.6	0.09	< 0.02
				7	0.12	0.40	0.06
				14	< 0.02	0.22	0.05
England, Wokingham, 2001 (Chariot) 3050/01	0.06	0.03	31	0	1.8	0.92	0.02
				7	0.13	0.50	0.09
				14	0.03	0.13	0.04
			37–42	0	1.9	0.12	< 0.02
				7	0.23	0.29	0.09
				14	0.03	0.10	0.05
France, Les Petites Loges, 2001 (Esterel) 3024/01	0.06	0.02	39	0	0.75 (0.84, 0.66)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)
				7	< 0.02 (< 0.02, < 0.02, < 0.02)	0.14 (0.14, 0.14, 0.14)	< 0.02 (< 0.02, < 0.02, < 0.02)
				14	< 0.02 (< 0.02, < 0.02, < 0.02)	0.18 (0.18, 0.18, 0.19)	0.05 (0.05, 0.05, 0.04)
			32	0	0.70 (0.69, 0.67, 0.74)	0.03 (0.03, 0.03, 0.03)	< 0.02 (< 0.02, < 0.02, < 0.02)
				7	0.02 (0.02, 0.02, 0.03)	0.19 (0.18, 0.21, 0.19)	< 0.02 (< 0.02, < 0.02, < 0.02)
				14	< 0.02 (< 0.02, < 0.02, < 0.02)	0.15 (0.14, 0.14, 0.16)	0.02 (0.02, 0.02, < 0.02)
France, Marsillargues, 2001 (Baraka) 3026/01	0.06	0.02	39	0	0.53	0.26	< 0.02
				7	0.04	0.14	0.03
				14	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02)
			32	0	0.60	0.36	< 0.02
				7	0.13	0.26	0.04
				14	0.05	0.16	0.04
France, St Porquier, 2001 (Volga) 3030/01	0.06	0.02	39	0	0.97	0.24	< 0.02
				7	0.02	0.15	0.03
				14	< 0.02	0.09	0.03
			31–32	0	1.3	0.73	< 0.02
				7	0.06	0.33	0.06
				14	< 0.02	0.19	0.04
Germany, Dabrun, 2001 (Barke) gba 30401	0.06	0.02	37–39	0	3.6	0.07	< 0.02
				7	< 0.02	0.29	0.04
				14	< 0.02	0.03	0.14
			31–32	0	3.0	0.22	< 0.02

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6
				7	0.02	0.36	0.06
				14	< 0.02	0.02	0.04
				28	< 0.02	0.03	< 0.02
Germany, Rohlstorf, 2001 (Barke) gba 10401	0.06	0.02	31–32	0	3.0	0.22	< 0.02
				7	0.02	0.36	0.06
				14	< 0.02	0.016	0.04
				28	< 0.02	0.03	< 0.02
			37–39	0	3.6	0.07	< 0.02
				7	< 0.02	0.29	0.04
				14	< 0.02	0.03	0.14
Italy, Bassano, 2002 (Baraka) 02-3004	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 41 days	0.02 (1^{st}) + 0.030 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	0	0.77	0.46	< 0.02
	0.06	0.03	39	0	0.77	0.31	< 0.02
Italy, Lungavilla, 2002 (Amillis) 02-3005	0.04 (1^{st}) + 0.06(2^{nd}) RTI = 37 days	0.02 (1^{st}) + 0.030 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	0	1.1	0.15	< 0.02
				14	0.02	0.17	0.04
	0.06	0.03	39	0	0.91	0.10 (0.10, 0.09, 0.11)	< 0.02 (< 0.02, < 0.02, < 0.02)
				14	0.02	0.17 (0.20, 0.15, 0.17)	0.03 (0.03, 0.03, 0.04)
Italy, Voghera, 2001 (Amillis) 3012/01	0.06 (1^{st}) + 0.04 (2^{nd}) RTI = 29 days	0.02(1^{st}) + 0.01 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	0	1.8	0.08	< 0.02
				7	0.10	0.34	0.03
				14	0.03	0.18	0.02
	0.06	0.02	39	0	1.9	0.02	< 0.02
				7	0.10	0.29	0.02
				14	0.04	0.22	0.03
Italy, Cascina, 2001 (Kelibia) 3013/01	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 29 days	0.01 (1^{st}) + 0.02 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	29	< 0.02	0.04	< 0.02
Spain, Valladolid, 2002 (Blanche) 02-3000	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 38 days	0.02 (1^{st}) + 0.03(2^{nd})	22–24 (1^{st}) + 47–51 (2^{nd})	0	2.0	0.80	0.07
	0.06	0.03	47–51	0	2.3	0.75	0.03
			31–39	0	2.2	0.05	< 0.02
Spain, Huesca, 2002 (Graphic) 02-3001	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 33 days	0.02 (1^{st}) + 0.03(2^{nd})	13–21 (1^{st}), 37–39 (2^{nd})	2	0.46	0.10	< 0.02
	0.06	0.03	37–39	0	1.2	0.04	< 0.02
				14	0.03	0.06	0.02
Spain, Valladolid, 2001 (Garbo) 3044/01	0.06	0.03	39	0	1.1	0.36	< 0.02
				7	0.12	0.34	0.11
				14	0.06	0.20	0.09

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2	M4	M6
	0.06	0.03	31–32	0	1.5	0.66	< 0.02
				7	0.05	0.48	0.12
				14	< 0.02	0.27	0.11

Table 47 Residues of pinoxaden in barley hay, ears and stalks in North American and European Regions

Location, year (variety), Trial No., Study code	Application			DALA	Portion Analysed	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6
Canada GAP	0.06	0.12	up to 37	30	Hay			
Canada, St-Pie-de Bagot, QC, 2003 (Grant) T550 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	29	hay	< 0.02 (< 0.02, < 0.02)	0.26 (0.26, 0.27)	0.14 (0.13, 0.14)
Canada, Elm Creek, MB, 2003 (Conlon) T551 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	33	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	0.02 (< 0.02, 0.03)
Canada, Wrentham, AB, 2003 (Stein) T552 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	48	hay	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)
Canada, Vanscoy, SK, 2003 (CDC Dolly) T553 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	28	hay	< 0.02 (< 0.02, < 0.02)	0.60 (0.63, 0.57)	0.12 (0.12, 0.13)
Canada, Lacombe, AB, 2003 (Metcalfe) T554 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	46	hay	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.05 (0.03, 0.06, 0.04, 0.07, 0.06, 0.06)	0.02 (0.03, < 0.02, 0.02, 0.03, 0.02, 0.03)
Canada, Lacombe, AB, 2003 (Bold) T555 CER0707/03	0.07	0.06	23 (up to the 4th tiller/3–6 leaf stage)	27	hay	< 0.02 (< 0.02, < 0.02)	0.22 (0.21, 0.24)	0.07 (0.06, 0.08)
				46	hay	< 0.02 (< 0.02, < 0.02)	0.08 (0.07, 0.08)	0.02 (0.02, < 0.02)
Canada, Rosthern, SK, 2003 (Kendall) T557 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	22	hay	< 0.02	0.08	0.03
				29	hay	< 0.02	0.09	0.05
				35	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)
				42	hay	< 0.02	0.03	< 0.02
				49	hay	< 0.02	0.04	< 0.02
Canada, Rosthern, SK, 2003 (AC Dolly) T 558 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	35	hay	< 0.02 (< 0.02, < 0.02)	0.03 (0.04, < 0.02)	< 0.02 (< 0.02, < 0.02)
Canada, Hepburn,	0.07	0.07	23 (up to the 4th	34	hay	< 0.02	0.26	0.08

Location, year (variety), Trial No., Study code	Application			DALA	Portion Analysed	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6
SK, 2003 (CDC Dolly) T559 CER0707/03			tiller/3–6 leaf stage)			(< 0.02, < 0.02)	(0.23, 0.29)	(0.06, 0.11)
Canada, Boissevain, MB, 2003 (Metcalfe) T561 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	33	hay	< 0.02 (< 0.02, < 0.02)	0.14 (0.12, 0.16)	0.06 (0.06, 0.07)
Canada, Boissevain, MB, 2003 (Robust) T562 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	28	hay	< 0.02 (< 0.02, < 0.02)	0.40 (0.26, 0.55)	0.08 (0.07, 0.09)
Canada, Minto, MB, 2003 (Conlon) T560 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	15	hay	< 0.02	0.40	0.18
				22	hay	< 0.02	0.10	0.05
				28	hay	< 0.02 (< 0.02, < 0.02)	0.10 (0.08, 0.12)	0.04 (0.04, 0.03)
				36	hay	< 0.02	0.05	0.03
				43	hay	< 0.02	0.03	< 0.02
Canada, Minto, MB, 2003 (Lacey) T563 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	34	hay	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.06 (0.05, 0.06, 0.06, 0.03,0.06, 0.07)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)
Canada, Penhold, AB, 2003 (Metcalfe) T556 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	46	hay	< 0.02 (< 0.02, < 0.02)	0.06 (0.05, 0.06)	0.02 (0.03, < 0.02)
Canada, Penhold, AB, 2003 (Bold) T564 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	46	hay	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.03)	0.02 (0.02, < 0.02)
Canada, Kipp, AB, 2003 (Stein) T565 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	26	hay	< 0.02 (< 0.02, < 0.02)	0.12 (0.09, 0.14)	0.06 (0.03, 0.08)
				46	hay	< 0.02 (< 0.02, < 0.02)	0.06 (0.06, 0.05)	< 0.02 (< 0.02, < 0.02)
USA GAP	0.06	0.30	up to 39	60	Hay			
USA, Tule Lake, CA, 2002 (Legacy) WD-HR-008-02, 825-02	0.07	0.04	post foliar	30	hay	< 0.02 (< 0.02, < 0.02)	0.50 (0.21, 0.78)	0.20 (0.09, 0.30)
USA, Wellington, CO, 2002 (Moravian) WH-HR-008-02, 825-02	0.07	0.05	47 (flag leaf visible)	30	hay	< 0.02 (< 0.02, < 0.02)	0.02 (0.02, 0.02)	< 0.02 (< 0.02, < 0.02)
USA, Geneva, MN, 2002 (Royal) NF-HR-010-02, 825-02	0.07	0.04	51 (heads showing)	30	hay	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
USA, Lake	0.07	0.37	32	30	hay	< 0.02	0.04	< 0.02

Location, year (variety), Trial No., Study code	Application			DALA	Portion Analysed	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6
Andes, SD, 2002 (Robust) NC-HR-008-02, 825-02						(< 0.02, < 0.02)	(0.03, 0.04)	(< 0.02, < 0.02)
USA, Dagmar, MT, 2002 (Robust) WI-HR-015-02, 825-02	0.07	0.05	33	30	hay	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.05)	< 0.02 (< 0.02, < 0.02)
USA, Dagmar, MT, 2002 (Conlin) WI-HR-016-02, 825-02	0.07	0.05	33	10	hay	0.08 (0.07, 0.09)	2.1 (2.0, 2.2)	0.51 (0.48, 0.54)
				20	hay	< 0.02 (< 0.02, < 0.02)	0.10 (0.09, 0.10)	0.06 (0.06, 0.06)
				30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.05</u> (0.05, 0.05)	0.02 (0.02, < 0.02)
				40	hay	< 0.02 (< 0.02, < 0.02)	0.02 (< 0.02, 0.02)	< 0.02 (< 0.02, < 0.02)
USA, Windsor, VA, 2002 (Nomini) EB-HR-009-02, 825-02	0.07	0.05	35	30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.20</u> (0.18, 0.22)	0.06 (0.06, 0.06)
USA, Ephrata, WA, 2002 (Baronesse) WF-HR-012-02, 825-02	0.07	0.04	51 (beginning of heading)	30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.24</u> (0.22, 0.26)	0.12 (0.14, 0.09)
USA, Richmond Township, WI, 2002 (Robust) NI-HR-010-02, 825-02	0.07	0.04	30	30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.02</u> (0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
USA, Eldridge, ND, 2002 (Robust) WI-HR-014-02, 825-02	0.07	0.04	41	10	hay	< 0.02 (< 0.02, < 0.02)	1.2 (1.0, 1.4)	0.48 (0.47, 0.48)
				20	hay	< 0.02 (< 0.02, < 0.02)	0.15 (0.14, 0.16)	0.04 (0.04, 0.05)
				30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.13</u> (0.13, 0.13)	0.03 (0.03, 0.03)
				40	hay	< 0.02 (< 0.02, < 0.02)	0.09 (0.09, 0.09)	0.02 (0.02, 0.02)
USA, Gardner, ND, 2002 (Robust) WI-HR-013-02, 825-02	0.07	0.06	23	30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.04</u> (0.03, 0.06)	< 0.02 (< 0.02, < 0.02)
USA, Jerome, ID, 2002 (Baronesse) WG-HR-016-02, 825-02	0.07	0.05	57	30	hay	< 0.02 (< 0.02, < 0.02)	<u>0.02</u> (0.02, 0.03)	< 0.02 (< 0.02, < 0.02)
Slovenia GAP	0.06	0.03	13–39	Not specified				
England, Suffolk, 2001 (Regina)	0.06	0.03	39–49	28	stalk	0.03	0.13	0.07
				34	stalk	0.02	0.11	0.07

Location, year (variety), Trial No., Study code	Application			DALA	Portion Analysed	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6
3048/01				28	ear	< 0.02	0.15	0.03
				34	ear	< 0.02	0.15	0.03
			31–32	28	stalk	< 0.02	0.21	0.08
				35	stalk	< 0.02	0.11	0.04
				28	ear	< 0.02	0.14	0.02
				35	ear	< 0.02	0.08	< 0.02
England, Wokingham, 2001 (Chariot) 3050/01	0.06	0.03	31	28	stalk	< 0.02	0.03	< 0.02
				35	stalk	< 0.02	0.02	< 0.02
				28	ear	< 0.02	< 0.02	< 0.02
				35	ear	< 0.02	< 0.02	< 0.02
			37–42	28	stalk	< 0.02	0.05	0.03
				35	stalk	< 0.02	0.05	0.04
				28	ear	< 0.02	0.06	< 0.02
				35	ear	< 0.02	0.05	< 0.02
France, Les Petites Loges, 2001 (Esterel) 3024/01	0.06	0.02	39	28	stalk	< 0.02	0.11	0.05
				35	stalk	< 0.02	0.09	0.05
				28	ear	< 0.02	0.08	< 0.02
				35	ear	< 0.02	0.05	< 0.02
			32	28	stalk	< 0.02	0.10	0.03
				35	stalk	< 0.02	0.06	0.02
				28	ear	< 0.02	0.07	< 0.02
				35	ear	< 0.02	0.05	< 0.02
France, Marsillargues, 2001 (Baraka) 3026/01	0.06	0.02	39	28	stalk	< 0.02	0.08	0.04
				35	stalk	< 0.02	0.07	0.04
				28	ear	< 0.02	0.08	< 0.02
				35	ear	< 0.02	0.07	< 0.02
			32	28	stalk	0.02	0.14	0.06
				35	stalk	< 0.02	0.11	0.05
				28	ear	< 0.02	0.12	0.02
				35	ear	< 0.02	0.07	< 0.02
France, St Porquier, 2001 (Volga) 3030/01	0.06	0.02	39	28	stalk	< 0.02	0.04	0.02
				35	stalk	< 0.02	0.04	0.03
				28	ear	< 0.02	0.06	0.03
				35	ear	< 0.02	0.05	< 0.02
			31–32	28	stalk	< 0.02	0.02	< 0.02
				35	stalk	< 0.02	0.02	< 0.02
				28	ear	< 0.02	0.04	< 0.02
				35	ear	< 0.02	0.02	< 0.02
Germany, Dabrun, 2001 (Barke) gba 30401	0.06	0.02	37–39	28	stalk	< 0.02	0.05	0.02
				35	stalk	< 0.02	0.05	0.03
				28	ear	< 0.02	0.06	0.02
				35	ear	< 0.02	0.04	0.02
			31–32	28	stalk	< 0.02	< 0.02	< 0.02
				35	ear	< 0.02	< 0.02	< 0.02
Germany, Rohlstorf, 2001 (Barke) gba 10401	0.06	0.02	31–32	35	stalk	< 0.02	< 0.02	< 0.02
				35	ear	< 0.02	< 0.02	< 0.02
			37–39	28	stalk	< 0.02	0.05	0.02
				35	stalk	< 0.02	0.05	0.03
				28	ear	< 0.02	0.06	0.02
				35	ear	< 0.02	0.04	0.02
Italy, Lungavilla, 2002 (Amillis) 02-3005	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 37 days	0.02 (1^{st}) + 0.030 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	35	stalk	< 0.02	0.09	0.04
				35	ear	< 0.02	0.06	< 0.02
	0.06	0.03	39	35	stalk	< 0.02	0.08	0.04
				35	ear	< 0.02	0.07	< 0.02
Italy, Voghera,	0.06	0.02(1^{st})	23–25 (1^{st}) + 39	28	stalk	< 0.02	0.07	0.03

Location, year (variety), Trial No., Study code	Application			DALA	Portion Analysed	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application			M2 [a]	M4	M6
2001 (Amillis) 3012/01	(1st) + 0.04 (2nd) RTI = 29 days	+ 0.01 (2nd)	(2nd)	35	stalk	< 0.02	0.05	0.02
				28	ear	< 0.02	0.06	0.03
				35	ear	< 0.02	0.03	< 0.02
	0.06	0.02	39	28	stalk	< 0.02	0.10	0.04
				35	stalk	< 0.02	0.05	0.02
				28	ear	< 0.02	0.07	< 0.02
				35	ear	< 0.02	0.03	< 0.02
Spain, Huesca, 2002 (Graphic) 02-3001	0.06	0.03	37–39	36	stalk	0.02	0.03	0.03
				36	ear	< 0.02	0.02	< 0.02

Table 48 Residues of pinoxaden in barley straw in North American and European Regions

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
Canada GAP	0.06	0.12	up to 37	60			
Canada, Branchton, ON, 2009 (HY 481-6R) T650 CER 07025/09	0.06	0.07	33–37 (flag leaf still visible)	70	< 0.02 (< 0.02, < 0.02)	0.53 (0.48, 0.58)	0.16 (0.14, 0.19)
Canada Woodlands, MB, 2009 (Trey) T651 CER 07025/09	0.06	0.07	12–13 (2–3 leaf stage)	80	< 0.02 (< 0.02, < 0.02)	0.02 (< 0.02, 0.03)	< 0.02 (< 0.02, < 0.02)
Canada, St-Pie-de Bagot, QC, 2003 (Grant) T550 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	57	< 0.02 (< 0.02, < 0.02)	0.05 (0.04, 0.06)	0.02 (0.02, 0.03)
Canada, Elm Creek, MB, 2003 (Conlon) T551 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	63	< 0.02 (< 0.02, < 0.02)	0.10 (0.12, 0.09)	0.06 (0.04, 0.07)
Canada, Wrentham, AB, 2003 (Stein) T552 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	78	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)
Canada, Vanscoy, SK, 2003 (CDC Dolly) T553 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	62	< 0.02 (< 0.02, < 0.02)	0.08 (0.07, 0.10)	0.04 (0.04, 0.04)
				69	< 0.02 (< 0.02, < 0.02)	0.10 (0.06, 0.13)	0.06 (0.05, 0.07)
Canada, Lacombe, AB, 2003 (Metcalfe) T554 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	84	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02)	0.04 (0.05, 0.06, 0.04, 0.03, 0.04, 0.05)	0.04 (0.03, 0.05, 0.04, 0.03, 0.04, 0.05)

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
Canada, Lacombe, AB, 2003 (Bold) T555 CER0707/03	0.07	0.06	23 (up to the 4th tiller/3–6 leaf stage)	84	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	0.02 (< 0.02, 0.02)
Canada, Rosthern, SK, 2003 (Kendall) T557 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	59	< 0.02	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
				66	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
				73	< 0.02	< 0.02	< 0.02
				80	< 0.02	< 0.02	< 0.02
Canada, Rosthern, SK, 2003 (AC Dolly) T 558 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	66	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
Canada, Rosthern, SK, 2009 (Copeland) T652 CER 07025/09	0.06	0.06	13–15 (3–5 leaf stage)	85	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
Canada, Hepburn, SK, 2003 (CDC Dolly) T559 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	58	< 0.02 (< 0.02, < 0.02)	0.1 (0.07, 0.13)	0.04 (0.03, 0.06)
Canada, Boissevain, MB, 2003 (Metcalfe) T561 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	60	< 0.02 (< 0.02, < 0.02)	0.07 (0.07, 0.07)	0.05 (0.05, 0.05)
Canada, Boissevain, MB, 2003 (Robust) T562 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	60	< 0.02 (< 0.02, < 0.02)	0.08 (0.07, 0.09)	0.04 (0.04, 0.04)
Canada, Minto, MB, 2003 (Conlon) T560 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	46	< 0.02	0.02	< 0.02
				54	< 0.02 (< 0.02, < 0.02)	0.03 (0.03, 0.03)	< 0.02 (< 0.02, < 0.02)
				60	< 0.02	0.04	< 0.02
				70	< 0.02	0.02	< 0.02
Canada, Minto, MB, 2003 (Lacey) T563 CER0707/03	0.07	0.04	23 (up to the 4th tiller/3–6 leaf stage)	57	< 0.02 (< 0.02, < 0.02, < 0.02,< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02,< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02, < 0.02, 0.03, < 0.02)
Canada, Penhold, AB, 2003 (Metcalfe) T556 CER0707/03	0.07	0.20	23 (up to the 4th tiller/3–6 leaf stage)	89	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
Canada, Penhold, AB, 2003 (Bold) T564 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	89	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
Canada, Kipp, AB, 2003 (Stein) T565 CER0707/03	0.07	0.07	23 (up to the 4th tiller/3–6 leaf stage)	74	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
USA GAP	0.06	0.30	up to 39	60			
USA, Tule Lake, CA, 2002 (Legacy)	0.07	0.04	post foliar	60	< 0.02 (< 0.02,	0.06 (0.05, 0.06)	< 0.02 (< 0.02,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
WD-HR-008-02, 825-02					< 0.02)		< 0.02)
USA, Wellington, CO, 2002 (Moravian) WH-HR-008-02, 825-02	0.07	0.05	47 (flag leaf visible)	60	< 0.02 (< 0.02, < 0.02)	0.15 (0.14, 0.16)	0.10 (0.09, 0.11)
USA, Geneva, MN, 2002 (Royal) NF-HR-010-02, 825-02	0.07	0.04	51 (heads showing)	60	< 0.02 (< 0.02, < 0.02)	0.12 (0.11, 0.12)	0.04 (0.04, 0.04)
USA, Lake Andes, SD, 2002 (Robust) NC-HR-008-02, 825-02	0.07	0.37	32	60	< 0.02 (< 0.02, < 0.02)	0.34 (0.25, 0.42)	0.14 (0.11, 0.18)
USA, Dagmar, MT, 2002 (Robust) WI-HR-015-02, 825-02	0.07	0.05	33	60	< 0.02 (< 0.02, < 0.02)	0.18 (0.18, 0.19)	0.06 (0.06, 0.06)
USA, Dagmar, MT, 2002 (Conlin) WI-HR-016-02, 825-02	0.07	0.05	33	46	< 0.02 (< 0.02, < 0.02)	0.24 (0.21, 0.26)	0.18 (0.15, 0.20)
				53	< 0.02 (< 0.02, < 0.02)	0.22 (0.21, 0.24)	0.16 (0.16, 0.17)
				60	< 0.02 (< 0.02, < 0.02)	0.22 (0.20, 0.24)	0.18 (0.18, 0.18)
				67	< 0.02 (< 0.02, < 0.02)	0.15 (0.14, 0.16)	0.14 (0.12, 0.15)
USA, Windsor, VA, 2002 (Nomini) EB-HR-009-02, 825-02	0.07	0.05	35	60	< 0.02 (< 0.02, < 0.02)	0.14 (0.17, 0.12)	0.05 (0.06, 0.04)
USA, Ephrata, WA, 2002 (Baronesse) WF-HR-012-02, 825-02	0.07	0.04	51 (beginning of heading)	60	< 0.02 (< 0.02, < 0.02)	0.04 (0.04, 0.04)	0.06 (0.05, 0.06)
USA, Richmond Township, WI, 2002 (Robust) NI-HR-010-02, 825-02	0.07	0.04	30	60	< 0.02 (< 0.02, < 0.02)	0.37 (0.34, 0.40)	0.12 (0.20, 0.05)
USA, Eldridge, ND, 2002 (Robust) WI-HR-014-02, 825-02	0.07	0.04	41	46	< 0.02 (< 0.02, < 0.02)	0.17 (0.20, 0.14)	0.10 (0.14, 0.07)
				53	< 0.02 (< 0.02, < 0.02)	0.26 (0.37, 0.15)	0.18 (0.26, 0.09)
				60	< 0.02 (< 0.02, < 0.02)	0.24 (0.32, 0.17)	0.18 (0.23, 0.12)
				67	< 0.02 (< 0.02, < 0.02)	0.15 (0.12, 0.18)	0.12 (0.08, 0.16)
USA, Gardner, ND, 2002 (Robust) WI-HR-013-02, 825-02	0.07	0.06	23	60	< 0.02 (< 0.02, < 0.02)	0.07 (0.08, 0.06)	0.04 (0.03, 0.04)
	0.22	0.19	23	60	< 0.02 (< 0.02, < 0.02)	0.15 (0.15, 0.15)	0.09 (0.09, 0.09)
USA, Jerome, ID, 2002 (Baronesse) WG-HR-016-02, 825-02	0.07	0.05	57	60	< 0.02 (< 0.02, < 0.02)	0.11 (0.09, 0.13)	0.16 (0.13, 0.19)
	0.36	0.25	57	60	< 0.02	0.71 (0.67,	1.0 (1.0,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
					(< 0.02, < 0.02)	0.75)	1.0)
Slovenia GAP	0.06	0.03	13–39	Not specified			
England, Suffolk, 2001 (Regina) 3048/01	0.06	0.03	39–49	61	< 0.02 (< 0.02, < 0.02)	0.12 (0.12, 0.13)	0.08 (0.08, 0.08)
			31–32	82	< 0.02 (< 0.02, < 0.02)	0.10 (0.10, 0.11)	0.04 (0.04, 0.05)
England, Wokingham, 2001 (Chariot) 3049/01	0.06	0.03	37–42	71	< 0.02 (< 0.02, < 0.02)	0.06 (0.06, 0.06)	0.03 (0.03, 0.03)
			31	90	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
England, Wokingham, 2001 (Chariot) 3050/01	0.06	0.03	31	71	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
			37–42	71	< 0.02 (< 0.02, < 0.02)	0.06 (0.06, 0.07)	0.03 (0.03, 0.03)
France, Les Petites Loges, 2001 (Esterel) 3024/01	0.06	0.02	39	71	< 0.02 (< 0.02, < 0.02)	0.10 (0.06, 0.14)	0.04 (0.02, 0.07)
			32	82	< 0.02 (< 0.02, < 0.02)	0.10 (0.06, 0.13)	0.04 (0.03, 0.05)
France, Marsillargues, 2001 (Baraka) 3026/01	0.06	0.02	39	76	< 0.02 (< 0.02, < 0.02)	0.06 (0.06, 0.07)	0.04 (0.03, 0.04)
			32	90	< 0.02 (< 0.02, < 0.02)	0.06 (0.07, 0.06)	0.04 (0.03, 0.04)
France, Le Puiset, 2001 (Prisma) 3029/01	0.06	0.02	39	59	< 0.02 (< 0.02, < 0.02)	0.10 (0.10, 0.11)	0.06 (0.06, 0.07)
			32	69	< 0.02 (< 0.02, < 0.02)	0.09 (0.09, 0.09)	0.05 (0.05, 0.05)
France, St Porquier, 2001 (Volga) 3030/01	0.06	0.02	39	49	< 0.02 (< 0.02, < 0.02)	0.08 (0.08, 0.09)	0.04 (0.04, 0.04)
			31–32	62	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)
France, Rueil-Malmaison, 2001 (Cork) 3031/01	0.06	0.02	39	53	< 0.02 (< 0.02, < 0.02)	0.08 (0.07, 0.09)	0.08 (0.07, 0.08)
			31–32	67	< 0.02 (< 0.02, < 0.02)	0.06 (0.06, 0.07)	0.05 (0.05, 0.05)
Finland, Jokioinen, 2006 (Saana) T000722-06	0.06	0.03	41–43	42	0.03	0.18	0.15
Germany, Dabrun, 2001 (Barke) gba 30401	0.06	0.02	37–39	74	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)
			31–32	74	< 0.02 (< 0.02,	< 0.02 (< 0.02,	< 0.02 (< 0.02,

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
					< 0.02)	< 0.02)	< 0.02)
Germany, Rohlstorf, 2001 (Barke) gba 10401	0.06	0.02	31–32	74	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02)
			37–39	74	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.04)	< 0.02 (< 0.02, < 0.02)
Italy, Bassano, 2002 (Baraka) 02-3004	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 41 days	0.02 (1^{st}) + 0.030 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	55	< 0.02 (< 0.02, < 0.02)	0.08 (0.08, 0.09)	0.06 (0.05, 0.06)
	0.06	0.03	39	55	< 0.02 (< 0.02, < 0.02)	0.10 (0.09, 0.10)	0.06 (0.06, 0.06)
Italy, Lungavilla, 2002 (Amillis) 02-3005	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 37 days	0.02 (1^{st}) + 0.030 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	61	< 0.02 (< 0.02, < 0.02)	0.09 (0.09, 0.09)	0.04 (0.04, 0.04)
	0.06	0.03	39	61	< 0.02 (< 0.02, < 0.02)	0.08 (0.08, 0.07)	0.03 (0.03, 0.03)
Italy, Voghera, 2001 (Amillis) 3012/01	0.06 (1^{st}) + 0.04 (2^{nd}) RTI = 29 days	0.02(1^{st}) + 0.01 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	62	< 0.02 (< 0.02, < 0.02)	0.08 (0.06, 0.09)	0.04 (0.03, 0.05)
	0.06	0.02	39	62	< 0.02 (< 0.02, < 0.02)	0.09 (0.06, 0.12)	0.04 (0.03, 0.06)
Italy, Cascina, 2001 (Kelibia) 3013/01	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 29 days	0.01 (1^{st}) + 0.02 (2^{nd})	23–25 (1^{st}) + 39 (2^{nd})	62	< 0.02 (< 0.02, < 0.02)	0.14 (0.13, 0.14)	0.08 (0.07, 0.08)
	0.06	0.02	39	62	< 0.02 (< 0.02, < 0.02)	0.19 (0.22, 0.16)	0.12 (0.10, 0.14)
Spain, Valladolid, 2002 (Blanche) 02-3000	0.04 (1^{st}) + 0.06 (2^{nd}) RTI = 38 days	0.02 (1^{st}) + 0.03(2^{nd})	22–24 (1^{st}) + 47–51 (2^{nd})	53	< 0.02 (< 0.02, < 0.02)	0.58 (0.57, 0.58)	0.25 (0.25, 0.25)
	0.06	0.03	47–51	53	< 0.02 (< 0.02, < 0.02)	0.34 (0.30, 0.39)	0.20 (0.19, 0.21)
			31–39	69	< 0.02 (< 0.02, < 0.02)	0.17 (0.17, 0.17)	0.07 (0.07, 0.07)
Spain, Huesca, 2002 (Graphic) 02-3001	0.04 (1^{st}) + 0.06 (2^{nd})	0.02 (1^{st}) + 0.03(2^{nd})	13–21 (1^{st}), 37–39 (2^{nd})	65	0.02 (0.02, < 0.02)	0.04 (0.04, 0.04)	0.02 (0.03, 0.02)

Location, year (variety), Trial No., Study code	Application			DALA	Residues, mg/kg		
	kg ai/ha	kg ai/hL	Crop growth stage (BBCH) at application		M2 [a]	M4	M6
	RTI = 33 days						
	0.06	0.03	37–39	65	< 0.02 (< 0.02, < 0.02)	0.04 (0.03, 0.05)	0.02 (0.03, < 0.02)
Spain, Grisalena-Burgos, 2001 (Cezzane) 3043/01	0.06	0.03	39–41	48	0.02 (0.02, 0.02)	0.44 (0.48, 0.40)	0.45 (0.40, 0.50)
			31–32	61	< 0.02 (< 0.02, < 0.02)	0.20 (0.19, 0.20)	0.16 (0.15, 0.16)
Spain, Valladolid, 2001 (Garbo) 3044/01	0.06	0.03	39	54	< 0.02 (< 0.02, < 0.02)	0.12 (0.10, 0.13)	0.10 (0.11, 0.10)
	0.06	0.03	31–32	58	< 0.02 (< 0.02, < 0.02)	0.08 (0.11, 0.05)	0.08 (0.08, 0.09)

[a] Only for the 2009 trials conducted in Canada are the residues measured as M2 and reported as pinoxaden equivalents. For all other trials, residues are measured as M2 and reported as M2.

Fate of residues during processing

In processing-nature of residues

Hydrolysis of [phenyl-1-^{14}C] pinoxaden (specific activity 53.51 µCi/mg), at 5 mg ai/L, was investigated in aqueous buffer solutions, at 90 °C and pH 4 for 20 min (simulating pasteurisation), at 100 °C and pH 5 for 60 min (simulating baking, brewing and boiling), and at 120 °C and pH 6 for 20 min (simulating sterilisation) (Stingelin, J., 2002).

Quantitative measurement of the radioactivity was carried out by LSC. Further analysis to quantify and identify the radiolabelled degradation products present in the test solutions was conducted using HPLC and TLC. Pinoxaden was identified by HPLC co-chromatography with a certified standard. Selected samples were analysed by TLC to confirm the presence of pinoxaden.

Table 49 Degradation of pinoxaden under various hydrolysis conditions

Condition	Pinoxaden [% AR]	M2 [% AR]	Unknowns [% AR]	Total Recovery [% AR]	Degradation [% AR]
pH 4, 90 °C	86.25 (85.47, 87.02)	5.34 (5.28, 5.40)	0.00	91.59 (90.75, 92.42)	5.34
pH 5, 100 °C	72.30 (72.75, 71.64)	20.25 (20.69, 19.82)	0.21 (0.41, 0.00)	92.75 (93.85, 91.65)	20.46
pH 6, 120 °C	53.54 (54.68, 52.41)	39.65 (38.39, 40.91)	0.00	93.20 (93.07, 93.32)	39.65

Pinoxaden showed some degradation under pasteurization conditions (pH 4, 90 °C, 20 minutes) accounting for 5.3% of the AR, while under baking, brewing and boiling conditions (pH 5, 100 °C, 60 minutes), 20% of the AR was degraded. Under sterilization conditions (pH 6, 120 °C, 20 minutes), up to 40% of the AR was degraded. The only hydrolysis product identified was the metabolite M2.

In processing-effect on the residue level

The Meeting received information on the fate of pinoxaden residues and its metabolites M2, M4 and M6 during the processing of wheat and barley grains.

Processing of wheat

One trial was conducted in the USA during the 2002 growing season where a single foliar spray application of an EC formulation, containing 100 g/L of pinoxaden, was applied to wheat at rates of 72 g ai/ha and 359 g ai/ha. Grain samples were collected 60 days after the last application and processed in accordance with commercial practices, into bran, flour, middlings, shorts and germ (Lin, 2004b).

In two trials conducted in Germany during the same growing season, an EC formulation, containing 100 g/L of pinoxaden, was applied to winter wheat at a rate of 180 g ai/ha. Treated grain samples were harvested 85 or 92 days following application and milled to straight flour, coarse bran, and middlings. Low grade meal (toppings) was further separated from the coarse bran and middlings, resulting in total bran (the remnants of the coarse bran and middlings). The straight flour and toppings were then mixed to form all-purpose flour (type 550). The wholemeal flour was generated by mixing the straight flour, coarse bran, and middlings. The wholemeal dough was made by mixing yeast, salt, and water with the wholemeal flour. Dough was kneaded, risen, and baked to make the whole meal bread.

The residues of M2 (expressed as pinoxaden equivalents), M4 and M6 were quantitated using method REM 199.02. The LOQ was determined to be 0.01 mg/kg/analyte for wheat grain and processed commodities. The residues in the treated wheat processed commodities as well as the processing factors are presented in the following tables 50 and 51.

Table 50 Pinoxaden wheat processing study conducted in USA

Location, year (variety) study code	Commodity	Treatment rate	Residues, mg/kg			Calculated Processing Factor			Mean Processing Factor	
		(g ai/ha)	M2	M4	M6	M2	M4	M6	M4	M6
USA, Colony, OK, 2002 (Coker) 824-02	Grain RAC	72	< 0.01	0.4	0.04	n.a.	n.a.	n.a.	n.a.	n.a.
		359	< 0.01	1.1	0.15	n.a.	n.a.	n.a.	n.a.	n.a.
	Aspirated grain fractions	72	< 0.01	0.04	0.02	n.a.	0.10	0.50		
		359	< 0.01	0.18	0.07	n.a.	0.16	0.47	0.13	0.48
	Bran	72	< 0.01	0.48	0.14	n.a.	1.20	3.50		
		359	< 0.01	5.2	0.6	n.a.	4.73	4.00	2.96	3.75
	Flour	72	< 0.01	0.06	0.02	n.a.	0.15	0.50		
		359	< 0.01	0.18	0.02	n.a.	0.16	0.13	0.16	0.32
	Middlings	72	< 0.01	0.23	0.02	n.a.	0.58	0.50		
		359	< 0.01	0.79	0.08	n.a.	0.72	0.53	0.65	0.52
	Shorts	72	< 0.01	0.37	0.05	n.a.	0.93	1.25		
		359	< 0.01	1.1	0.15	n.a.	1.00	1.00	0.96	1.13
	Germ	72	< 0.01	0.23	0.03	n.a.	0.58	0.75		
		359	< 0.01	0.79	0.16	n.a.	0.21	0.20	0.39	0.48

n.a = Not applicable

Table 51 Pinoxaden wheat processing studies conducted in Germany

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
Germany, 2002 (winter wheat) gwh049002	Grain RAC	180	< 0.01 (< 0.01, < 0.01)	0.08 (0.07, 0.08)	0.02 (0.01, 0.02)	n.a.	n.a.	n.a.
	Purified grain	180	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.07)	0.01 (0.01, 0.01)	n.a.	0.75	0.50
	Offal	180	0.01 (0.01, < 0.01)	0.04 (0.05, 0.02)	0.01 (0.01, < 0.01)	n.a.	0.5	0.50
	Straight flour	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.25	0.50
	Middlings	180	< 0.01 (< 0.01, < 0.01)	0.20 (0.20, 0.20)	0.03 (0.03, 0.03)	n.a.	2.5	1.50
	Coarse bran	180	< 0.01 (< 0.01, < 0.01)	0.26 (0.25, 0.28)	0.04 (0.04, 0.04)	n.a.	3.25	2.00
	Total bran	180	< 0.01 (< 0.01, < 0.01)	0.30 (0.31, 0.29)	0.04 (0.04, 0.05)	n.a.	3.75	2.00
	Low grade meal (toppings)	180	< 0.01 (< 0.01, < 0.01)	0.10 (0.11, 0.10)	0.02 (0.02, 0.02)	n.a.	1.25	1.00
	Flour (all-purpose/type 550) including toppings	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.25	0.50
	Wholemeal flour	180	< 0.01 (< 0.01,	0.08 (0.08,	< 0.01 (< 0.01,	n.a.	1	0.50

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
			< 0.01)	0.08)	< 0.01)			
	Wholemeal dough	180	< 0.01 (< 0.01, < 0.01)	0.04 (0.04, 0.05)	< 0.01 (< 0.01, < 0.01)	n.a.	0.5	0.50
	Wholemeal bread	180	< 0.01 (< 0.01, < 0.01)	0.04 (0.04, 0.05)	< 0.01 (< 0.01, < 0.01)	n.a.	0.5	0.50
	Wheat germ	180	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.02 (0.02, 0.02)	n.a.	0.375	1.00
Germany, Wuhnitz, 2002 (winter wheat) gwh043102	Grain RAC	180	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.01 (0.01, < 0.01)	n.a.	n.a.	n.a.
	Purified grain	180	< 0.01 (< 0.01, < 0.01)	0.07 (0.06, 0.08)	0.01 (0.01, 0.01)	n.a.	1.17	1
	Offal	180	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.07)	0.01 (0.01, 0.01)	n.a.	1.00	1
	Straight flour	180	< 0.01 (< 0.01, < 0.01)	0.01 (0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.17	1
	Middlings	180	< 0.01 (< 0.01, < 0.01)	0.18 (0.16, 0.20)	0.02 (0.02, 0.03)	n.a.	3.00	2
	Coarse bran	180	< 0.01 (< 0.01, < 0.01)	0.28 (0.26, 0.31)	0.04 (0.04, 0.04)	n.a.	4.67	4
	Total bran	180	< 0.01 (< 0.01, < 0.01)	0.30 (0.34, 0.26)	0.04 (0.04, 0.04)	n.a.	5.00	400
	Low grade meal (toppings)	180	< 0.01 (< 0.01, < 0.01)	0.07 (0.07, 0.07)	0.01 (0.01, 0.01)	n.a.	1.17	1
	Flour (all-purpose/type 550) including toppings	180	< 0.01 (< 0.01, < 0.01)	0.01 (0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.17	1
	Wholemeal flour	180	< 0.01 (< 0.01, < 0.01)	0.07 (0.06, 0.08)	< 0.01 (< 0.01, < 0.01)	n.a.	1.17	1
	Wholemeal dough	180	< 0.01 (< 0.01, < 0.01)	0.04 (0.05, 0.04)	< 0.01 (< 0.01, < 0.01)	n.a.	0.67	1
	Wholemeal bread	180	< 0.01 (< 0.01, < 0.01)	0.04 (0.03, 0.04)	< 0.01 (< 0.01, < 0.01)	n.a.	0.67	1
	Wheat germ	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	0.02 (0.02, 0.02)	n.a.	0.33	2

	Wheat Processed Commodity	Mean Processing Factor	
		M4	M6
	Purified grain	0.96	0.75
	Offal	0.75	0.75
	Straight flour	0.21	0.75
	Middlings	2.75	1.75
	Coarse bran	3.96	3.00
	Total bran	4.38	201.00
	Low grade meal (toppings)	1.21	1.00
	Flour (all-purpose/type 550) including toppings	0.21	0.75

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
	Wholemeal flour					1.08		0.75
	Wholemeal dough					0.58		0.75
	Wholemeal bread					0.58		0.75
	Wheat germ					0.35		1.50

n.a: Not applicable

Processing of barley

One trial was conducted in the USA during the 2002 growing season where a single foliar spray application of an EC formulation, containing 120 g/L of pinoxaden, was applied to barley at rates of 72 g ai/ha and 359 g ai/ha. Grain samples were collected 60 days after treatment and processed in accordance with commercial practices, into pearled barley, flour and bran (Lin, 2004a).

In two trials conducted in Germany during the same growing season, an EC formulation, containing 100 g/L of pinoxaden, was applied to barley at a rate of 180 g ai/ha. Treated grain samples were harvested 71 days following application and hulled to produce pearl barley and abrasion (the waste from hulling). Grains were also sprouted to produce malt sprouts for brewing. Malt sprouts were mashed and extracted with water to produce wort and spent grains (the used malt). Hops were added to the wort and boiled. The spent hops were then removed from the wort. Yeast was added to the wort and then fermented, producing beer.

The residues of M2 (expressed as pinoxaden equivalents), M4 and M6 were quantitated using methods 117-01 (USA) and REM 199.02 (Germany). The LOQ was determined to be 0.01 mg/kg/analyte for barley grain and processed commodities. The residues in the treated barley processed commodities as well as the processing factors are presented in the following Tables 52 and 53.

Table 52 Pinoxaden barley processing study conducted in USA

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing factors			Mean Processing Factor	
			M2	M4	M6	M2	M4	M6	M4	M6
USA Jerome, ID, 2002 (Baronesse) 825-02	Grain	72	< 0.01	0.20	0.07	n.a.	n.a	n.a	n.a.	n.a.
		359	< 0.01	1.3	0.35	n.a.	n.a	n.a		
	Pearled barley	72	< 0.01	0.25	0.06	n.a.	1.25	0.86	1.05	0.84
		359	< 0.01	1.1	0.29	n.a.	0.85	0.83		
	Flour	72	< 0.01	0.10	0.01	n.a.	0.50	0.14	0.46	0.23
		359	< 0.01	0.55	0.11	n.a.	0.42	0.31		
	Bran	72	< 0.01	0.53	0.14	n.a.	2.65	2.00	1.71	1.50
		359	< 0.01	1.0	0.35	n.a.	0.77	1.00		

n.a: Not applicable

Table 53 Pinoxaden barley processing studies conducted in Germany

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
Germany, 2002 (Spring barley) gba039002	Grain	180	< 0.01 (< 0.01, < 0.01)	0.18 (0.17, 0.18)	0.10 (0.09, 0.10)	n.a.	n.a.	n.a.
	Clean grain	180	< 0.01 (< 0.01, < 0.01)	0.16 (0.14, 0.19)	0.08 (0.08, 0.09)	n.a.	0.89	0.8
	Offal	180	< 0.01	0.12	0.07 (0.07,	n.a.	0.67	0.7

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
			(< 0.01, < 0.01)	(0.12, 0.13)	0.07)			
	Pearled barley	180	< 0.01 (< 0.01, < 0.01)	0.09 (0.09, 0.09)	0.04 (0.04, 0.05)	n.a.	0.50	0.4
	Abrasion	180	< 0.01 (< 0.01, < 0.01)	0.36 (0.33, 0.38)	0.18 (0.17, 0.20)	n.a.	2.00	1.8
	Malt (after drying)	180	< 0.01 (< 0.01, < 0.01)	0.21 (0.19, 0.23)	0.16 (0.14, 0.17)	n.a.	1.17	1.6
	Malt sprouts	180	< 0.01 (< 0.01, < 0.01)	0.06 (0.05, 0.07)	0.03 (0.03, 0.03)	n.a.	0.33	0.3
	Malt (before brewing)	180	< 0.01 (< 0.01, < 0.01)	0.20 (0.17, 0.22)	0.10 (0.10, 0.11)	n.a.	1.11	1
	Spent grain	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.01, 0.02)	< 0.01 (< 0.01, < 0.01)	n.a.	0.11	0.1
	Wort (before cooking)	180	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.02 (0.02, 0.02)	n.a.	0.17	0.2
	Wort (after cooking)	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	0.02 (0.01, 0.02)	n.a.	0.11	0.2
	Spent hops	180	< 0.01 (< 0.01, < 0.01)	0.04 (0.04, 0.05)	0.02 (0.02, 0.03)	n.a.	0.22	0.2
	Young beer	180	< 0.01 (< 0.01, < 0.01)	0.03 (0.03, 0.03)	0.02 (0.02, 0.02)	n.a.	0.17	0.2
	Beer	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	0.02 (0.02, 0.01)	n.a.	0.11	0.2
Germany, 2002 (Spring barley) gba033102	Grain	180	< 0.01 (< 0.01, < 0.01)	0.13 (0.13, 0.13)	0.04 (0.04, 0.05)	n.a.	n.a.	n.a.
	Clean grain	180	< 0.01 (< 0.01, < 0.01)	0.12 (0.12, 0.11)	0.04 (0.04, 0.04)	n.a.	0.92	1
	Offal	180	< 0.01 (< 0.01, < 0.01)	0.10 (0.09, 0.11)	0.06 (0.06, 0.06)	n.a.	0.77	1.5
	Pearled barley	180	< 0.01 (< 0.01, < 0.01)	0.06 (0.06, 0.06)	0.01 (0.01, 0.01)	n.a.	0.46	0.25
	Abrasion	180	< 0.01 (< 0.01, < 0.01)	0.30 (0.28, 0.31)	0.12 (0.12, 0.11)	n.a.	2.31	3
	Malt (after drying)	180	< 0.01 (< 0.01, < 0.01)	0.16 (0.16, 0.15)	0.08 (0.08, 0.08)	n.a.	1.23	2
	Malt sprouts	180	< 0.01 (< 0.01, < 0.01)	0.08 (0.08, 0.09)	0.02 (0.02, 0.03)	n.a.	0.62	0.5
	Malt (before brewing)	180	< 0.01 (< 0.01, < 0.01)	0.16 (0.15, 0.16)	0.06 (0.05, 0.06)	n.a.	1.23	1.5
	Spent grain	180	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.08	0.25

Location, year (variety) study code	Commodity	Treatment rate (g ai/ha)	Residues, mg/kg			Processing Factors		
			M2	M4	M6	M2	M4	M6
	Wort (before cooking)	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	0.01 (0.01, < 0.01)	n.a.	0.15	0.25
	Wort (after cooking)	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.03)	0.02 (0.02, 0.01)	n.a.	0.15	0.5
	Spent hops	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.01)	0.01 (0.01, 0.01)	n.a.	0.15	0.25
	Young beer	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	0.01 (0.01, < 0.01)	n.a.	0.08	0.25
	Spent yeast	180	< 0.01 (< 0.01, < 0.01)	0.01 (0.01, < 0.01)	< 0.01 (< 0.01, < 0.01)	n.a.	0.08	0.25
	Beer	180	< 0.01 (< 0.01, < 0.01)	0.02 (0.02, 0.02)	< 0.01 (< 0.01, < 0.01)	n.a.	0.15	0.25

Barley Processed Commodity	Mean Processing Factors	
	M4	M6
Clean grain	0.91	0.90
Offal	0.72	1.10
Pearl barley	0.48	0.33
Abrasion	2.15	2.40
Malt (after drying)	1.20	1.80
Malt sprouts	0.47	0.40
Malt (before brewing)	1.17	1.25
Spent grain	0.09	0.18
Wort (before cooking)	0.16	0.23
Wort (after cooking)	0.13	0.35
Spent hops	0.19	0.23
Young beer	0.12	0.23
Beer	0.13	0.23

n.a: Not applicable

Residues in animal commodities

Dairy Cattle

One dairy cattle feeding study was conducted where eleven dairy cows (Holstein, 2–3 years old, 202–250 kg bw) were divided into four test groups (Oakes, T., 2003). The first group consisted of a single cow as a control while the remaining three groups consisted of three cows each. Animals were dosed with M4 once daily by means of gelatine capsules administered with a balling gun. Treatments were made in the evening following milking for 28 consecutive days. The doses administered to the low, mid and high dose treatment groups were 1.11, 3.01, and 10.12 mg of M4/kg feed/day, respectively. Cows were dosed for 29–30 consecutive days and sacrificed 20–24 hours after administration of the last dose.

Milk samples were collected on Days 0 (pre-dose), 2, 5, 8, 12, 15, 19, 22 and 28. All milk samples were frozen at –20 °C and analysed within 71 days. Tissue samples collected at sacrifice included liver, kidney, peri-renal fat, omental fat, round muscle and tenderloin muscle. All tissue samples were stored frozen and analysed within 60 days of collection. The stability of M4 and M6 has already been demonstrated in milk, liver and meat for 90 days (Study No. T001241-03).

Samples were analysed for residues of M4 and M6 using the LC-MS/MS analytical method T001530-03. Tissue or milk samples were refluxed with 1 N HCl for 2 hours. An aliquot of the extract was then filtered through two solid-phase extraction (SPE) cartridges for clean-up. The eluate

was evaporated and the final solution was diluted with 0.2% formic acid prior to analysis. The LOQ for M4 and M6 in milk is 0.01 mg/kg/analyte, while the LOQ in tissue is 0.02 mg/kg/analyte.

In milk, no quantifiable (< LOQ) residues of M4 or M6 were observed in the high dose treatment group. Hence, samples from the low and mid dose groups were not analysed.

Table 54 Residues in whole milk following 28 days of oral administration of M4 to dairy cows

Day	High dose (10.12 mg/kg feed/day)	
	M4 (mg/kg)	M6 (mg/kg)
0	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
2	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
5	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
8	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
12	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
15	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
19	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
22	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)
28	< 0.01 (< 0.01, < 0.01, < 0.01)	< 0.01 (< 0.01, < 0.01, < 0.01)

In liver and kidney, no quantifiable residues of M4 or M6 were observed in the high dose treatment group. Therefore, samples from the low and mid dose experiments were not analysed.

Table 55 Residues in liver and kidney following 28 days of oral administration of M4 to dairy cows

Dose (mg/kg feed/day)	Liver		Kidney	
	M4 (mg/kg)	M6 (mg/kg)	M4 (mg/kg)	M6 (mg/kg)
10.12	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)

In muscle and fat, no quantifiable residues of M4 or M6 were observed in the high dose treatment group. As such, samples from the low or mid dose treatment groups were not analysed.

Table 56 Residues in fat and muscle following 28 days of oral administration of M4 to dairy cows

Dose (mg/day)	Omental fat		Perirenal fat		Round Muscle		Tenderloin muscle	
	M4 (mg/kg)	M6 (mg/kg)	M4 (mg/kg)	M6 (mg/kg)	M4 (mg/kg)	M6 (mg/kg)	M4 (mg/kg)	M6 (mg/kg)
10.12	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)

Poultry

The hen feeding study was conducted with 100, 34-week-old white Leghorn laying hens (Oakes, T., 2003). The hens weighed on average 1.45 kg with an egg production of ≥ 0.77 eggs per day. The hens were assigned to four different groups with 15 hens each; one control and three treatment groups. Each of these groups was separated into three subgroups of five animals each. The four treatment groups were fed rations treated with M4 at rates of 0.5 mg/kg feed, 1.5 mg/kg feed and 5.0 mg/kg feed per day for 28 consecutive days. The hens were sacrificed between 20–24 hours after removing the treated feed.

Composite egg samples were collected on Days 0 (pre-dose), 1, 3, 6, 9, 13, 16, 20, 23, and 28. One composite sample was collected per subgroup by pooling the eggs of all five hens together (i.e. three composite samples per treatment group). The eggs were frozen and stored at –20 °C until analysis. Composite tissue samples of skin plus attached fat, peritoneal fat, liver and breast plus thigh muscle were collected for each subgroup and stored frozen until analysis. No sample was stored for longer than 99 days (approximately 3 months). The stability of M4 and M6 has already been demonstrated in eggs, liver, and meat for 90 days (Study No. T001241-03).

All samples were analysed for residues of M4 and M6 using LC-MS/MS analytical method T001530-03. Briefly, tissue and egg samples were refluxed with 1 N HCl for 2 hours. An aliquot of the extract was then filtered through two solid-phase extraction (SPE) cartridges for clean-up. The organic solvent was then evaporated and the final solution was diluted with 0.2% formic acid prior to analysis. The LOQ for M4 and M6 in eggs and tissue is 0.02 mg/kg/analyte.

In eggs, no quantifiable (< LOQ) residues of M4 or M6 were detected in the high dose treatment group. Because of this, no samples from the low and mid dose groups were analysed.

Table 57 Residues in eggs following 28 days oral administration of M4 to laying hens

Day	High dose (5 mg/kg feed)	
	M4 (mg/kg)	M6 (mg/kg)
0	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
1	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
3	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
6	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
9	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
13	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
16	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
20	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
23	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
28	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)

In muscle, liver, and fat, no quantifiable residues of M4 or M6 were detected in the 10× treatment group. Because of this, no samples from the low and mid dose groups were analysed.

Table 58 Residues in muscle, liver and fat following 28 days oral administration to laying hens

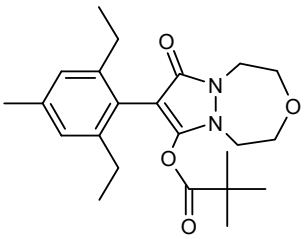
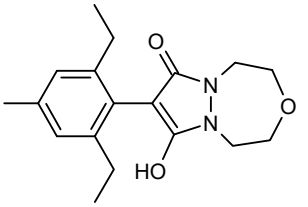
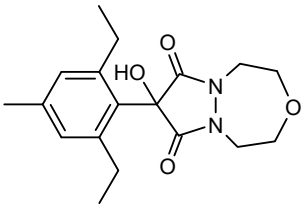
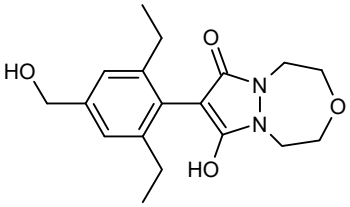
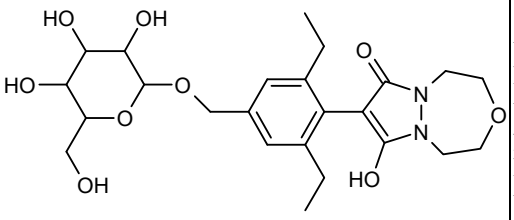
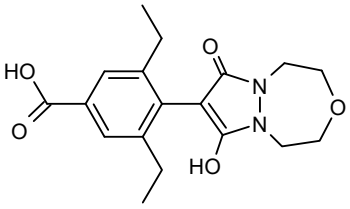
Commodity	High dose (5 mg/kg feed)	
	M4 (mg/kg)	M6 (mg/kg)
Thigh and breast muscle	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
Liver	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
Peritoneal fat	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)
Skin and attached fat	< 0.02 (< 0.02, < 0.02, < 0.02)	< 0.02 (< 0.02, < 0.02, < 0.02)

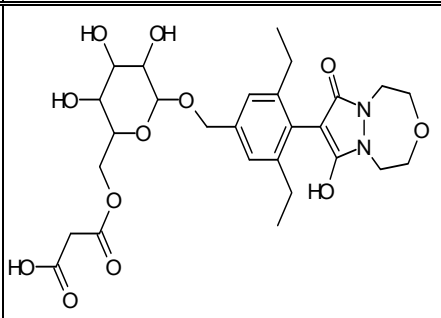
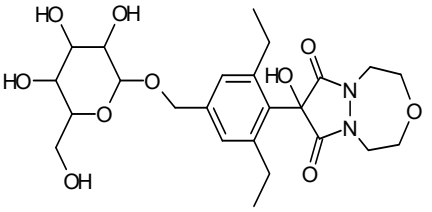
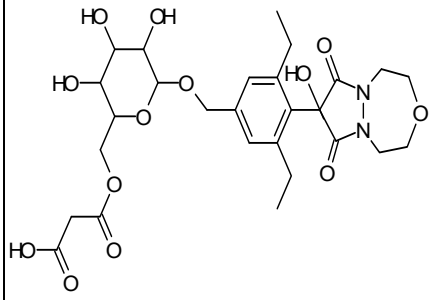
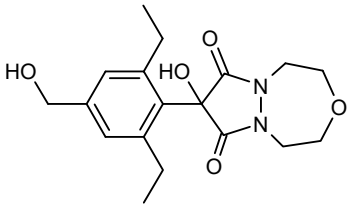
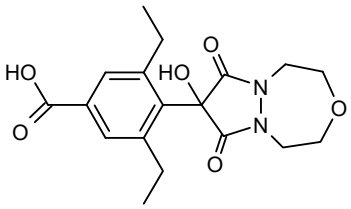
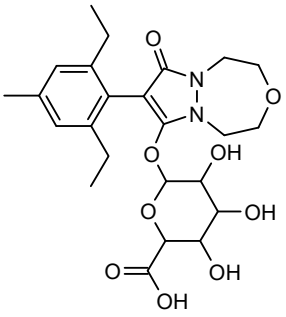
APPRAISAL

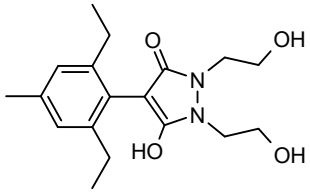
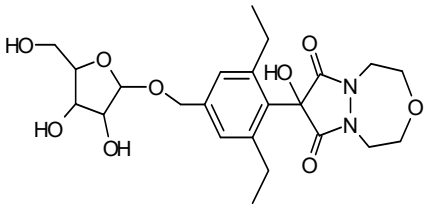
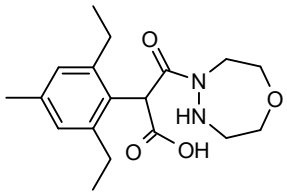
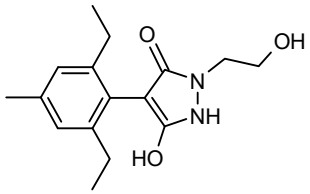
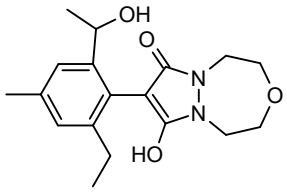
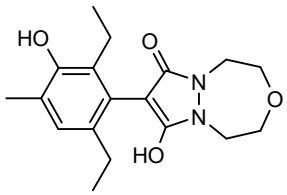
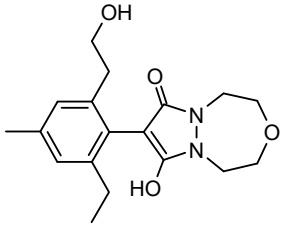
Pinoxaden is a selective post-emergence herbicide for the control of annual grass weeds in cereal crops. Pinoxaden belongs to the phenylpyrazole class of herbicides which act by inhibiting the enzyme acetyl-CoA carboxylase (ACCase). The compound was evaluated for the first time by the 2016 JMPR for both toxicology and residues.

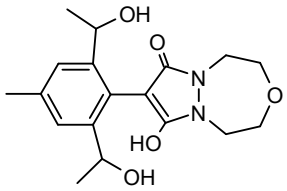
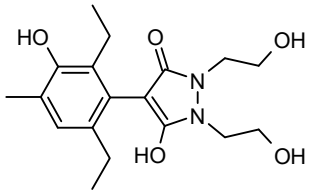
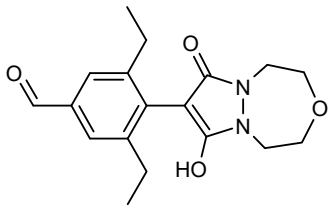
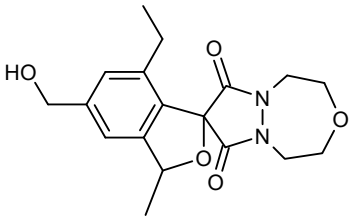
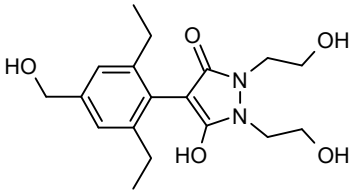
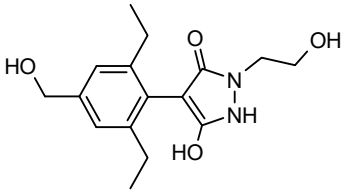
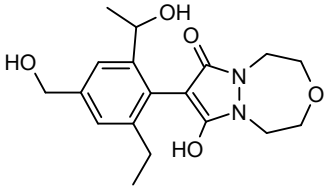
The Meeting received information on the metabolism of pinoxaden in lactating goats, laying hens, wheat and rotational crops, methods of residue analysis, freezer storage stability, GAP information, supervised residue trials and processing studies on wheat and barley as well as livestock transfer studies in both dairy cattle and poultry.

In this document, the code names, chemical structures and chemical names of the metabolites were as follows:

Compound Name	Structure	IUPAC-Name	Occurrence in
Pinoxaden NOA 407855 = M1		8-(2,6-diethyl-p-tolyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropionate	Plants and animals
NOA 407854 = M2		8-(2,6-Diethyl-4-methyl-phenyl)-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat (early intervals) Spring Wheat (early intervals) Goat Hen (excreta) Rat
NOA 447204 = M3		8-(2,6-Diethyl-4-methyl-phenyl)-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Hen Rotational Wheat Rotational Lettuce
SYN 505164 = M4		8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Goat Hen Rat
M5 (glucose conjugate of M4)		8-[2,6-Diethyl-4-(3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-yloxymethyl)-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Rat
SYN 502836 = M6		3,5-Diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzoic acid	Winter Wheat Spring Wheat Hen Goat Rat

Compound Name	Structure	IUPAC-Name	Occurrence in
M7 (malonyl-glucose conjugate of M4)		Malonic acid mono-{6-[3,5-diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzyloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-ylmethyl} ester	Winter Wheat Spring Wheat
M8 (glucose conjugate of M10)		8-[2,6-Diethyl-4-(3,4,5-trihydroxy-6-hydroxymethyl-tetrahydro-pyran-2-yloxymethyl)-phenyl]-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Spring Wheat
M9 (malonyl-glucose conjugate of M10)		Malonic acid mono-{6-[3,5-diethyl-4-(8-hydroxy-7,9-dioxo-hexahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzyloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-ylmethyl} ester	Winter Wheat
SYN 505887 = M10		8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-8-hydroxy-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione	Winter Wheat Spring Wheat Goat Rat
SYN 504574 = M11 = ME7		3,5-Diethyl-4-(8-hydroxy-7,9-dioxo-hexahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzoic acid	Winter Wheat Spring Wheat Rat Rotational crop forage
M12		6-[8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-yloxy]-3,4,5-trihydroxy-tetrahydro-pyran-2-carboxylic acid	Goat Rat

Compound Name	Structure	IUPAC-Name	Occurrence in
M13		4-(2,6-diethyl-4-methyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat Rat
M14 (pentose conjugate of M4)		8-[4-(3,4-Dihydroxy-5-hydroxymethyl-tetrahydro-furan-2-yloxymethyl)-2,6-diethyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d] [1,4,5]oxadiazepin-7-one	Winter Wheat Spring Wheat Rat
M19		2-(2,6-diethyl-4-methyl-phenyl)-3-[1,4,5]oxadiazepan-4-yl-3-oxo-propionic acid	Goat Rat
M20		4-(2,6-diethyl-4-methyl-phenyl)-5-hydroxy-1-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat Rat
M22		8-[2-ethyl-6-(1-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M23		8-(2,6-diethyl-3-hydroxy-4-methyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M24		8-[2-ethyl-6-(2-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat

Compound Name	Structure	IUPAC-Name	Occurrence in
M26		8-[2,6-bis-(1-hydroxy-ethyl)-4-methyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Goat Rat
M27		4-(2,6-diethyl-3-hydroxy-4-methyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Goat
M31		3,5-Diethyl-4-(9-hydroxy-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-8-yl)-benzaldehyde	Winter Wheat Hen
M32		7-ethyl-5-(hydroxymethyl)-3-methyl-3H-spiro[2-benzofuran-1,8'-pyrazolo[1,2-d][1,4,5]oxadiazepine]-7',9'-dione	Winter wheat Spring Wheat Rotational Crops
M33		4-(2,6-diethyl-4-hydroxymethyl-phenyl)-5-hydroxy-1,2-bis-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Hen
M34		4-(2,6-diethyl-4-hydroxymethyl-phenyl)-5-hydroxy-1-(2-hydroxy-ethyl)-1,2-dihydro-pyrazol-3-one	Hen Rat
M35		8-[2-ethyl-6-(1-hydroxy-ethyl)-4-hydroxymethyl-phenyl]-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one	Hen Rat

Plant metabolism

The metabolism of pinoxaden, labelled in the [pyrazol-3,5-^{14}C], [phenyl-1-^{14}C] and the [oxadiazepin-3,6-^{14}C] rings, was investigated in spring and winter wheat grown under outdoor conditions.

Foliar treatment

Winter wheat (variety Galaxie) was treated as an autumn application with pinoxaden, labelled in the **pyrazole** ring and formulated as an emulsifiable concentrate formulation containing the safener cloquintocet-mexyl. The test material was applied once at growth stage BBCH 13 as a foliar spray at a rate of 68.5 g ai/ha. Samples of forage (immature plant) were harvested 0, 14, 42, and 209 days after application. Mature plants were harvested 264 days after application and separated into grain, straw and husk.

Overall total radioactive residues (TRRs) in mature grain were very low (0.004 mg eq/kg) and hence further identification was not conducted. For straw, approximately 64% of the TRRs were extracted using acetonitrile/water. Acid hydrolysis of the unextracted radioactivity, accounting for 35% of the TRR (0.013 mg/kg) released an additional 13% of the TRR. The only metabolite observed was the metabolite M10 (<3.3% of the TRR).

Stem injection

A stem injection experiment was conducted in order to generate grain and straw samples containing higher measurable residues to aid in metabolite identification. At early booting stage (BBCH 41), 50 µg of -pyrazole-labelled pinoxaden was directly injected into the stem, approximately 1–2 cm above the first node, of each spring wheat plant (variety Toronit), grown in a growth chamber. Wheat was sampled after 14, 28 and 56 days, but only the mature plants (56 DAT) were separated into grain, husk and straw and used for analysis.

The TRR in grain was considerably higher (1.5 mg eq/kg) than that following foliar application, allowing for the identification of the metabolites. Soxhlet extraction of the residue remaining following acetonitrile/water extraction released 12% of the TRR, with M4 and M6 being the only metabolites observed (concentrations not reported in the study). Further hydrolysis work on the unextracted residue (23% of the TRR) indicated that a low amount of the radioactivity (about 2% of the TRR) was incorporated into starch. When extracted with 0.05 N NaOH and hydrolysed using 1 N HCl at 100 °C for 6 hours, the metabolites M4 and M6 (both accounting for < 16% of the TRR; < 0.24 mg eq/kg) were identified.

Conversely, direct acid hydrolysis of whole grain released 100% of the TRRs and after clean-up, the majority of the radioactivity was shown to be M4 (86% of the TRR) with a small amount of M6 (8% of the TRR). This demonstrated that the majority of the radioactivity in grain consisted of conjugates of M4.

Differences in the metabolite pattern between the foliar and the stem injection experiments were noted. Moreover, in the field experiment, the presence of the metabolite M10 was likely due to uptake of the soil metabolite M3 which is subsequently hydroxylated in the plant to the metabolite M10.

Winter wheat (variety Galaxie) was treated as an autumn application with pinoxaden, labelled in the **phenyl** ring and formulated as an emulsifiable concentrate formulation. The test material was applied once at growth stage BBCH 49 as a foliar spray at rates of 64 g ai/ha (1 × rate) or 318 g ai/ha (5 × rate).

At 28 days after treatment (DAT), ears were sampled while mature plants were harvested at 55 DAT and separated into grain, straw and husks.

TRRs in the 5 × grain and straw, accounting for 0.84 mg eq/kg and 16 mg eq/kg, respectively, were 3-fold higher than those from the 1 × experiment.

Extractability of TRRs in grain was higher for the 5 × samples (76% of the TRR) in comparison with the 1 × samples (60% of the TRR). The predominant metabolites in grain were M4

(18–20% of the TRR; 0.05–0.15 mg eq/kg), its malonyl conjugate M7 (4–11% of the TRR; 0.01–0.09 mg eq/kg) and M6 (9.6–12% of the TRR; 0.02–0.11 mg eq/kg). Minor metabolites included M5, M8 and M10 (each representing ≤ 10% of the TRR; ≤ 0.01 mg eq/kg). The unextracted residue in the 1 × grain accounted for 46% of the TRR (0.11 mg eq/kg) while it accounted for 19% of the TRR (0.16 mg eq/kg) in the 5 × grain. To characterize the bound residues, grain samples from the 1 × experiment were subjected to acid hydrolysis with 1 N HCl for 6 hours at 100 °C. Metabolite M4 accounted for the majority of the released radioactivity (79% of the TRR) with M6 accounting for about 11% of the TRR, indicating that the grain unextracted residues predominantly consisted of M4 and M6 or conjugates thereof.

Approximately 78% of the TRRs in straw were extracted with an 80% acetonitrile solution. The predominant metabolites were M4 (15–37% of the TRR; 1.8-2.0 mg eq/kg) and M10 (1 × experiment only: 13% of the TRR; 0.7 mg eq/kg). Several minor metabolites were found in straw from both the 1 × and 5 × experiments including M3, M6, M7, M8, M11, M14 and M31 with M32 only found in the straw sample from the 5 × rate, none of which accounted for > 10% of the TRR). Unextracted radioactivity in the straw sample from the 1 × experiment accounted for 17% of the TRR (0.93 mg eq/kg). Acid hydrolysis of this fraction released 6.2% of the TRR and subsequent base hydrolysis released a further 8.2% of the TRR. The major metabolites released upon hydrolysis were M4 (29–60% of the TRR) and M6 (17–18% of the TRR). The unextracted residues of the straw sample from the 5 × experiment (25% of the TRRs, 3.1 mg eq/kg) were not further subjected to identification/characterisation procedures.

Spring wheat (variety Toronit) was treated with pinoxaden, labelled in the phenyl and oxadiazepine rings and formulated as an emulsifiable concentrate formulation containing the safener cloquintocet-mexyl. The test material was applied once at growth stage BBCH 37–39 as a foliar spray at a rate of 62 g ai/ha for the phenyl label and 66 g ai/ha for the oxadiazepine label. Samples of grain and straw were collected 67 DAT for both labels.

In general, TRRs were similar for both labels, especially at maturity for grain (0.14–0.16 mg eq/kg) and straw (0.91–1.3 mg eq/kg).

In grain nearly 80% of the radioactivity was extracted using acetonitrile/water followed by microwave extraction with 80% n-propanol. Hydrolysis of the cold and microwave extracts with 1N HCl released up to 92% of the TRR. In the case of the phenyl label, the released radioactivity consisted almost entirely of M4 (58% of the TRR) and M6 (6.8% of the TRR). For the oxadiazepine label, the major metabolites M4 and M6 accounted for 65% and 12% of the TRRs, respectively.

Up to 79% of the TRR was extracted from straw using acetonitrile/water (80:20, v/v). The major metabolite was M4 accounting for 34-36% of the TRR (0.33-0.44 mg eq/kg). The metabolite M6 was also found at levels up to 9% of the TRR. Several minor metabolites were identified including M3, M5, M7, M10, M11 and M32, each representing ≤ 9% of the TRR; ≤ 0.08 mg eq/kg). Unextracted radioactivity in straw accounted for 22% of the TRR (0.20 mg eq/kg) for the phenyl label and 28% of the TRR (0.36 mg eq/kg) for the oxadiazepine label. A significant amount of this residue was released by acid hydrolysis, and was attributed to metabolites M4 (0.8–1.3% of the TRR) and M6 (2.4–2.7% of the TRR).

In summary, the major metabolic pathway in wheat proceeds via ester hydrolysis of pinoxaden to M2 and subsequently to M4 followed by conjugation. Oxidation of M4 resulted in the formation of M10 which was subsequently conjugated. Lastly, further oxidation of the methyl-hydroxy function of M4 leads to the corresponding carboxylic acid M6.

The Meeting noted that all metabolites observed in wheat were also identified in the rat metabolism.

Animal metabolism

Metabolism studies were conducted in lactating goats where they were dosed orally once daily for 4 consecutive days with [**phenyl-1-^{14}C**]-pinoxaden at a dose level equivalent to 115–126 ppm feed. The major route of elimination of the radioactivity was via the urine which accounted for 45–48% of the

total administered dose (AD), while feces accounted for 15–21% of the AD and milk accounted for ≤ 0.01% of the AD. The tissue burden was very low (< 1% of the AD) considering the dosing levels. The overall recovery of administered radioactivity averaged 86%.

The total radioactive residues (TRRs) were highest in kidney (1.7–4.6 mg eq/kg) followed by liver (0.9–1.4 mg eq/kg), muscle (0.06–0.1 mg eq/kg for both leg muscle and loin muscle), fat (0.01–0.04 mg eq/kg) and milk (0.01–0.02 mg eq/kg). Sequential extractions of tissues and milk with acetonitrile and acetonitrile/water released greater than 92% of the TRR.

Pinoxaden was not observed in any tissue or milk. The hydrolysis product of the parent compound, M2, was the major metabolite in all these tested matrices accounting for 79–90% of the TRR. Several minor metabolites were observed, none of which exceeded 10% of the TRR.

The metabolism of the major plant metabolite M4 was also investigated in lactating goats dosed orally once daily for 4 consecutive days with [Pyrazole-5-^{14}C]-M4 at a dose level of 9–11 ppm feed.

The major route of elimination of the radioactivity was via the feces which accounted for 58–62% of the AD, while urine accounted for 8–9% of the AD and milk accounted for ≤ 0.01% of the AD. The tissue burden was very low (< 0.1% of the AD). The overall recovery of administered radioactivity averaged 92%.

The total radioactive residues (TRRs) were highest in kidney (0.05 mg eq/kg) followed by liver (0.02–0.03 mg eq/kg). TRRs in milk were < 0.002 mg eq/kg while those in fat and muscle were each < 0.011 mg eq/kg, demonstrating very limited transfer of residues. As the radioactivity in muscle, fat and milk were low, the nature of the residues in these matrices was not further elucidated. In liver and kidney, approximately, 88–92% of the TRR was extracted with acetonitrile/water.

The major component identified in kidney and liver was unchanged M4 (41–55% of the TRR; 0.01-0.02 mg eq/kg). Minor amounts of the hydroxylated metabolite M10 were also identified (≤ 9% of the TRR; ≤ 0.004 mg eq/kg). Therefore, the predominant metabolic route was hydroxylation of M4 at the 8-position to form M10.

Leghorn laying hens were dosed orally once daily for 4 consecutive days with [**phenyl-1-^{14}C**] labelled pinoxaden at dose levels equivalent to 97 ppm feed. Approximately 85% of the AD was recovered, most of which (75% of the AD) was excreta-related. TRRs in egg white and egg yolk accounted for about 0.007% of AD (0.003% AD in egg white plus 0.004% AD in yolk). The TRR levels in egg white reached a plateau by Day 3 of dosing, however, no plateau was observed in egg yolk. The tissue burden was very low (< 0.2% of the AD) with highest concentrations found in kidney (1.8 mg eq/kg) followed by liver (0.62 mg eq/kg), skin (0.12 mg eq/kg), lean meat (0.06 mg eq/kg)and peritoneal fat (0.04 mg eq/kg). Sequential extractions of tissues and egg whites with acetonitrile, acetonitrile/water and methanol/water released greater than 92% of the TRR while for egg yolks the extractability was 67% of the TRR.

No pinoxaden was detected in any of the samples. The major metabolites in all tissues and eggs were M2 (1.7–46% of the TRR), M4 (18–44% of TRR) and M6 (13–45% of TRR; only observed in egg yolks). Four minor metabolites were also observed in these matrices, none of which exceeded 10% of the TRRs.

The Meeting concluded that, in all species investigated, the total administered radioactivity was predominantly eliminated in excreta. While the metabolic profiles differed quantitatively between the species, qualitatively there are no major differences; the routes and products of metabolism in animals were similar across the studies resulting from the hydrolysis of the parent compound to the major metabolite M2 followed by hydroxylation of the 4-methyl group of the phenyl moiety to the metabolite M4. This was followed by further oxidation of M4 to M6.

Environmental fate

The FAO Manual (FAO, 2016) explained the data requirements for studies of environmental fate. The focus should be on those aspects that are most relevant to MRL setting. For pinoxaden, supervised

residue trials data were received for foliar spray on annual crops. Therefore, according to the FAO Manual, only studies on rotational crops (confined, field), aerobic degradation, hydrolysis and photolysis were evaluated.

Confined rotational crops

The Meeting received three confined rotational crop studies where pinoxaden was labelled in the **[phenyl-1-^{14}C], [oxadiazepin-3,6-^{14}C]** and both [**phenyl-1-^{14}C**] and [**oxadiazepin-3,6-^{14}C1**] rings and formulated as emulsifiable concentrate formulations. The radioalabelled material was applied once to soil at rates of 60.3–70 g ai/ha. Lettuce, radish and wheat (spring and winter) were planted 29-30, 120, 168–177 (wheat only) and 361–365 days after soil treatment. Spring wheat, mustard greens and turnip were also planted at a 15-day PBI.

The TRRs in all crop fractions planted following the longer PBIs (168-365 days) were well below 0.01 mg/kg. Hence no further work was conducted on samples from these intervals. Therefore, analysis was only conducted on fractions where residues were above 0.01 mg eq/kg. For all tested matrices, residues of the parent compound, pinoxaden, were not detectable.

Several metabolites were identified including M2, M3, M8, M9, M11 and M32, none of which exceeded 0.01 mg eq/kg, however, the metabolite M3 generally accounted for the highest proportions (9–29% of the TRR; 0.0006–0.012 mg eq/kg) in all tested commodities. Enzymatic hydrolysis of some of the extracted residues as well as acid hydrolysis of the unextracted residues revealed that 5–55% of the TRRs were attributed to free and conjugated M10 (< 0.001–0.008 mg eq/kg).

In summary, the main metabolite observed in rotational crops was M3 which was in turn hydroxylated to M10. These metabolites were all identified in the primary crop (wheat) metabolism studies, albeit at non-detectable levels in grain.

Field rotational crops

Pinoxaden, formulated as an emulsifiable concentrate formulation, was applied to the primary crop, wheat, as a single application at a rate of 69 g ai/ha, equivalent to the registered GAP. Spinach, radish, and oat crops were planted 60 and 90 days after the application (60 and 90-day plant-back intervals (PBI)).

At the 60-day PBI, no quantifiable residues (< 0.01 ppm) of the metabolite were found in any of the edible portions of the harvested commodities.

Based on this information, measurable residues of M3 are not expected in follow crops, when planted in rotation with wheat and barley treated in accordance with the registered GAP.

Soil degradation

The Meeting received soil degradation studies where **^{14}C-phenyl-, ^{14}C-pyrazole- and ^{14}C-oxadiazepine** labelled pinoxaden were each applied to soil and incubated at 20–25 °C in the dark under aerobic conditions. The soil samples were analysed after 181 days (phenyl label) and 100 days (pyrazole and oxadiazepine labels).

The volatiles were identified exclusively as carbon dioxide, demonstrating mineralization which accounted for > 45% of the applied radioactivity.

Pinoxaden was rapidly hydrolysed to M2 followed by oxidation to M3, which was further degraded. The maximum observed concentration of M2 was 88% of the AR (after 1 day), and the maximum observed concentration of M3 was 17% of the AR (between 7 and 30 days).

Under aerobic conditions pinoxaden was degraded rapidly by hydrolysis of the ester bond to M2. M2 was then degraded with a half-life of 2–16 days, forming M3 that was in turn degraded with a half-life of 7–51 days.

The Meeting also received a soil degradation study which investigated the rate of aerobic degradation of **^{14}C-pyrazole ring labelled M3** in three different soils. ^{14}C-labelled M3 was applied at a dose rate equivalent to a single field application rate of 63 g ai/ha (representing the maximum registered seasonal application rate). The soils were incubated under aerobic conditions in the laboratory under dark conditions at 20 °C ± 2 °C for up to 120 days.

Mineralization to carbon dioxide reached comparable levels in all soils with maximum levels ranging from 13-19% of the applied dose by the end of the incubation.

The amount of unchanged M3 extracted from the soil decreased continuously throughout the study in all three soil types, with DT_{50} values between 130 to 220 days. In conclusion, the degradation of pinoxaden in soil maintained under aerobic conditions is rapid with formation of the major degradation products M2 and M3. Neither pinoxaden nor the metabolite M2 are persistent in soil ($DT_{50} \leq 16$ days), however, the metabolite M3 appears to be relatively more persistent ($DT_{50} \leq 220$ days).

Hydrolytic degradation

^{14}C-phenyl-labelled pinoxaden was incubated in diluted aqueous buffer solution at a concentration of 5 mg/L at temperatures of 15 °C (pH 7 and pH 9), 25 °C (pH 5, 7, and 9) under sterile conditions in the dark.

Pinoxaden was relatively stable to hydrolysis at pH 5 and 7 (DT_{50} of 10–23 days) but undergoes rapid hydrolysis at pH 9 (DT_{50} of ≤ 0.6 days), suggesting that hydrolysis is a significant route of degradation and occurs faster at higher pHs. The main hydrolysis degradate was M2 which was stable at all pHs and temperatures tested.

^{14}C-pyrazole labelled M3 was incubated in dilute aqueous buffer solution at a concentration of 5 mg/L under sterile conditions in the dark under the following conditions:at pH 7 at 25 °C (30 days of incubation).

Under neutral conditions (pH 7) M3 hydrolysed with a DT_{50} of 58 days at 25 °C.

Four minor metabolites resulting from the hydrolysis of the metabolite M3 were observed, however, none accounted for >10% of the AR. In summary, hydrolysis is a major degradation route of pinoxaden, with metabolites M2 and M3 being less susceptible to hydrolysis under environmental conditions.

Photolysis

During irradiation at 25 °C, pinoxaden degraded rapidly to M2, with a DT_{50} of 22 days. M2 was further photolytically degraded by the light with a DT_{50} of 8 days. In the dark, pinoxaden was also hydrolytically degraded to M2, with a comparable DT_{50} of 18 days yet M2 was not further degraded in the dark. Therefore, photolysis appears to be a major route of degradation of pinoxaden.

Methods of analysis

Methods have been reported in the scientific literature for the analysis of pinoxaden in food, including multi-residue methods. These methods do not involve a hydrolysis step, therefore, the measured residue is reported as pinoxaden, *per se*.

The wheat metabolism studies demonstrated that pinoxaden was only detected in forage samples harvested soon after application, however, as the plant matured, pinoxaden was rapidly hydrolysed to the major metabolite M2 followed by hydroxylation/oxidation and subsequent conjugation. Therefore, any residues of pinoxaden that may be present in wheat and barley commodities would be converted to M2 and all conjugates of the metabolites M4 and M10 would undergo hydrolysis. Consequently, the methods REM199.02/199.03 and 117-01, which involve extraction with 1N HCl by boiling under reflux for 2 hours, were deemed adequate to quantify residues of M2, M4 (and its conjugates), M6 and M10 (and its conjugates) in wheat and barley supervised trials and processing studies

To validate the extraction efficiency of methods REM 199.02/199.03 and 117-01, samples of grain, straw and husks from the winter wheat metabolism study were extracted by heating under reflux in 1N HCl for 2 hours or by heating under reflux in 1M HCl:acetonitrile (90:10, v:v). The overall extractabilities achieved with the analytical methods REM199.02/199.03 and 117-01 were comparable to those achieved using the procedure in the metabolism study. Therefore, these analytical methods are capable of successfully extracting residues for quantitative analysis.

A QuEChERS method was also developed for the metabolites M4 and M6 in plant commodities, but did not include a hydrolysis step. Therefore, this method was found unsuitable for measuring residues of the conjugated forms of the metabolite M4.

The Meeting also received the description and validation data for an analytical method capable of quantifying residues of the metabolites M4 and M6 in animal commodities.

All residue analytical methods rely on LC-MS/MS. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.02 mg/kg/analyte. Methods were successfully validated by independent laboratories, demonstrating good reproducibility.

Stability of pesticide residues in stored analytical samples

The Meeting received storage stability studies under conditions at -18 °C for pinoxaden and its relevant metabolites M2, M4, M6 and M10 for the duration of the storage of 28 months in wheat whole plant, straw, grain and processed commodities. The Meeting concluded that residues of pinoxaden and M2, M4, M6 and M10 are stable for at least 28 months in cereal commodities.

Freezer storage stability studies on animal matrices demonstrated that residues of M4 and M6 in milk, egg, chicken muscle, and beef liver, when stored frozen at -20 °C or lower, were stable for 90 days.

Definition of the residue

In wheat metabolism studies, the parent compound was rapidly hydrolysed to the metabolite M2 which was subsequently hydroxylated to the major metabolite M4 (≤ 20% of the TRRs in grain and ≤ 37% of the TRR in wheat straw) followed by conjugation (up to 28% of the TRR). Oxidation of the methyl-hydroxy function of M4 also lead to the corresponding carboxylic acid M6 which accounted for up to 14% of the TRRs in grain and less than 10% of the TRRs in straw. Therefore, while pinoxaden may be observed in forage harvested soon after application, there is no expectation of significant pinoxaden residues in mature grain and straw.

The major metabolites M4 (and its conjugates) and M6 in wheat were not identified in rotational crops. Metabolites M3, M10, M11 and the conjugates of M10 were found at (>10% of the TRRs) in all crop commodities at the 15-day, 29-30 day and 120-day plant-back intervals, but at low concentrations. Under field conditions, residues of these metabolites are expected to be low (i.e., <0.01 mg/kg), following uptake from soil.

The free and conjugated forms of the metabolite M4 represent the majority of the residues in primary crops. This is further supported by the results of the wheat and barley crop field trials where residues of free and conjugated M4 in wheat and barley grain accounted for up to 7-fold and 50-fold the residues of the metabolites M6 and M10, respectively. Therefore, the Meeting decided to define the residue for enforcement/monitoring for plant commodities as the free and conjugated forms of the metabolite M4.

Based on toxicity studies reviewed by the Meeting, the metabolite M4 was one of the major metabolites observed in rats. Further to this, toxicity studies on the metabolite M6 showed lower toxicity than pinoxaden. Therefore M6 is not considered relevant for the residue definition for dietary risk assessment. The Meeting decided to define the residue for dietary risk assessment for plant commodities as the free and conjugate metabolite M4.

In the future, should the use of pinoxaden be expanded to any crop other than a cereal crop, the Meeting recommends that additional plant metabolism studies be provided.

The metabolite M4, occurring as a major plant metabolite, was administered to lactating goats in the metabolism study. The predominant component identified in kidney and liver, the only matrices for which there was measurable radioactivity, was the unchanged metabolite M4. A laying hen metabolism study with M4 was not conducted.

In the livestock feeding studies, poultry and dairy cattle were both dosed with M4. While all matrices were analysed for the metabolites M4 and M6, no quantifiable residues of these metabolites were observed in milk, eggs and all tissues collected from animals administered the highest dose tested. Being the major compound observed in metabolism and feeding studies, M4 could be included in the residue definition for enforcement as a marker compound. Since the analytical method is capable of analysing M4, the Meeting agreed to define the residue for enforcement/monitoring and dietary intake for livestock commodities as the metabolite M4.

Neither the goat metabolism study nor the dairy cattle feeding study showed a partition of the metabolite M4 into the fat tissues or milk at any dose level. Similarly in the laying hen metabolism study and the poultry feeding study, the partitioning of the metabolite M4 into the fatty tissues and eggs was not observed. Since this metabolite did not sequester to fatty matrices in animals, the Meeting does not consider the residue fat soluble.

Definition of the residue for compliance with the MRLs and dietary intake for plant commodities: Sum of free and conjugated M4 (SYN 505164; *8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one*), expressed as pinoxaden equivalents.

Definition of the residue for compliance with the MRLs and dietary intake for animal commodities: M4 (SYN 505164; *8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one*), expressed as pinoxaden equivalents.

Results of supervised residue trials on crops

Cereal grains

Results from supervised field trials on wheat and barley conducted in Canada, USA and Europe were provided to the Meeting.

A total of 142 supervised trials were conducted in Canada, the USA, Germany, the Netherlands, United Kingdom, France, Italy, Spain, Switzerland and Greece on wheat (92) and barley (50). The GAP in Canada, the USA and Slovenia for cereal grains allows a single early post-emergence application at growth stages ranging from BBCH 13–39 at a rate of 0.06 kg ai/ha, with a PHI of 60 days for grain (PHI not specified on the Slovenia label). For the 2013 European trials, where grain samples, collected from trials conducted at 0.06 kg ai/ha, were analysed using the QuEChERS method, these residues were not considered in the MRL recommendation as they do not reflect the proposed residue definition for MRL compliance/enforcement.

Residues of total M4 (free and conjugated and expressed as parent equivalents) in wheat grain from 30 Canadian and USA independent trials and 26 European independent trials matching the Canadian and USA critical GAPs were: <0.01 (6), 0.01 (2), 0.02 (4), 0.04 (3), 0.05 (4), 0.06 (2), 0.07 (4), 0.08 (2), 0.10, 0.11 (6), 0.13 (4), 0.14 (2), 0.16 (2), 0.17, 0.18, 0.19, 0.22, 0.23, 0.29 (2), 0.31 (2), 0.35, 0.37, 0.38, 0.50, 0.66 mg/kg (n = 56).

Based on the combined residue data for wheat grain, the Meeting estimated a maximum residue level of 0.7 mg/kg, and an STMR of 0.10 mg/kg.

Residues of total M4 (free and conjugated and expressed as parent equivalents) in barley grain from 21 independent Canadian and USA trials and 17 independent European trials matching the Canadian and USA critical GAPs were: <0.01, 0.02(3), 0.04 (4), 0.05 (4), 0.06, 0.07(4), 0.08(2), 0.10 (4), 0.12, 0.13, 0.14(2), 0.17 (3), 0.18, 0.19 (2), 0.32, 0.34, 0.36, 0.56 (2) mg/kg (n = 38).

Based on the combined residue data for barley grain, the Meeting estimated a maximum residue level of 0.7 mg/kg and an STMR of 0.09 mg/kg.

Animal feed items

Wheat and barley forage, hay and straw

Supervised field trials on wheat forage/whole plant, hay and straw and barley hay and straw were provided to the Meeting.

These trials were conducted in Canada, the USA, Germany, the Netherlands, United Kingdom, France, Italy, Spain, Switzerland and Greece on wheat and barley.

The GAP in Canada for cereal grains allows a single early post-emergence application at growth stages up to BBCH 37 at a rate of 0.06 kg ai/ha, with a grazing interval of 7 days for forage and PHIs of 30 days for hay and 60 days for straw.

In the USA, the GAP allows for a single early post-emergence application at growth stages up to BBCH 39 at a rate of 0.06 kg ai/ha, however, the forage can only be harvested for hay 30 days after application and the PHI for straw is 90 days.

While the GAP in Slovenia is the same as the Canadian and USA GAPs with applications permitted within growth stages BBCH 13-39, no grazing restrictions or PHIs for feed are specified.

Forage and whole plant of wheat

Residues of total M4 (free and conjugated expressed as parent equivalents) in wheat forage from 9 independent Canadian trials and wheat whole plant from 3 independent European trials, matching the Canadian critical GAP were: 0.24, 0.35, 0.40, 0.73, 1.27, 1.33, 1.48, 1.67, 1.94, 2.24, 2.38, 3.54 mg/kg (n = 12).

Based on the combined residue data from Canada and Europe for wheat forage and whole plant, the Meeting estimated a highest residue of 3.54 mg/kg and a median residue of 1.41 mg/kg.

Hay of wheat and barley

Average residues of total M4 (free and conjugated and expressed as parent equivalents) in wheat hay, as received, from 32 independent Canadian and USA trials matching the Canadian and USA critical GAPs were: <0.02(3), 0.04(2), 0.05(3), 0.06, 0.08, 0.11, 0.13 (2), 0.16, 0.19 (2), 0.20, 0.24, 0.26, 0.53, 0.62, 0.66, 0.73, 0.74, 0.82, 0.86 (2), 0.89, 1.22, 1.36, 1.44 mg/kg (n = 32).

Average residues of total M4 (free and conjugated expressed as parent equivalents) in barley hay, as received, from 20 independent Canadian and USA trials matching the Canadian and USA GAPs were: < 0.02, 0.02(3), 0.05(4), 0.11, 0.12, 0.14, 0.16, 0.24, 0.25, 0.29, 0.31(2), 0.48, 0.60, 0.72 mg/kg (n = 20).

Noting that hay of small cereal grains (wheat and barley) are very similar and difficult to distinguish in trade, and, residue populations for wheat and barley hay are not significantly different (Kruskal-Wallis), the Meeting decided to combine the residues (as received): < 0.02(4), 0.02(3), 0.04(2), 0.05(7), 0.06, 0.08, 0.11(2), 0.12, 0.13 (2), 0.14, 0.16(2), 0.19 (2), 0.20, 0.24(2), 0.25, 0.26, 0.29, 0.31(2), 0.48,0.53, 0.60, 0.62, 0.66, 0.72, 0.73, 0.74, 0.82, 0.86 (2), 0.89, 1.22, 1.36, 1.44 mg/kg (n = 52).

Straw of wheat and barley

Residues of total M4 (free and conjugated and expressed as parent equivalents) in wheat straw, as received, from 31 independent Canadian and USA trials and 26 independent European trials matching the Canadian and USA critical GAPs were: < 0.02(2), 0.04, 0.05(4), 0.06(2), 0.07(3), 0.08, 0.11(3), 0.12, 0.13, 0.17(2), 0.18, 0.19 (2), 0.20 (4), 0.24(3), 0.25(2), 0.29, 0.30, 0.32, 0.34(2), 0.35(2), 0.37, 0.38(2), 0.42(3), 0.43, 0.47, 0.62, 0.68, 0.77, 0.83, 0.89, 0.98, 1.08, 1.31 mg/kg (n = 57).

Residues of total M4 (free and conjugated and expressed as parent equivalents) in barley straw, as received, from 22 independent Canadian and USA trials and 18 independent European trials matching the Canadian and USA critical GAPs were: <0.02(3), 0.02, 0.05(5), 0.06, 0.07(4), 0.08,

0.10(5), 0.11, 0.12(6), 0.13, 0.14 (3), 0.17, 0.18, 0.20, 0.23, 0.24, 0.26, 0.29, 0.41, 0.44, 0.64 mg/kg (n = 40).

Similar to hay, noting that straw of small cereal grains (wheat and barley) are very similar and difficult to distinguish in trade, and, residue populations for wheat and barley straw are not significantly different (Kruskal-Wallis), the Meeting decided to combine the residues (as received): <0.02(5), 0.02, 0.04, 0.05(9), 0.06(3), 0.07(7), 0.08(2), 0.10(5), 0.11(4), 0.12(7), 0.13(2), 0.14(3), 0.17(3), 0.18(2), 0.19(2), 0.20(5), 0.23, 0.24(4), 0.25(2), 0.26, 0.29(2), 0.30, 0.32, 0.34(2), 0.35(2), 0.37, 0.38(2), 0.41, 0.42(3), 0.43, 0.44, 0.47, 0.62, 0.64, 0.68, 0.77, 0.83, 0.89, 0.98, 1.08, 1.31 mg/kg (n = 97).

As the residues of M4 (expressed as parent equivalents) were higher in hay (dry weight basis) compared to straw (dry weight basis), the Meeting estimated a maximum residue level for *wheat and barley straw and fodder* of 3 mg/kg (dry weight basis), a highest residue of 1.44 mg/kg and a median residue of 0.16 mg/kg, all based on wheat hay.

Fate of residues during processing

High temperature hydrolysis

No high temperature hydrolysis studies, simulating the degradation of the metabolite M4 during pasteurization, baking, brewing, boiling and sterilization were provided,

Processing

The Meeting received information on the fate of pinoxaden residues and its metabolites M2, M4 and M6 during the processing of wheat and barley grains.

Processing factors calculated for the processed commodities of the cereal grains are shown in the tables below. Processing factors, best estimates and STMR-Ps were calculated for M4.

Wheat

Commodity	Calculated Processing Factor	Best Estimate	STMR-P or median
Aspirated grain fractions	0.10, 0.16	0.13 (mean)	0.01
Unprocessed bran	1.20, 4.73, 4.38	4.38 (median)	0.44
Flour	0.15, 0.16, 0.21	0.16 (median)	0.02
Middlings	0.58, 0.72, 2.75	0.72 (median)	0.07
Shorts	0.93, 1.0	0.96 (mean)	0.10
Germ	0.21, 0.35, 0.58	0.35 (median)	0.04
Low grade meal (toppings)	1.21	1.21	0.12
Wholemeal flour	1.08	1.08	0.11
Wholemeal bread	0.58	0.58	0.06

Barley

Commodity	Calculated Processing Factors	Best Estimate	STMR-P or median
Pearled barley	1.25, 0.85, 0.48	0.48 (median)	0.04
Flour	0.50, 0.42	0.46 (mean)	0.04
Unprocessed bran	2.65, 0.77	1.71 (mean)	0.15
Malt (after drying)	1.20	1.20	0.11
Malt sprouts	0.47	0.47	0.04
Malt (before brewing)	1.17	1.17	0.11
Beer	0.13	0.13	0.01

As the residue concentrations of M4 in all processed commodities are not higher than the estimated maximum residue levels for wheat and barley grain, separate maximum residue levels will not be estimated for any of the cereal grain processed commodities.

Residues in animal commodities

Farm animal feeding studies

The Meeting received information on the residue levels arising in tissues and milk when three groups of dairy cows were fed with a diet containing 1.11, 3.01, and 10.12 mg of M4/kg feed for 29–30 consecutive days.

In milk, liver, kidney, muscle and fat, no quantifiable (<LOQ) residues of M4 or M6 were observed in the 10× treatment group. Hence, samples from the low and mid dose experiments were not analysed.

The Meeting also received information on the residue levels arising in tissues and eggs when groups of laying hens were fed with a diet containing M4 at rates of 0.5 mg/kg feed, 1.5 mg/kg feed and 5.0 mg/kg feed per day for 28 consecutive days.

In eggs, muscle, liver, and fat, no quantifiable (<LOQ) residues of M4 or M6 were detected in the 10x treatment group. Because of this, no samples from the low and mid doses were analysed.

Estimated dietary burdens of farm animals

Maximum and mean dietary burden calculations for pinoxaden are based on the feed items evaluated for cattle and poultry as presented in Annex 6. The calculations were made according to the livestock diets from Australia, the EU, Japan and US-Canada in the OECD feeding table.

The foliar application of pinoxaden to wheat and barley resulted in residues in the following feed items: wheat forage/whole plant, wheat and barley hay, straw and grain (including aspirated grain fractions, bran, meal and milled by-products). Based on the named feed items, the calculated maximum animal dietary burden for dairy or beef cattle was in Australia, followed by EU and US-Canada. For poultry broiler or layer, the calculated maximum dietary burden was in EU, followed by US-Canada and Australia.

	Livestock dietary burden, M4 (expressed as parent equivalents), ppm of dry matter							
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0.49	0.28	3.2	1.3	14.2	5.6	0.32	0.32
Dairy cattle	2.8	1.1	2.8	1.1	8.5	3.4	0	0
Poultry - broiler	0.25	0.25	0.10	0.10	0.10	0.10	0.02	0.02
Poultry-layer	0	0	1.4[A]	0.56[B]	0	0	0	0

[A] Suitable for MRL estimates for eggs, meat, fat and edible offal of poultry

[B] Suitable for STMR estimates for eggs, meat, fat and edible offal of poultry

Animal commodities maximum residue level estimation

As the feeding levels from the dairy cattle feeding study did not address the maximum dietary burdens for cattle in Australia, the Meeting could not estimate MRLs for M4 (expressed in parent equivalents) for milk, meat from mammals, mammalian fat and edible offal (mammalian).

As there were no quantifiable residues of M4 detected in eggs, muscle, liver and fat collected from laying hens dosed 5 mg M4/kg feed (ca. 3-fold the maximum dietary burden in poultry (layer)), the Meeting estimated maximum residue levels of M4, expressed as parent equivalents, of 0.02* mg/kg for eggs and 0.02* mg/kg for edible offal, meat and fats of poultry. The HRs and STMRs for eggs, edible offal, meat and fat were each 0.02 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IESTI and IEDI assessments.

Definition of the residue for compliance with the MRLs and dietary intake for plant commodities: Sum of free and conjugated M4 (SYN 505164; *8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one*), expressed as pinoxaden.

Definition of the residue for compliance with the MRLs and dietary intake for animal commodities: M4 (SYN 505164; *8-(2,6-Diethyl-4-hydroxymethyl-phenyl)-9-hydroxy-1,2,4,5-tetrahydro-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-one*), expressed as pinoxaden.

The residue is not fat soluble.

	Commodity	MRL, mg/kg	HR, HR-P	STMR, STMR-P
CCN	Name	Proposed	Mg/kg	mg/kg
GC 0640	Barley	0.7		0.09
GC 0654	Wheat	0.7		0.10
AS 0640	Barley straw and fodder, dry	3 (dry weight)	1.44 (as received)	0.16 (as received)
AS 0654	Wheat straw and fodder, dry	3 (dry weight)	1.44 (as received)	0.16 (as received)
PM 0110	Poultry meat	0.02*		0.02
PF 037	Poultry fats	0.02*		0.02
PO 038	Poultry, edible offal of	0.02*		0.02
PE 039	Eggs	0.02*		0.02

For calculating animal dietary burden

	Commodity	STMR, STMR-P	HR
CCN	Name	mg/kg	mg/kg
	Wheat forage	1.41	3.54
	Barley unprocessed bran	0.15	
	Wheat aspirated grain fractions	0.01	
	Wheat milled byproducts (unprocessed bran)	0.44	
	Low grade meal (toppings)	0.12	

For calculating dietary intake

	Commodity	STMR, STMR-P
CCN	Name	mg/kg
	Pearled barley	0.04
	Barley flour	0.04
	Malt (after drying)	0.11
	Malt sprouts	0.04
	Malt (before brewing)	0.11
	Beer	0.01
CM 0654	Wheat bran (unprocessed)	0.44
CF 1211	Wheat flour	0.02
CF 1210	Wheat germ	0.04
CF 1212	Wholemeal flour	0.11
CP 1212	Wholemeal bread	0.06

DIETARY RISK ASSESSMENT

Long-term dietary exposure

The International Estimated Dietary Intakes (IEDIs) of pinoxaden were calculated for the 17 GEMS/Food cluster diets using STMRs and STMR-Ps estimated by the current Meeting (Annex 3 to

the 2016 Report). The ADI is 0–0.1 mg/kg bw and the calculated IEDIs were 0–1% of the maximum ADI. The Meeting concluded that the long-term exposure to residues of pinoxaden resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term dietary exposure

The ARfD for pinoxaden is 0.3 mg/kg bw. The International Estimate of Short Term Intake (IESTI) for pinoxaden were calculated for the food commodities for which STMRs or HRs were estimated by the present Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2016 JMPR Report. The IESTIs were 1% of the ARfD for the general population including children. The Meeting concluded that the short-term dietary exposure to residues of pinoxaden, from the uses that have been considered by the present Meeting, is unlikely to present a public health concern.

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