Australian Pesticides &
Veterinary Medicines Authority

The reconsideration of approvals of selected sheep ectoparasiticide products and their associated label

Preliminary Review Findings

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CHAPTER 1 - DIAZINON

1.1 INTRODUCTION

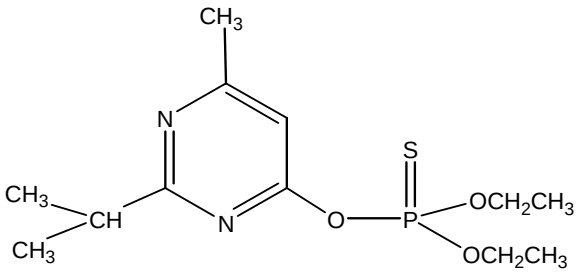
Eighteen diazinon products were nominated for review in accordance with the APVMA Gazette of 7 September. This review is applicable only to those products currently registered for use as ectoparasiticides in long wool sheep (>6 weeks wool growth). It based on data provided by Novartis and Schering-Plough Pty Ltd, as well as published and previously assessed data.

Diazinon is an organophorphorus insecticide with widespread uses. Its major use is for the control of lice, blowflies, ked, ticks in sheep, cattle, goats and dogs etc. Diazinon is specifically under review in the APVMA's Chemicals Review Program and a draft environmental assessment report is available on the Internet (APVMA, 2003).

This report will focus on the wool scouring effects as a result of the veterinary uses on sheep.

1.2 CHEMICAL IDENTITY

Chemical name:	O,O-Diethyl O-(2-isopropyl-6-methylpyrimidine-4-yl) phosphorothioate [CAS]
Common name:	Diazinon
Manufacturer's code:	GS 24480
CAS Registry number:	333-41-5
Molecular formula:	$C_{12}H_{21}N_2O_3PS$
Structural formula:	



Molecular weight: 304.3

1.3 PHYSICO-CHEMICAL PROPERTIES

The following physico-chemical properties refer to the pure active constituent unless otherwise stated. The technical grade material is >90.2% pure.

Appearance:	Colourless liquid. The active constituent is a clear yellow to brown liquid.
Odour:	Not specific
Boiling Point:	83-84 ˚C @ 0.002 mm Hg
Specific Gravity/Density	Active constituent approximately 1.11 @ 20 ˚C
Vapour Pressure:	4.7×10^{-3} Pa @ 20 ˚C
Solubility in Water	40 mg/L @ 20 ˚C
Octanol-Water Coefficient.	Log $P_{ow} = 3.95$
Henry's Constant	3.53×10^{-7} atm.m^3/mol
Dissociation Constant:	Given as Ka = 230 ± 0.05.

1.4 ENVIRONMENTAL EXPOSURE

1.4.1 Volume

As indicated in the most recent AWI survey (see Section 1.6.1), use of diazinon as a sheep ectoparasiticide is very widespread, with over 50% of wool in the survey having detectable residues.

1.4.2 Application and Use Pattern

Veterinary usage is the major use, with most use for control of lice, ked and blowfly on sheep by dipping or jetting. The approved label rates for dips, jetting and hand spraying are shown in Table 1.1. Note that some products are used in combination with other active constituents.

Table 1.1: The maximum application rates for the registered diazinon products used as ectoparasiticides on sheep. Products used for plunge and conventional shower dips have additional instructions for replenishment (topping up) and reinforcement (dipping out).

Product	Pests	Routes of Administration	Application rates
Coopers 4-in-1 Dip	Lice, ked itch mite and blowfly	Plunge and shower dip (short wool only)*	150 g ai/1000 L
Cooper Di-Jet Sheep Dip/Jetting Fluid, Cattle and Pig Spray	Lice and ked	Plunge and shower dip	100 & 200 g ai/1000 L
	Blowfly	Plunge and shower dip Jetting	200 g ai/1000 L Unclear**
Di-shield Sheep and Jetting Fluid	Lice and ked	Plunge and shower dip	100 & 200 g ai/1000 L
	Blowfly	Plunge and shower dip Jetting	200 g ai/1000 L 400 g ai/1000 L
Virbac Jetdip Sheep Dip Jetting Fluid And Blowfly Dressing	Lice, ked, itchmite and blowfly	Plunge and shower dip Jetting	200 g ai/1000 L 400 g ai/1000 L
WSD Diazinon for Sheep, Cattle, Goats and Pigs	Lice and ked	Plunge and shower dip	100 g ai/1000 L
	Blowfly	Plunge, mobile plunge and shower dip	200 g ai/1000 L
		Jetting	400 g ai/1000 L
Topclip Blue Shield Sheep Dip, Jetting Fluid and Blowfly Dressing	Lice and Ked	Plunge and shower dip	100 g ai/1000 L
	Blowfly	Plunge and shower dip	200 g ai/1000 L
		Jetting	400 g ai/1000 L

* No mention of jetting or instructions on label

** No dilution instructions on label which indicates "jet along backline from poll to rump with a strip 18-20 cm wide, taking care to wet the wool to the skin".

Based on the registered use patterns in Table 1.1, it is apparent that the maximum application rate is 400 g ai/1000 L by jetting for the treatment of blowfly strike on sheep with a wool withholding period (WWP) of not less than 2 months.

1.5 ENVIRONMENTAL CHEMISTRY AND FATE

1.5.1 Residue depletion studies in wool

1.5.1.1 Modelling of depletion rates

A model has been devised based on the results of the experimental application of organophosphates, synthetic pyrethroids and insect growth regulators on sheep at the recommended dose rates (Campbell et al. 1998). The model relates the decomposition of the chemicals to the chemicals used, the method of application and the length of the wool at the time of treatment. The results indicate that organophosphates break down very quickly when applied to the surface of the wool (initial half-life of 9-12 days), but

the rate of breakdown gradually slows as the proportion of pesticides near the surface of the wool decreases. When the pesticide is applied deep into the wool by hand jetting or dipping, the rate of breakdown is slower (average half-life of 27-42 days). The results for the breakdown of diazinon in wool, based on the available data, are shown in Table 1.2.

Table 1.2: The rate of breakdown and final concentration of diazinon on wool estimated by the Campbell et al (1998) model from the various routes of administration

Method of application	**Wool growth (months)**	**Chemical applied per sheep (g)**	**Average half-life (days)[a]**	**Range of half-lives (days)**	**Mean final concentration (mg/kg)[b]**	**Range of concentration (mg/kg)**
Plunge dip	4	2.8	37	34-41	5.8	3.7-9.1
Hand jet	4	1.23	29	27-33	0.6	0.3-1.0
Hand jet	6	1.08	37	33-41	6.9	4.6-10
Hand jet	9	1.76	43	37-52	79	62-102
Hand jet	8	1.28	41	34-54	31	19-49
Jetting race	8	1.68	28	22-40	5.4	2.2-14
Harrington AJR[c]	8	0.64	18	15-23	0.4	0.1-1.2

a denotes average half-life over the entire period based on the estimated amount applied, estimated amount at 12 months after shearing and the total time
b denotes final concentration on wool 12 months after the previous shearing estimated by the model
c Automatic Jetting Race

The model allows for different breakdown rates due to the method of application, the length of wool and the changes in the rate of breakdown between application and shearing. The model can be used to estimate the expected residues on wool at any time after a specified treatment provided the amount of the chemical applied is known. The results indicate that the highest residue was observed in sheep with 9 month's wool growth treated by hand jetting.

1.5.1.2 Fleece Residues Trial for Long Wool Sheep

Information on diazinon residues resulting from application to sheep with long wool is available from a study by Burman *et al* (1997). Two groups (each n = 10 animals) were jetted with *Topclip Blue Shield* (Ciba Geigy) at 200 mg/L diazinon at nine or ten months from shearing. An untreated control group of ten animals was used to monitor wool growth rates. Wool samples were taken from a 5 cm circumferential strip around each of five sheep in each group. Samples were taken on days 7, 30, 60 and 90 after treatment for 9 months wool growth, and on days 7, 30 and 60 after treatment for 10 months wool growth. The final sampling occurred when the sheep had 12 months wool growth and was equivalent to the next shearing. The mean values for diazinon residues (mg/kg) are listed in the Table 1.3 below.

Table 1.3: Mean diazinon concentration (mg/kg) on wool at sampling points of 7, 30, 60 and 90 days after treatment for 9 or 10 months wool growth

Days post treatment	9 months wool growth	10 months wool growth
	Mean diazinon concentration mg/kg (range of values)	Mean diazinon concentration mg/kg (range of values)
7	128 (80-175)	83 (45-120)
30	50 (40-60)	70 (45-95)
60	52 (30-75)	63 (40-85)
90	30 (10-50)	-

The results indicate that diazinon concentrations on long wool degrade slowly over time. This is largely due to the dilution effect caused by the wool growth with time and the protection of the residues from sunlight in long wool. It is noted that the dose rate of 200 mg/L is only half of the current maximum dose rate of 400 mg/L for the product *Topclip Blue Shield*. It appears that under the current use pattern, the diazinon concentration in greasy wool would be at least 63 mg/kg for treatment with 10 month's wool growth at the current WWP of not less than 60 days.

It is impossible to accurately calculate a half-life value from these data as the diazinon concentration immediately after treatment was not recorded. However, the registrant has presented an estimate of the half-life for diazinon by manipulating the results for individual sheep. The results are shown in Table 1.4.

Table 1.4: Half-lives of depletion of diazinon on sheep treated at 9 or 10 months wool growth

Treatment	Sheep No.	Half-life (days)
Sheep treated at 9 months wool growth and wool sampled on days 7, 30, 60 and 90 after treatment	0107 0129 0142 0147 0166	111 35 27 61 57
	Mean	58
Sheep treated at 10 months wool growth and wool sampled on days 7, 30 and 60 after treatment	0141 0152 0158 0164 0175	47 75 40 no degradation no degradation
	Mean	>54

The registrant did not provide the details of the calculation of the half-lives under the trial conditions. It appears that the half-lives of degradation are significantly different between the treatments at 9 or 10 months wool growth as no degradation occurred in two of the five sheep with 10 months wool growth. However, the limited samples points (7, 30 and 60) used for the half-life calculation for treatment at 10 months wool growth may incur significant error. It is noted that for sheep No. 0107, the half-life of 111 days is significantly different from those of other animals treated at 9 months wool growth. The half-lives are also longer than those calculated by Campbell et al (1998, see Table 1.2). However, the diazinon concentrations measured in this experiment

were in turn lower than those reported in Savage (1998) from two experiments conducted in Victoria where band sampling was also used (see Table 1.5).

The Victorian experiments involved the application of 1.3 g of diazinon to sheep by hand jetting to sheep with nine months wool in the first year and six months wool in the second year. In the experiment conducted by Burman *et al* (1997) 0.9 g of diazinon was contained in the volume of jetting fluid applied and 0.3 g was assumed to be retained in the wool. However, some stripping is likely to have occurred but without measurements of the jetting fluid draining from the sheep it is impossible to estimate the degree of stripping or the concentration of diazinon in the fleece immediately after application.

Table 1.5: Comparison of the diazinon concentrations in long wool sheep from the Victorian experiments (Savage 1998) and Burman (1997)

Year 1 Victoria (Savage, 1998)		Year 2 Victoria (Savage, 1998)		Burman (1997)	
Weeks from application	**Diazinon concentration mg/kg**	**Weeks from application**	**Diazinon concentration mg/kg**	**Weeks from application**	**Diazinon concentration mgkg**
1	-	1	-	1	128
2	251	2	-	2	-
4	162	4	181	4	50
8	148	8	-	8	52
9	-	9	95	9	-
12	112	12	-	12	31
17	-	17	53	17	-
26	-	26	8	26	-

Although the intervals between treatment and sampling sometimes varied between experiments it can be seen from Table 1.5 that residue levels in the wool measured by Burman *et al* were much lower than those recorded in the Victorian experiments. For example, in the Victorian experiments the concentrations of diazinon were 148 and 95 mg/kg at eight and nine weeks after treatment respectively in comparison to a concentration of 52 mg/kg after eight weeks measured by Burman *et al* (1997). At twelve weeks from treatment the difference is greater with a concentration of 112 mg/kg found in the Victorian experiment in year one and 31 mg/kg found by Burman *et al*. This has resulted from the use of diazinon at 200 mg/L (a minor use permit rate for lice control) in comparison to the full label rate of 400 mg/L.

1.5.1.3 Fleece Residue Trial (AVCARE 1994)

One hundred merino wethers were used in this trial. The sheep had been previously dipped in diazinon. At the trial site the sheep were drenched for nematode parasites (ivermectin) and liver fluke (triclabendazole) at the recommended dose rates. After one month of grazing to allow adjustment to the trial site, the sheep were grouped into 10 groups of 10 animals. Each group was treated with a different active constituent except for one group that was used as the untreated control. All sheep for plunge dipping were shorn on the same day and were dipped 6 weeks after shearing. The sheep for jetting were treated at 9 months' wool growth.

The sheep were treated with the registered product *Topclip Blue Shield Dip, Jetting Fluid and Blowfly Dressing* at the registered label dose rates of 100 mg/L and 400 mg/L for dipping and jetting, respectively. Approximately 5 L of fluid per sheep was

administered by jetting along the backline and around the crutch. Plunge dipping was done in a 2200 L concrete-lined in-ground sump. Data were obtained from 5 sheep per group. Wool samples were taken from the flank and backline of the untreated controls, and of the treated sheep on 1, 6, 12, 26 and 42 weeks after dipping and on 1, 6 and 12 weeks after jetting. Wool samples were stored at –15°C prior to analysis by HPLC. The results are shown in Tables 1.6 and 1.7.

Table 1.6: Diazinon residues in wool (mg/kg greasy wool) from sheep with 6 weeks wool growth dipped with the registered product *Topclip Blue Shield* at the label dose rate of 100 mg/L

Weeks post-treatment	**Diazinon residues in wool (mg/kg wool)**		**Mean diazinon residues in wool ± SD (mg/kg wool)**	
	Backline	**Flank**	**Backline**	**Flank**
1	494, 586, 308, 320, 731	943, 1052, 312, 793, 965	488 ± 180	813 ± 295
6	69, 18.7, 37, 19.6, 10.1	58, 86, 65, 67, 121	31 ± 23	79 ± 26
12	3.2, 2.5, 5.0, 1.8, 1.8	15.1, 15.1, 147, 6.5, 18.7	2.8 ± 1.3	41 ± 60
26	0.60, 2.5, 0.35, 1.53, 0.49	2.00, 0.78, 0.76, 1.27, 1.76	1.1 ± 0.9	1.3 ± 0.6
46	0.43, 0.52, 0.17, 2.30, 0.94	0.36, 0.60, 0.70, 13.90, 22.10	14.0 ± 1.9	15 ± 3.5

Limit of detection = 2 mg/kg for weeks 1, 6 and 12, and 0.1 mg/kg for weeks 26 and 46
ND – Non-detectable level
Diazinon residues in wool of untreated controls were at non-detectable level

Table 1.7: Diazinon residues in wool (mg/kg) from sheep with 9 months wool growth jetted with the product *Topclip* at the maximum label dose rate of 400 mg/L

Weeks post-treatment	**Diazinon residues in wool (mg/kg wool)**		**Mean diazinon residues in wool ± SD (mg/kg wool)**	
	Backline	Flank	Backline	Flank
1	964, 1316, 1236, 1330, 787	20, 70, 50, 136, 24	1126 ± 240	60 ± 47
6	122, 286, 434, 181, 331	10.0, 11.7, 15.0, 16.9, 26	271 ± 123	16 ± 6
12	107, 210, 218, 66, 81	11.9, 13.1, 7.9, 3.6, 14.9	136 ± 72	10 ± 5

Limit of detection = 2 mg/kg
ND – Non-detectable level
Note that mean diazinon residues in backline and flank of untreated controls were 4.7 and 4.2 mg/kg, respectively. This probably reflects the residual from the previous diazinon dipping treatment. Levels are low compared with the combined 1 week post treatment levels.

The data indicate that the concentration of diazinon in wool decreased with increasing wool withholding periods (WWP) for both long and short wool treatments. Diazinon residues in backline samples were higher in the long wool treatment than the short wool treatment at the corresponding sampling points, reflecting the difference in the backline treatment and the amount added. This may be further accounted for by the fact that the active constituent was presumably protected from photolysis by the long wool. For the short wool treatment by dipping, the diazinon residues were higher in the flank than the backline. This could be due to more backline areas being exposed to photolysis for short wool treatment. Conversely, higher diazinon residues were

observed in the backline area than flank area for the long wool treatment by jetting. It is likely that residues were retained more readily in the backline by long wool but little ran off to the flank.

1.5.1.4 Conclusions

Depletion studies of residues in wool were performed on sheep with varying length of wool growth. The results indicate the rate of degradation appears to decrease with increased wool length. This suggests that the degradation of diazinon is more rapid in the early season than that of the later season accounting for the fact that diazinon is protected from photolysis by the long wool.

1.5 2 Environmental fate

The following is an editing of the summaries in the Environmental Assessment Section of the draft Chemical Review report for diazinon (APVMA, 2003), focussing on the information relevant to the degradation and mobility of diazinon used as a sheep ectoparasiticide.

1.5.2.1 Abiotic degradation

Hydrolysis of diazinon is relatively slow at pH 7 and 9, but is faster at pH 5. Hydrolysis could be a significant contributor to the overall degradation of diazinon in the environment under acidic conditions.

Laboratory studies using artificial sunlight lamps indicate photodegradation in water is possible but that degradation in natural sunlight is slower. The half-lives for the former ranged from 55.9 to 122 hours, while that of the latter was 49 days. 6-hydroxy-2-isopropyl-4-methylpyrimidine is the major metabolite. Direct aquatic photodegradation of diazinon is unlikely under environmental conditions.

In soil photolysis studies using natural sunlight, the half-life of diazinon was calculated to be between 17.5 and 37.4 hours, with the same major metabolite as above. In studies using artificial light, the half-lives were determined as 55 hours and 5.5 days. Photodegradation in soil could be a route of environmental degradation in Australia, given the high light levels during summer.

1.5.2.2 Soil/water degradation

The degradation in soil of diazinon under aerobic conditions is moderate to fast, with a half-life of 4.5 to 8 days at 20°C in the most reliable study under a range of temperature and soil moisture conditions. In other studies the half-life ranged between 11 to 59 days in 4 different soils. As above, the initial product is 6-hydroxy-2-isopropyl-4-methylpyrimidine, which is then slowly degraded and mineralised to carbon dioxide.

From a review of literature studies on the degradation of diazinon in soil, the time for 50% degradation is between 2 and 4 weeks. This is dependent on temperature, moisture and pH value. However, in a fen soil (17% om) the DT50 is given as 5 weeks and after 7 months there was still 10% remaining.

The degradation of diazinon in aerobic aqueous conditions is relatively fast, with a half-life of between 7-15 days in natural river and pond water/soil systems. Diazinon largely stays in the water column. The degradation pathway appears to be hydrolysis followed by mineralisation of the hydrolysis product. In an older study, the concentration of diazinon in water and pond sediment decreased from the initial 32 mg/L to 0.8 mg/L after 9 days, representing 93% degradation.

In a literature study, the degradation of diazinon in three flooded clay soils was studied using both non-sterile and sterile soil/water systems. The results show that diazinon disappeared with half-lives between 8.8-17.4 days for non-sterile systems.

While diazinon will largely stay in the water column, it may be concluded that any diazinon in sludge from scours disposed of to land will not be persistent. Similarly diazinon released to waters in sewage effluent will not persist.

1.5.2.3 Mobility

Batch equilibrium studies of diazinon in six soils show that diazinon is moderately absorbed with K_{oc} values ranging from 255 to 496. In a literature report on the mobility of diazinon in 25 different soils, the K_{oc} values ranged from 207 to 4222 with an average of 496. The K_{oc} values were highly correlated with organic matter of the soils with significant correlations with silt and clay for soils with organic matter <2%.

In soil column leaching studies using eight different soils, there was no leaching of diazinon but the metabolites were detected in the leachate. In 3 aged soil leaching studies with 6 soils, it was shown that the metabolites from soil degradation are more mobile than diazinon itself, in particular the hydrolysis product, and these could leach.

The level of volatilisation of diazinon recorded from two loam soils (48 ng/cm^2/hr) indicates volatility from soil is low. The volatility from plants indicated the radioactivity lost over 24 hours was 9% of the applied. Volatilisation of diazinon from soils is not expected to be a significant route for its dissipation from soil.

1.5.2.4 Field Dissipation Studies

Ten bare soil studies involving a single treatment were available, with German soils classified as silt loams and US soils as loamy sands or sandy soils. The results clearly show that even under conditions conducive to leaching, the movement of diazinon was minimal. The major metabolite did show some leaching but significant contamination of ground water would not be expected. The half-life of diazinon ranged from 4-16 days, with one at 27 days, and for the principal metabolite between 7-24 days in the upper 15 cm of 5 soils.

Six field crop studies were performed as above, except that between 4-7 multiple applications were made. The study sites were largely the same as those used for the bare soil studies and the results and conclusions were similar. The first half-life of diazinon was between 2.8 to 13 days and for the principal metabolite between 8 to 24 days in the top 15 cm of 4 soils.

The results confirm laboratory indications that diazinon will not persist or leach in soils.

1.5.2.5 Run-off Monitoring Studies

Three agricultural run-off and pond monitoring studies, undertaken in three different apple orchards in the USA, were performed as special studies. The orchards were treated 6 times with diazinon under normal commercial practice. At each site there was a pond beside the orchards that received run-off from the orchards.

The data showed that run-off from treated areas could cause relatively high concentrations in ponds, and that the highest levels occurred immediately after application. The maximum concentration in ponds due to run-off only was 5.6 μg/L, which occurred some 14 days after the last application followed by heavy rain. The half-lives determined in these ponds under environmental conditions mainly in the USA summer ranged from 2.2 days to 19.7 days and corresponds closely with that in the aquatic metabolism study of 7 to 15 days. Levels in sediment were low.

1.5.2.6 Bioaccumulation

From a fish bioaccumulation study, the steady state bioaccumulation factors were determined to be low, with the highest being 540X for non-edible tissues. Elimination of diazinon from these tissues was rapid, with a half-life of between 1 and 3 days, indicative of rapid depuration.

A bio-concentration study using aged soil metabolites was performed. A sandy loam soil was dosed with diazinon and then aerobically aged for 14 days, then covered with water and the system equilibrated for 3 days before channel catfish were introduced into the system. The bioaccumulation phase lasted for 28 days before the fish were placed into clean flowing water for 14 days. The study showed that there is unlikely to be bioaccumulation of diazinon or the metabolites, confirming the above.

1.6 ENVIRONMENTAL TOXICOLOGY

Again the following is an editing of the summaries in the Environmental Assessment Section of the draft Chemical Review report for diazinon (APVMA, 2003), which focusses on the information relevant to the toxicity of diazinon used as a sheep ectoparasiticide.

1.6.1 Aquatic

The toxicity to aquatic organisms, especially invertebrates, is very high. The acute toxicity to fish from submitted studies (9 species) ranges from an LD50 of 2.16 mg/L for common carp to 23.4 mg/L for crucian carp. Life cycle studies have not been performed but the maximum acceptable tolerated dose (MATC) to embryonic and larval life stages of the fathead minnow was determined to be between 0.092 and 0.17 mg/L. Early life stages are normally considered to be the most sensitive. In a database of regulatory-type studies that have been reviewed by US EPA[1], the toxicity to fish of

[1] The database is maintained by the Ecological Fate and Effects Division of the Office of Pesticide Programs database, US EPA. Contact: Brian Montague, U. S. Environmental Protection Agency (7507C), Ariel Rios Building, 1200 Pennsylvania Ave., N.W., Washington, D.C.,20460. Phone:703-305-6438 FAX:703-305-6309 EMAIL Address: Montague.Brian@epa.gov.

diazinon ranged from an LC50 of 0.09 mg/L for rainbow trout to an LC50 of 7.8 mg/L for fathead minnow.

Diazinon is extremely toxic to invertebrates, which is typical for an organophosphate, with acute toxicity figures (EC50) for *Ceriodaphnia* of between 0.36-0.6 µg/L and for the mysid shrimp, normally a very sensitive test species, the EC50 = 4.2 µg/L. The MATC for chronic toxicity to daphnia was found to be between 0.17 and 0.32 µg/L. The US EPA database on reviewed regulatory studies (see footnote 3) gives the most sensitive species as the scud, with an EC50 = 0.2 µg/L, and least sensitive invertebrate as the grass shrimp, EC50 = 28 µg/L. The acute EC50 for *Daphnia magna* (three studies) in this database ranged from 0.96 to 1.1 µg/L.

Diazinon is moderately toxic to green algae, with EC50s of 8.5 and 6.4 mg/L for two species of *Scenedesmus*.

1.6.2 Mesocosms

In a detailed long term study, diazinon was applied to several mesocosms at several treatment rates. The maximum average concentrations of diazinon, which mainly occurred immediately after the sixth (last) application, were 2.3 µg/L for level 1, 4.3 µg/L for level 2, 9.2 µg/L for level 3, 15.7 µg/L for level 4 and 29.7 µg/L for level 5. In treatment levels 4 and 5, one pond (replicate) showed consistently lower concentrations and more rapid degradation than the other two ponds. Also, the half-life of diazinon decreased with increasing number of applications, and ranged from 10-26 days after the first application to 5.5-8.5 days after the sixth application, suggesting acclimatisation of the microbial species present.

There were no detrimental effects on fish or plants at any treatment except for diatoms and green algae. Diatoms were significantly affected at the highest treatment with occasional reductions at lower levels, but green algae were affected only occasionally.

Invertebrates were significantly affected by diazinon. For zooplankton, Cladocerans were the most sensitive taxon (with a significant reduction at all levels), followed by rotifers and Copepods. For higher macroinvertebrates, Trichoptera were the most sensitive order and were reduced at all treatments, with Diptera and Ephemeroptera intermediate and gastropods essentially unaffected. All organisms had recovered by the end of the study period, with Cladocerans taking the longest, up to 4 months.

It is concluded that while diazinon can significantly affect aquatic organisms at relatively low concentrations, especially invertebrates, affected organisms are likely to recover and there is unlikely to be significant long term effects on populations, provided organisms are given adequate time to recover.

The toxicity data is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable).

1.6.3 Non-Target Invertebrates

The LD50 for diazinon toxicity of to earthworms was calculated as 130 mg/kg of soil. The toxicity of diazinon to earthworms has been tested under semi-field conditions at 4 and 20 mg/kg, corresponding to 4 and 20 kg ai/ha for soil 7.5 cm deep. There was a maximum of 20% mortalities at the highest level, indicating that there is unlikely to be significant mortalities of earthworms at normal levels resulting from spreading on land.

1.6.4 Micro-organisms

Diazinon has limited effects on micro-organisms. In tests using two different soil types, there was minimal effect on soil respiration and nitrification at 16 and 80 mg/kg soil, corresponding to 12 and 60 kg ai/ha. Literature reports give the EC50 as 10.3 mg/L to bacteria used in the Microtox system. There were only limited effects on respiration of sewage micro-organisms at 100 mg/L.

1.6.5 Phytotoxicity

There was greater than 25% effect on the vegetative growth of tomato, cucumber, onion, lettuce and carrot seedlings when these were oversprayed at 11.2 kg/ha. There were some relatively minor effects on seedling germination and emergence when tested at the highest rate used in the US. At rates likely to be contained in sewage sludge spread on land in Australia, effects on non-target plants are expected to be minimal.

1.6.6 End Point used in Hazard Assessment

From the US EPA ecotoxicological database, the most sensitive aquatic species is considered to be the scud with an EC50 of 0.2 μg/L. As this is a core result (see footnote 4), this will be used as the environmental end-point for the hazard calculations arising from the scouring effluent. Due to the extent of the data, an assessment factor of 10 will be used, resulting in a PNEC of 20 ng/L.

1.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

Aquatic exposure may be high to organisms exposed to wool scouring effluents that may contain residues washed from treated fleece. The discharge of the effluent containing chemical residues may have an adverse effect on the aquatic organisms, which would be the major environmental concern.

1.7.1 Residue Levels in the Australian Wool Clip

Diazinon represents a significant contaminant of the Australian wool clip. Monitoring data in 1997-1998 found a mean concentration of 5.4 mg/kg wool (Savage, 1998). In 1997-1998, 76% of the national flock was treated with diazinon, which represented most of the organophosphate (OP) residue in the clip of 5.8 mg/kg in the wool. Total OP residues from 1992 to 1998 ranged from 10.4 to 4.3 mg/kg. For the last two years of this period, OP residues were steadily declining, consistent with the declining use of OPs for long-wool jetting to control flies due to both fly resistance and OH&S concerns.

The mean total concentration of OP residues on Australian fleece wool for the year 2000-1 was 1.51 mg/kg greasy wool (I Russell, pers comm) based on the AWI wool residue survey. Of the samples that contained diazinon, the average concentration was

2.6 mg/kg and the maximum concentration was 56 mg/kg. These samples contained 87.6% of the total mass of OPs on the clip.

The declining trend was confirmed in the 2001-2002 results (S Williams AWI, personal communication) where the mean residue was 1.3 mg/kg. For 2002-2003 and 2003-2004 (I Russell, 2004) the mean residue of diazinon on all wool was 1.2 and 1.0 mg/kg, respectively. In the latest survey 33.7% of samples had residues above the Limit of Resolution (LoR), the mean residue when treated was 2.7 mg/kg, with the highest residue found being 65 mg/kg.

As it is the most recent survey, the 2003-2004 mean residue in all wool value of 1.0 mg/kg will be used in the hazard calculations below. For comparison, the mean residue when treated value of 2.7 mg/kg will also be used, covering a potential "hot spot". For a processing lot to contain that level of residue it would have to result from an area of grazing country where most farmers use diazinon and the wool grown is such that little if any mixing occurs prior to processing. Given that over 1/3 of sheep still appear to be treated with diazinon, the probability of this is occurring is relatively high.

1.7.2 Australian Model

The Australian model (Savage 1998) has been used by the Department of the Environment and Heritage (DEH) to predict the worst case level of diazinon present in sewage effluent entering the Barwon waters from the Black Rock treatment plant. The results of the calculation performed take into consideration the following parameters as shown in Table 1.8.

Table 1.8: Determination of Q values by DEH using 2003-2004 wool clip survey results

Parameter	Mean residue in clip	Mean residue when treated
Concentration of diazinon in wool at harvest (mg/kg)	1.0	2.7
Mass of wool scoured in one day (tonnes)	50	50
Mass of diazinon entering scouring plant on wool (g)	50	135
Percentage remaining on scoured wool (%)	4	4
Percentage removed with grease during scouring (%)	30	30
Percentage removed during sewage treatment (%)	50	50
Mass of diazinon discharged (g)	16.8	45.36
Flow rate of sewage treatment plant (ML/d)	50	50
Predicted concentration in sewage outflow (ng/L)	336	907.2
Dilution in plume#	0.02	0.02
Predicted environmental concentration (PEC) (ng/L)	**6.72**	**18.1**
Predicted No Effect Concentration (PNEC) (ng/L)	20	20
Quotient (PEC/PNEC)	**0.34**	**0.91**

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).

The Q value of <1 derived from the hazard calculations by DEH for both situations indicate that there is unlikely to be an environmental hazard associated with use of diazinon-containing products according to their approved labels. However, the safety margin is relatively narrow, particularly when the mean residue when treated of 2.7 mg/kg is used. The use of the mean represents a scour lot of wool containing only wool treated with diazinon, a potential "hot spot" situation, as discussed below.

1.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall based on the PNEC used. The result is shown in Table 1.9.

Table 1.9: Calculated concentration of diazinon (ng/L) in raw greasy wool based on the target concentration of 20 ng/L at the ocean outfall for diazinon

Parameters	**DEH's estimates**
Target concentration (ng/L)	20
Load entering the ocean which takes into account the plume dilution factor of 1/50 (ENV) (g)	50 ML X 20 ng/L X 50 = 50
Load entering sewage treatment plant (STP) (g)	100/50 X 50 = 100
Load entering wax recovery (WAX) (g)	100/70 X 100 = 142.8
Load entering scour (SCR) (g)	100/96 X 142.8 = 148.7
Concentration of residues on wool (mg/kg)	148.7/50 = 2.97

The calculation indicates that there is unlikely to be an environmental hazard based on the latest monitoring data of 1.0 mg/kg mean residues in wool for diazinon. However, again the safety margin is narrow and the possiblity that potential "hot spots" occur which may pose an unacceptable hazard needs to be taken into account. If the mean residue when treated of 2.7 mg/kg, coming from an area of grazing country where most farmers use diazinon (quite possible as over 30% of sheep still appear to be treated with diazinon) and the wool grown is such that little if any mixing occurs prior to processing, is used the hazard is still acceptable. However, the margin is very narrow, and it may also be possible that some processing lots will contain diazinon residues >3.0 mg/kg, leading to a potentially unacceptable hazard. Therefore it cannot be concluded that current use of diazinon according to the approved label would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment when treated wool is scoured in Australia.

1.8 TRADE

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours.

1.8.1 UK/EU EQS/MAC Requirements

In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry to meet environmental standards. Savage (1998) noted the AA and MAC values for organophosphates were 10 and 100 ng/L, respectively. These were UK 'draft operational standards' and subject to review. The EQualS^{TM} Version 3.0 database[2] confirms these

[2] The EqualS^{TM} database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk

values have been proposed for diazinon in fresh water in the UK. However, this was the situation in 1999 and the former website[3] (http://www.basicweb.fsnet.co.uk/index.htm) included the more recently proposed values of an AA of 30 ng/L and an MAC of 100 ng/L respectively. These are confirmed as final values for freshwater in Annex G of of the Scottish Environmental Protection Agency web site[4]. Therefore the latter have been used to calculate wool residue levels on the basis of EU/UK requirements as shown in Table 1.10.

Table 1.10: Predicted concentration of diazinon (ng/L) in river based on the EU/UK model by DEH

Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of diazinon in wool at harvest (mg/kg)	1.0	1.0
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of diazinon entering scouring plant on wool (g)	27.6	27.6
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	50	50
Mass of diazinon discharged (g)	2.65	2.65
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	**17.8**	**37.3**
UK/EU proposed requirement (ng/L)*	30	100

* UK is the 'worst case scenario' for the EU and has freshwater EQSs of AA and MAC of 30 and 100 (ng/L), respectively, for diazinon.

On the basis of the 2003-2004 AWI monitoring data for diazinon, the calculations in Table 1.10 indicate that the predicted environmental concentrations will meet proposed UK/EU requirements for the AA and MAC. However, the margin of safety is low. If the mean residue when treated of 2.7 mg/kg, representing a potential "hot spot", is used, the predicted environmental concentrations in the river would be 48.1 and 100.7 respectively, which are well above and very close to the proposed UK AA and MAC EQS values respectively.

1.8.2 DEH's Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report the maximum mean concentration in raw wool can be estimated from the target concentration at the river outfall as shown in Table 1.11.

Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[3] Available from 2001 but removed in mid 2003.

[4] Available on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf

Table 1.11: Calculated concentration of diazinon (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 10 (AA) and 100 (MAC) ng/L.

DEH's calculations based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)*	30	100
Load entering the river (ENV) (g)	149 ML X 30 ng/L = 4.47	71 ML X 100 ng/L = 7.1
Load entering sewage treatment plant (STP) (g)	100/50 X 4.47= 8.94	100/50 X 7.1 = 14.2
Load entering on-site treatment plant (OST) (g)	100/20 X 8.94 = 44.7	100/20 X 14.2 = 71
Load entering scour (SCR) (g)	100/96 X 44.7 = 46.563	100/96 X 71 = 74
Concentration of residues on wool (mg/kg)	46.563/27.6 = 1.69	74/27.6 = 2.68

On the basis of the above model, the mean residue of 1.0 mg/kg diazinon on all wool in the 2003-2004 AWI monitoring data is likely to lead to concentrations in the river that are below the proposed UK requirements for AA of 30 ng/L, but the safety margin is narrow. While there is a more acceptable safety margin with the proposed MAC of 2.68 mg/kg, the possibility of processing lots containing hot spots such as average residues of 2.7 mg/kg, which as noted above is quite possible, needs to be taken into account. This level is likely to lead to concentrations in the river that are well above the proposed EQS AA and very close to the proposed MAC. Taking into account that the same limits are proposed for total organophosphates, it cannot therefore be ruled out that the registered use of diazinon might adversely prejudice Australia's export trade if the UK tests for diazinon in scouring effluents.

1.9 WOOL WITHHOLDING PERIOD FOR DIAZINON

As noted above (Section 1.4.2), a wool withholding period (WWP) of not less than 2 months is stipulated on labels for the treatment of blowfly strike on sheep by jetting. Note that in some cases although the two month WWP interval is applicable the statement has not been included on current labels.

Horton and Campbell (1999) estimated the wool withholding period (WWP) based on the model (see Section 1.5.1.1 above) for the breakdown of diazinon residues on wool to meet the proposed individual sale lot maximum residue limits for the processing of greasy wool. This required the use of a computer program that incorporates the model to predict the expected results after using any given method of treatment in any length wool, with sheep shorn at any time after treatment. On the basis of this model, WWPs could be calculated to ensure the diazinon residues on wool remained below 9 mg/kg for individual wool sale lots (Savage 1998). The results are shown in Table 1.12.

Table 1.12: Calculated wool withholding period necessary to keep diazinon residues on wool below 9 mg/kg for individual wool sale lots (taken from Savage 1998)

Method of administration	Time after shearing before treatment	WWP (weeks)
Dip (lice)	Off-shears	9
Dip (lice)	6 weeks	17
Dip (lice)	12 weeks	27
Dip (lice)	18 weeks	34
Dip (flystrike)	6 weeks	22
Dip (flystrike)	12 weeks	33
Dip (flystrike)	15 weeks	37
Jetting	6 weeks	7
Jetting	12 weeks	12
Jetting	18 weeks	16
Jetting	24 weeks	19
Jetting	31 weeks	21

These data suggest that diazinon breaks down at a faster rate in short wool than long wool and indicate that sheep treated with longer wool growth will result in a longer WWP irrespective of the method of application.

Proposed WWPs for organophosphates have recently been recalculated (Horton and Campbell 2001) based on the wool residue breakdown model by using the more recent survey data and the increase in processing lot targets described by Russell (2000). The results are shown in Table 1.13.

Table 1.13: Suggested days from treatment to shearing using the Withholding/Blending Model

Organophosphates	UK EQS (days)	UK MAC (days)	Australia (days)
Diazinon off-shears backliner	26	24	43
Diazinon lice dipping	65	63	98
Diazinon fly control dipping	80	72	118
Diazinon jetting	0	0	64

There is insufficient information to allow independent verification of these calculations, which are based on processing lot maximum limits of 2.6 (UK EQS), 12.6 (UK MAC) and 3 (Australia) mg/kg, as compared with figures proposed in this report of 1.69, 2.68 and 2.97 mg/kg, respectively. The former were derived from limits of 30, 470 and 1000 ng/L respectively, compared with 30, 100 and 20 ng/L in this report. Even given this there are some puzzling aspects, as most results are the opposite of the DEH calculations. In particular it is unclear why the Australian WWPs should be all longer than those estimated for the UK, and why there is a nil WWP for diazinon jetting which is expected to be the most widely used method for long wool treatment.

What is clear is that based on the calculations for the hazard from Australian scouring, the current WWP of 2 months (60 days) is barely adequate and may not totally prevent a hazard occurring from some "hot spot" situations. It is also clear that the current WWP is not sufficient to avoid potential incidents that may adversely prejudice Australia's export trade.

There are insufficient data to allow DEH to recalculate an acceptable WWP and DEH does not have the ability to estimate WWPs or even to do separate calculations for the contribution from short and long wooled treatments.

1.10 CONCLUSIONS

On the basis of this assessment the DEH is unable to conclude that the use of selected sheep ectoparasiticide products containing diazinon in accordance with approved labels under Australian scouring conditions and the current WWP would not be likely to have an effect that is harmful to animals, plants or things or to the Australian environment under Australian scouring conditions. The main concern is possible "hot spots" from areas of grazing country where most farmers use diazinon and the wool grown is such that little if any mixing occurs prior to processing.

In addition, the DEH concludes there is a potential prejudice to trade associated with the use of products containing diazinon, based on a comparative analysis of likely scour residues and their likely future impact on exports of Australian raw wool.

1.11 REFERENCES

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CHAPTER 2 - PROPETAMPHOS

2.1 INTRODUCTION

The products *Ectomort® Plus Lanolin Sheep Dip, Young's Ectomort plus Lanolin Sheep Dip* and *Nufarm Seraphos 360 Dip and Jetting Fluid for Sheep* containing propetamphos were selected for the Sheep Ectoparasiticide Review in accordance with the APVMA Gazette of 7 September 1999.

The registered products are used for the control of lice (*Bovicola ovis*) and ked (*Melophagus ovinnus*) on short wool sheep by dipping and to assist in the control of OP susceptible blowfly (*Lucilia cuprina*) strike on sheep by jetting.

The only current registrations for propetamphos within Australia are for sheep.

This report is based on the published literature and data supplied by Novartis Animal Health Australasia Pty Limited for propetamphos. To date no information has been provided by either Nufarm or Tomen.

In accordance with the Gazette statement of 7 September 1999, this report considers only the long wool treatment by jetting for blowfly control. However, it is not clear from the label statement at what stage of wool growth the sheep would be treated. A Wool Withholding Period (WWP) of 2 months is specified on the label for *Ectomort*, but no WWP is specified on the label for *Seraphos.*

2.2 CHEMICAL IDENTITY

Chemical Name: 1-methylethyl (E)-3-[[(ethylamino)methoxyphosphinothioyl]oxy]-2-butenoate

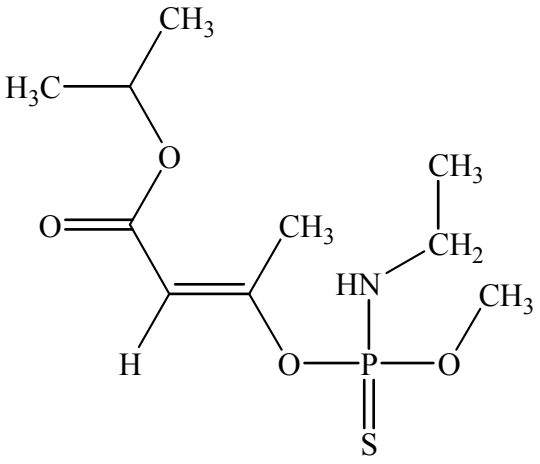
Common Name: Propetamphos

CAS Number: 31218-83-4

Molecular formula: $C_{10}H_{20}NO_4PS$

Molecular weight: 281.3

Structural Formula:



2.3 PHYSICO-CHEMICAL PROPERTIES

Appearance:	Yellowish oily liquid
Boiling Point:	87-89°C
Vapour Pressure:	1.9 mPa (at 20°C)
Water Solubility:	Moderately soluble (110 mg/L at 24°C). Readily miscible with acetone, ethanol, methanol, hexane diethyl ether, dimethyl sulfoxide, chloroform and xylene
Partition Coefficient:	Log K_{ow}= 3.82
Dissociation Constant:	pKa = 13.67 (23°C)

2.4 ENVIRONMENTAL EXPOSURE

2.4.1 Volume

Based on the most recent AWI survey, use of propetamphos is very low compared with diazinon, with residues found in only 1.5% of all wool tested in 2001-2002.

2.4.2 Application Rate and Use Pattern

Ectomort and *Seraphos* are used for the control of lice (*Bovicola ovis*) and ked (*Melophagus ovinnus*), and to assist in the control of OP susceptible blowfly (*Lucilia cuprina*) under strike conditions on sheep. Indications are for the treatment of lice, ked and fly as a plunge or shower dip at the maximum recommended dose rate of 1/1250 dilution (1/1250 X 360 g/L = 288 mg/L) of the product with water, and for assisting the control of blowfly strike by jetting at a maximum recommended dose rate of 1/1000 dilution (1/1000 X 360 g/L = 360 mg/L) of the product with water. In

accordance with the products' label instructions sheep are not to be dipped more than 6 weeks after shearing. Hence this treatment applies to off-shears.

The amount of propetamphos that will be administered to sheep by jetting and how much of the administered dose stays on the sheep is unclear from the label, which indicates standard jetting procedures are to be used, saturating the treated area to the skin. However, in the AVCARE (1994) trial described below 5 L (1.8 g) was applied along the backline and around the crutch.

2.5 ENVIRONMENTAL CHEMISTRY AND FATE

2.5.1 Residue depletion studies in wool

2.5.1.1 Summary of half-life calculations

A registrant provided data on the breakdown of propetamphos in wool as modelled by Campbell et al. (1998) and Campbell et al. (1999) using available and published data. The average half-lives from treatment to shearing for propetamphos from experimental studies estimated by the Campbell model are shown in Table 2.1.

Table 2.1: Average half-life of propetamphos from treatment to shearing determined by the Campbell model

Method of treatment	Time of treatment after shearing	Range (days)	Mean half-life (days)	Reference
Plunge dip	6 weeks	32-40	36	AVCARE (1994)
Shower dip	6 weeks	31-36	34	Campbell et al. (1999)
Hand jet	6 months	33-41	37	Campbell et al. (1998)
Hand jet	8 months	33-56	41	Campbell et al. (1998)
Hand jet	9 months	30-44	36	AVCARE (1994)
Hand jet	9 months	39-49	43	Campbell et al. (1998)

The data indicate that the mean half-life of propetamphos calculated by the Campbell model is consistent irrespective of the time of treatment and the method of application. The half-life estimations indicate that the degradation of propetamphos in wool is quite rapid with an average half-life of 37 days.

2.5.1.2 Fleece Residue Trial (AVCARE 1994)

One hundred merino wethers were used in this trial. The sheep had been previously dipped in diazinon. At the trial site the sheep were drenched for nematode parasites (ivermectin) and liver fluke (triclabendazole) at the recommended dose rates. After one month of grazing to allow adjustment to the trial site, the sheep were grouped into 10 groups of 10 animals. Each group was treated with a different active constituent except for one group that was used as the untreated control. All sheep for plunge dipping were shorn on the same day and were dipped 6 weeks after shearing. The sheep for jetting remained unshorn and were treated at 9 months' wool growth.

The sheep were treated with the products at the approved label dose rates of 180 mg/L and 360 mg/L for dipping (*Seraphos*) and jetting (*Ectomort*), respectively. Approximately 5 L of fluid per sheep were administered by jetting along the backline and around the crutch. Plunge dipping was done in a 2200 L concrete-lined in-ground sump. Data were obtained from 5 sheep per group. Wool samples were taken from

the flank (at the shoulder and midline) and backline (at the shoulder and rump) of the untreated controls, and from the treated sheep 1, 6, 12, 26 and 46 weeks after dipping and 1, 6 and 12 weeks after jetting. Two backline samples were combined, thoroughly blended and a sub-sample of 2.0 g was taken for analysis. This procedure was repeated for the flank samples. Wool samples were stored at -15°C prior to analysis by HPLC. The results are shown in Tables 2.2 and 2.3.

Table 2.2: Propetamphos residues in wool (mg/kg greasy wool) from sheep with 6 weeks wool growth dipped with *Seraphos* at the label dose rate of 180 mg/L

Weeks post-treatment	**Propetamphos residues in wool (mg/kg wool)**		**Mean propetamphos residues in wool ± SD (mg/kg wool)**	
	Backline	**Flank**	**Backline**	**Flank**
1	400, 326, 334, 453, 454	622, 577, 664, 640, 815	393 ± 25	664 ± 60
6	2.90, 14.5, 24.0, 9.30, 12.4	36, 30, 89, 81, 90	12.6 ± 4.9	65 ± 7
12	ND, ND, 5.7, ND, ND	3.8, 11.3, 12.2, 13.1, 8.1	1.1 ± 1.6	9.7 ± 3
26	0.14, ND, 0.39, ND, ND	ND, 0.51, 0.78, 0.26, 0.25	0.11 ± 0.10	0.36 ± 0.15
46	ND, ND, ND, 0.83, 0.67	0.14, 0.70, 0.71, 0.10, 0.39	0.30 ± 0.10	0.41 ± 0.12

Limit of detection = 2 mg/kg for weeks 1, 6 and 12, and 0.1 mg/kg for weeks 26 and 46
ND – Non-detectable level
Propetamphos residues in wool of untreated controls were at non-detectable level

Table 2.3: Propetamphos residues in wool (mg/kg) from sheep with 9 months wool growth jetted with *Ectomort* at the maximum label dose rate of 360 mg/L

Weeks post-treatment	**Propetamphos residues in wool (mg/kg wool)**		**Mean propetamphos residues in wool ± SD (mg/kg wool)**	
	Backline	Flank	Backline	Flank
1	948, 1471, 1722, 1179, 1287	7.9, 14.3, 35, 14.3, 45	1321 ± 159	23.3 ± 5.4
6	653, 646, 588, 350, 396	9.4, 5.6, 24, 37, 5.6	527 ± 41	16.3 ± 5.5
12	97, 36, 153, 168, 183	18.7, 3.1, 6.6, 9.4, 2.4	127 ± 26	8.0 ± 3.8

Limit of detection = 2 mg/kg
Note that the mean propetamphos residues in the backline and flank of wool sampled 1 week prior to treatment were 7.4 and 13.2 mg/kg, respectively. This possibly reflects residual from a previous treatment with propetamphos, or less likely (since HPLC was used), the previous diazinon treatment.

The data indicate that the concentration of propetamphos in wool decreases with time for both the long and short wool treatments, with the mean half-lives (see Table 2.1) identical at 36 days. The levels of propetamphos found prior to jetting should not affect these calculations greatly, since they were low (~20 mg/kg) compared with the combined 1 week post-treatment levels (~ 1345 mg/kg).

Higher propetamphos residues were observed in the backline than flank area for the long wool treatment, with residues clearly being retained by the long wool and with little running off to the flank. Propetamphos residues in the backline samples were also higher in the long wool treatment than the short wool treatment at the corresponding sampling points. For the short wool dipping treatment, propetamphos

residues were higher in the flank than the backline, possibly due to more of the backline areas being exposed to photolysis, whereas the active constituent was more protected from photolysis by the long wool.

2.5.2 Environmental Fate

No information was provided by registrants on environmental fate. The following has been obtained from the readily available literature.

2.5.2.1 Hydrolysis

Results of a study summarised in the draft Registration Eligibility Decision (RED) assessment of propetamphos (US EPA, 1998) indicate that it is stable to hydrolysis at pH 6 and 25°C with a half-life of 365 days. Propetamphos hydrolyses slowly in acidic (pH 3) and in alkaline solutions (pH 9) with half-lives of 11 days and 41 days, respectively. At pH 7 the half-life was 17 days in solution maintained at an elevated temperature of 45°C. Thus hydrolysis of propetamphos occurs slowly in the environmental pH range (pH 5-9) at 25°C, with a half-life between 41 and 365 days. Isopropyl acetoacetate was an intermediate degradation product, which further degraded to isopropanol, acetone and carbon dioxide.

2.5.2.2 Photolysis

According to the Extoxnet database (UC Davis, 2003), propetamphos is rapidly degraded in water in the presence of sunlight.

2.5.2.3 Other data

There appear to be no data currently available on the breakdown of propetamphos in soil, groundwater or on vegetation.

2.5.2.4 Conclusion

On the basis of the available fleece residue data, the calculated mean depletion half-lives in wool based on the Campbell model indicate that propetamphos degrades quite rapidly after use according to label instructions.

Hydrolysis of propetamphos occurs slowly in the environmental pH range (pH 5-9) at 25°C, with a half-life between 41 and 365 days. In water in the presence of sunlight, propetamphos is said to be unstable. No other fate data appear to be available.

2.6 ENVIRONMENTAL TOXICOLOGY

No data were provided by registrants regarding the effects of propetamphos in the environment. The following ecotoxicological data were obtained from Tomlin (1997), the Extoxnet database (UC Davis, 2003), the database of the Environmental Fate and Effects Division of the Office of Pesticide Programs[5], and the draft RED (US EPA, 1998).

[5] The database is maintained by the Ecological Fate and Effects Division of the Office of Pesticide Programs database, US EPA. Contact: Brian Montague, U. S. Environmental Protection Agency (7507C), Ariel Rios Building, 1200 Pennsylvania Ave., N.W., Washington, D.C.,20460. Phone:703-305-6438 FAX:703-305-6309 EMAIL Address: Montague.Brian@epa.gov.

2.6.1 Aquatic Toxicity

2.6.1.1 Aquatic invertebrates/flora

Propetamphos is highly toxic on an acute basis to water fleas (*Daphnia magna*) with a LC50 (48 hour exposure) of 3.3 or 14.5 μg/L (US EPA, 1998; see also footnote 5 - database of the Environmental Fate and Effects Division of the Office of Pesticide Programs; note both considered as Core results) and moderately toxic with a LC50 (96 h exposure) of 2.9 mg/L for green algae (Tomlin 1997).

According to Extoxnet's Pesticide Information Profile (UC Davis 2003), propetamphos may be very highly toxic to aquatic invertebrates with reported LC50 values ranging between 0.68 and 14.5 μg/L in *Daphnia magna*.

2.6.1.2 Fish

The LC50 values reported (96 h exposure) are 4.6 mg/kg diet for rainbow trout and 7.0 mg/L for carp, indicating that propetamphos is moderately toxic to both species (Tomlin 1997). In addition Table 2.4 is derived from the database of the Environmental Fate and Effects Division of the Office of Pesticide Programs[5].

Table 2.4: Data for the effects of propetamphos on rainbow trout and bluegill sunfish

Species	**Weight (g)**	**LC50 (ppm); 96 h exposure**	**Year reviewed – Rating (footnote 4)**
Rainbow trout (*Oncorhynchus mykiss*)	1.1	0.94	1979 - Supplementary
	1.3	2.6	1990 – Core
Bluegill sunfish (*Lepomis macrochirus*)	1.1	0.28	1975- Core
	0.7	0.19	1979 – Core
	1.8	1.1	1990 - Core

Extoxnet (UC Davis 2003) notes that the LC50 values for propetamphos range from 0.13 mg/L in bluegill and 0.36 mg/L in rainbow trout (highly toxic) to 3.7-8.8 mg/L in carp. These are in line with the above.

2.6.2 End Point used in Hazard Assessment

The most sensitive aquatic species to propetamphos with the most reliable result is the water flea (*Daphnia magna*) with a 48 h EC50 of 3.3 μg/L, which has been accepted as a core result by the US EPA. Though the literature contains lower values, these cannot be independently confirmed and 3.3 μg/L will be used as the environmental end point for propetamphos in the hazard assessment of ocean discharge. However, since the data are limited and none of the original test reports have been able to be reviewed, an AF of 100 will be applied and the value of 33 ng/L will be used as the PNEC in the hazard assessment for Australian conditions.

The toxicity data is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable).

2.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN WOOL SCOURING

Aquatic organisms are most at risk from the use of propetamphos on sheep via the discharge of effluent from wool scours that have been processing propetamphos treated fleeces.

2.7.1 Residue levels in the Australian wool clip

The mean total concentration of OP residues on Australian fleece wool for 2000-1 based on the 2000-1 AWI wool residue survey was 1.51 mg/kg greasy wool (I. Russell CSIRO, personal communication). Of the samples that contained propetamphos, the average concentration was 1.2 mg/kg and the maximum concentration was 3.4 mg/kg. These samples contained 1.2% of the total mass of OPs on the clip, corresponding to 1.2% X 1.51 mg/kg = 0.018 mg/kg of the total OP concentration in the clip.

These levels have been confirmed in the 2001-2002 (S Williams AWI, personal communication), 2002-2003 and 2003-2004 results (I Russell, 2004), with clear indications of a declining trend. The mean residue of propetamphos on all wool was <0.1 mg/kg, with between 0.8-1.5% of samples with residues above the Limit of Resolution (LoR), the mean residue when treated being in the range 1.2-1.7 mg/kg, with the highest residue found being from 2.6-12 mg/kg. Therefore a maximum value of 0.1 mg/kg will be used in the hazard calculations below. For comparison, the mean residue when treated value of 1.7 mg/kg will also be used, covering a potential "hot spot".

2.7.2 Australian Model

The environmental model (Savage 1998) was used by DEH to predict the worst case level of propetamphos present in sewage effluent entering Barwon Waters from the Black Rock treatment plant.

The hazard calculations take into consideration the following parameters as shown in Table 2.5.

Table 2.5: Determination of Q values by DEH

Parameters	Mean residue in clip	Mean residue when treated
Concentration of propetamphos in wool at harvest (mg/kg)	0.1*	1.7
Mass of wool scoured in one day (tonnes)	50	50
Mass of propetamphos entering scouring plant on wool (g)	5	85
Percentage remaining on scoured wool (%)	4	4
Percentage removed with grease during scouring (%)	30	30
Percentage removed during sewage treatment (%)	50	50
Mass of propetamphos discharged (g)	1.68	28.56
Flow rate of sewage treatment plant (ML/d)	50	50
Predicted concentration in sewage outflow (ng/L)	33.6	571.2
Plume dilution factor	0.02	0.02
Predicted Environmental concentration (PEC) (ng/L)	**0.67**	**11.4**
Predicted No Effect Concentration (PNEC) (ng/L)	33	33
Quotient (PEC/PNEC)	**0.02**	**0.35**

* Based on the 2003-2004 AWI wool residue survey

The quotient of 0.02 based on the mean residue in the 2003-2004 wool clip indicates there is unlikely to be an environmental hazard when the propetamphos products are used as labelled, in particular considering the conservative nature of the calculation (assessment factor of 100 and maximum wool residues of 0.1 mg/kg assumed – the latter is probably much lower). This is confirmed by the Q value still being acceptable when the mean residues when treated value of 1.7 mg/kg is used. However, this is not the case if the maximum residue of 12 mg/kg in the 2002-2003 AWI wool survey is used as Q = 2.44.

The latter is very unlikely to occur. As noted above over the past three seasons propetamphos residues were detected in only 0.8-1.5% of all wool tested by the AWI, with a mean level of 1.2-1.7 mg/kg in sales lots when contaminated, and <0.1 mg/kg across the whole clip. For a processing lot to contain that level of residue it would have to result from a very small pocket of grazing country where most farmers use propetamphos and the wool grown is such that little if any mixing occurs prior to processing. The probability of this is very low.

Assuming that the 1.5% wool contaminated is a surrogate for market share, and that as a worst case 15% of a processing lot is contaminated with residues at this level, the maximum residue in a processing lot may be estimated as 1.7 X 0.15 = 0.255 mg/kg. In this case Q = 0.05, confirming that an aquatic hazard is unlikely from wool scouring under Australian conditions. For an unacceptable hazard to occur over 50% of wool would need to be contaminated with the maximum level of 8 mg/kg found in the 2001-2002 AWI residue level survey.

2.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target PNEC at the ocean outfall under Australian conditions. The result is shown in Table 2.6.

Table 2.6: Calculated concentration of propetamphos (ng/L) in raw greasy wool based on the target concentration of 33 ng/L at the ocean outfall for propetamphos

Parameters	**DEH's estimates**
Target concentration (ng/L)	33
Load entering the ocean which takes into account the plume dilution factor of 1/50 (ENV) (g)	50 ML X 33 ng/L X 50 = 82.5
Load entering sewage treatment plant (STP) (g)	100/50 X 82.5 = 165
Load entering wax recovery (WAX) (g)	100/70 X 165 = 235.7
Load entering scour (SCR) (g)	100/96 X 23.57 = 245.5
Concentration of residues on wool (mg/kg)	245.5/50 = 4.9

On the basis of the last 3 seasons' AWI wool residue survey data for propetamphos, there is unlikely to be an environmental hazard arising from use in accordance with currently approved labels for propetamphos as long as levels in processing lots remain below 4.9 mg/kg (note again the conservative assumptions used). As noted above, the maximum levels in a processing lot may be estimated as 0.255 mg/kg, well below this figure.

In conclusion, treatment of sheep according to the approved label (including a 2 month WWP) and scouring of wool under Australian conditions would not be likely to have

an unintended effect that is harmful to animals, plants or things or to the environment, even if the levels of use increased significantly over current levels.

2.8 TRADE

2.8.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, environmental quality standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry to meet environmental standards. The former website[6] (http://www.basicweb.fsnet.co.uk/index.htm) includes the recently proposed values of an AA of 30 ng/L and an MA of 100 ng/L respectively. These are confirmed as tentative values for freshwater in Annex G of of the Scottish Environmental Protection Agency web site[7]. The calculated wool residue levels on the basis of the proposed EU/UK requirements are shown in Table 2.7.

Table 2.7: Predicted concentration of propetamphos (ng/L) in river based on the EU/UK model

DEH EU/UK models estimate		
Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of propetamphos in wool at harvest (mg/kg)	0.1	0.1
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of propetamphos entering scouring plant on wool (g)	2.76	2.76
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	50	50
Mass of propetamphos discharged (g)	0.265	0.265
Flow rate of river (ML/d)	149	71
Predicted environmental concentration in river (PEC) (ng/L)	**1.78**	**3.73**
UK/EU expected requirement (ng/L)	30	100

The PECs for both the EQS AA and MAC based on the mean residue of propetamphos on all wool in the current AWI monitoring data readily meet the UK/EU expected requirements. However, if the mean residue when treated of 1.7 mg/kg from the 1.5% of samples with residues above the Limit of Resolution (LoR) is used, the PECs are 30.3 and 63.4, just over the AA and approaching the MAC respectively, suggesting trade implications are possible from the registered use of propetamphos. However, as noted above this is very unlikely to happen, with the maximum residues in a processing lot estimated as 0.255 mg/kg, where the Q values are acceptable at 0.45 and 0.095 respectively. Further the AA is a mean annual average, which could be exceeded at least for some of the time.

[6] Available from 2001 but removed in mid 2003.
[7] Available on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf

2.8.3 DEH's Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction of this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the river outfall as shown in Table 2.8.

Table 2.8: Calculated concentration of propetamphos (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 30 (EQS) and 100 (MAC) ng/L for propetamphos.

Based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)*	10	100
Load entering the river (ENV) (g)	149 ML X 30 ng/L = 4.47	71 ML X 100 ng/L = 7.1
Load entering sewage treatment plant (STP) (g)	100/50 X 4.47 = 8.94	100/50 X 7.1 = 14.2
Load entering on-site treatment plant (OST) (g)	100/20 X 8.94 = 44.7	100/20 X 14.2 = 71
Load entering scour (SCR) (g)	100/96 X 44.7 = 46.563	100/96 X 71 = 74
Concentration of residues on wool (mg/kg)	46.563/27.6 = 1.69	74/27.6 = 2.68

* UK is 'worst case scenario' for the EU and has tentative EQS and MAC of 30 and 100 ng/L for propetamphos, respectively.

On the basis of the mean residue of propetamphos on all wool in the recent AWI wool survey data propetamphos will meet the target concentrations for AA and MAC. As noted above the maximum residues in a processing lot are estimated as 0.255 mg/kg and at current use levels propetamphos is unlikely to unduly prejudice Australia's export trade.

2.9 CONCLUSIONS

The DEH notes that products that are sheep ectoparasiticides containing propetamphos currently constitute a very minor proportion of the total OP market (estimated maximum residue in a processing lot of 0.255 mg/kg). The DEH is therefore satisfied that the use of selected sheep ectoparasiticide products containing propetamphos in accordance with approved label instructions and the current WWP would not be likely to have an effect that is harmful to animals, plants, or things or to the Australian environment under Australian scouring conditions.

In addition, the DEH concludes there is unlikely to be a potential prejudice to trade associated with the use of products containing propetamphos, based on a comparative analysis of likely scour residues and their likely future impact on exports of Australian raw wool.

2.10 REFERENCES

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US EPA (1998), Office of Prevention, Pesticides and Toxic Substance. EFED Integrated Science Chapter for Propetamphos (draft RED)

CHAPTER 3 - TEMEPHOS

3.1 INTRODUCTION

Coopers Assassin Sheep Dip is a currently registered veterinary product that has not been marketed for some years. It contains temephos, an organophosphate insecticide, which in other registered products is currently used in the control of mosquitoes and midges, fleas in dogs and cats, as a pour-on insecticide for the control of lice on cattle and for dipping/jetting of sheep.

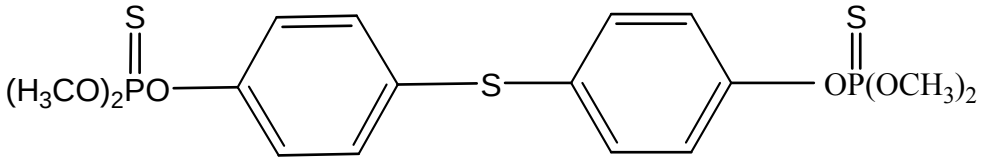
Coopers Assassin Sheep Dip is the only registered product containing temephos for use on sheep. The product is used for the control of body lice (including synthetic pyrethroid resistant strains) on wet or dry short wool sheep by plunge or shower dipping and for the treatment of body lice on long wool sheep by hand jetting.

This report is based on the data submitted for the original registration, and additional data provided for the Sheep Ectoparasiticide Review in March 2000. A Wool Withholding Period (WWP) of 3 months is currently stated on the product label based on the assessment of the original data.

3.2 CHEMICAL IDENTITY

Name CAS:	Phosphorothioic acid, *O,O'*-(thiodi-4,1-phenylene)-*O,O,O',O'*-tetramethyl ether
Common name:	Temephos
Trade name:	*Coopers Assassin Sheep Dip*
CAS number:	3383-96-8
Molecular formula:	$C_{16}H_{20}O_6P_2S_3$
Molecular weight:	466.4

Structural formula:



Purity:	Not less than 93%

3.3 PHYSICO-CHEMICAL PROPERTIES

Appearance:	Amber liquid with mercaptan-like odour (active constituent)
Melting Point:	30.0-30.5^{o}C (pure active); 10-15^{o}C (active constituent)
Relative Density:	1.33 g/mL at 20^{o}C
Vapour Pressure:	7.17 X 10^{-8} mm Hg at 25^{o}C
Water Solubility:	0.03 $\pm$ 0.007 mg/L at 25^{o}C
Partition Coefficient:	Log P_{OW} = 4.9 (measured and estimated values between 3.9 and 6.2 have been reported in the scientific literature).
Dissociation Constant:	Not applicable since temephos does not dissociate.
Stability:	Temephos appears to be thermally and hydrolytically stable for extended periods at normal temperatures.

3.4 ENVIRONMENTAL EXPOSURE

3.4.1 Volume

Most recent estimates by the registrant indicate between 0.5-2.5 tonnes of temephos per annum may be used for this purpose, with the majority used off shears.

3.4.2 Application and Use Pattern

3.4.2.1 Short wool

Sheep are treated using plunge or shower dips, up to 6 weeks off shears. Treatment within 2 weeks of shearing is not recommended. The label directs users to initially charge plunge and shower dips at 100 mL/100 L of water (35 g ai/100 L), and to top up at 100 mL/100 L.

The label instructs users to yard sheep overnight and preferably dip early in the morning to allow sheep to dry before nightfall. The dip should be topped up before its volume drops by more than 25%, and dipped out when excessively fouled (generally when one sheep has been dipped for every 2 L of original sump volume) or at the end of each day for shower dips. The label advises against leaving fouled plunge dips for more than a day in mild or warm weather, recommending that a disinfectant be added when dipping has finished for the day should retention for a longer period be unavoidable. Sheep must be thoroughly wetted. Inspection of the first few sheep to emerge from shower dips is recommended to ensure this. The label instructs users to

ensure each sheep swims for at least 30 seconds in plunge dips and has its head submerged twice.

3.4.2.2 Long wool

The product is registered for use on sheep with up to 9 months wool (i.e. up to 3 months before shearing). It is diluted at a rate of 100 mL to every 100 L of water and applied by hand jetting from the poll to the rump of the sheep in a band 15-25 cm in width with some fluid sprayed into the shoulder wool. The label instructs to apply fluid to wet backline fleece to skin level, and to use approximately 0.5 L of fluid (concentration of 100/100,000 X 350 g /L = 0.35 g ai/L) for each month of wool growth, with a minimum of 2.5 L per sheep, and a maximum of 4.5 L for sheep with 9 months wool growth. This equates to a range of 0.875 to 1.575 g of temephos applied per sheep.

3.4 Environmental fate

A detailed assessment of the environmental fate of temephos, with particular reference to coastal environments, is contained in DEH's publicly available environmental assessment report of July 1994 (can be provided on request). In the original submission the registrant provided some general literature references to the environmental characteristics of temephos, and recommended reference to that report for more detail. A brief summary of DEH's conclusions follows.

3.4.3.1 Abiotic degradation (hydrolysis, photolysis)

Temephos is hydrolytically stable but susceptible to photochemical oxidation about the thioether linkage. Product information indicates that hydrolysis may be expected after prolonged periods at high pH, suggesting possible hydrolytic degradation during wool scouring.

3.4.3.2 Metabolism in soils

The main degradative pathway operating in the environment is likely to be microbial metabolism, which proceeds by way of oxidation of the thioether and thiophosphate functionalities and phosphate hydrolysis to a range of products that break down further to carbon dioxide.

3.4.3.3 Aerobic aquatic metabolism

An aerobic study with lakewater and a sandy sediment indicated that around 30% of the applied radiolabel was in the water and 50% in the sediment by the end of the 30-day study. Temephos degraded with an estimated half-life of 17.2 days to give at least 5 products of which three were identified as the sulphoxide, the bis(phenol) derivative and its sulphone. The degradation is largely an oxidative one, impacting on the thiophosphate and thioether functionalities.

3.4.3.4 Anaerobic aquatic metabolism

Aside from a total absence of evolved carbon dioxide, the degradation pathway did not differ under anaerobic conditions carried out similarly to the above but under a N_2 atmosphere. The rate of degradation appeared faster initially but slowed thereafter. As in the aerobic study, temephos partitioned initially to sediment. However, by the end of the 1 year study, >90% of applied radioactivity was present in water. Of the

remainder <4% of the applied radioactivity was unextractable from the sediment at any stage.

3.4.3.5 Persistence

Temephos is non-persistent to slightly persistent in soils and aquatic systems, with half-lives of a few days or weeks being typical in the field. Biphasic dissipation, consisting of rapid sorption to organic matter followed by more gradual metabolism, occurs in water.

3.4.3.6 Sorption

Temephos sorbs strongly to soils and can be considered a non-leacher. However, its phenolic metabolites are more hydrophilic and mobile. In aquatic systems, temephos sorbs rapidly to sediment, where it is immobile.

3.4.3.7 Volatilisation

Model calculations indicate that volatilisation may also be a significant pathway for dissipation of temephos from water. A study by Prasad and Jain (1988) tends to support these predictions in that dissipation of Emulsifiable Concentrate (EC) formulations, which would leave significant amounts of temephos as a surface film, was more rapid than for granular formulations. This study also suggested a significant contribution from volatilisation during the first 24 hours after application to soil.

3.4.3.8 Bioaccumulation

A bioaccumulation factor of 2,300 and a depuration half-life of 8 days were obtained for bluegill sunfish exposed to ^{14}C-temephos under flow through conditions at an average level of 0.65 µg/L for 28 days in the laboratory. Residues in whole fish reached 1500 µg/kg during the uptake phase and appeared to be still increasing, but had declined to 380 µg/kg after 14 days depuration. The metabolite profile was not investigated. This is indicative of a moderate level of bioaccumulation and slow depuration, which has been confirmed in the field.

3.4.3.9 US EPA Assessment

Note that since DEH's 1994 assessment the US EPA has published a Re-registration Eligibility Document (RED, US EPA, 1999a), and a Revised Environment Fate and Effects Document (EFED, US EPA, 1999b). Apart from field studies more relevant to the mosquito application, this does not contain any additional relevant fate data.

3.4.4 Residue depletion studies in wool

3.4.4.1 Short wool

The significance of the scouring source will depend on the residues in the fleece before scouring and their fate in the scouring process. Information on fleece residues from use on short wool is summarised in a study designed to determine the likely exposure of shearers to temephos (Martin 1994).

The study involved shower dipping of ten sheep three weeks after shearing, followed by fleece sampling (5 X 5 cm) of backline and flank at 1, 6, 12 and 26 weeks. Backline and flank were assumed to contribute 30 and 70% to the total fleece weight, respectively. Results are tabulated as mg/kg greasy wool as shown in Table 3.1. The reduction of

fleece residues with time represents a combination of growth dilution and degradation. No initial levels were determined, and the half-life for degradation cannot be determined accurately from these data. However, it is concluded that use on short wool should not leave residues in excess of 1 mg/kg at shearing (see further discussion below).

Table 3.1: Temephos residue levels in wool at different sites of the sheep

Site	**Weeks post-treatment**			
	1	**6**	**12**	**26**
Backline (mg/kg)	868	10.2	4.2	ND
Flank (mg/kg)	906	6.5	2.5	0.9
Combined (mg/kg)	895	7.6	3.0	0.6

3.4.4.2 Long wool

Information on temephos residues resulting from application to sheep with long wool is available from a study by Burman *et al* (1997). Five groups of 10 medium wool Merino sheep were selected. At nine months from shearing one group was treated with temephos at 350 mg/L and another was treated with diazinon at 200 mg/L. At ten months from shearing one of the remaining three groups was treated with temephos and another was treated with diazinon. The final group remained untreated and was used to monitor wool growth rates. Wool samples were taken from a 5 cm circumferential strip around each of five sheep in each group. Sampling began before treatment and at 1 week, 1, 2 and 3 months or 1 week, 1 and 2 months after treatment. The final sampling occurred when the sheep had 12 months wool growth and was equivalent to the next shearing. The mean values for temephos residues (mg/kg) are listed in Table 3.2 below.

Table 3.2: Mean wool residue levels in sheep with 9 or 10 months wool growth sampled on days 7, 30, 60 and 90 after treatment

9 months wool growth				**10 months wool growth**		
Days post treatment	**Fleece weight (kg)***	**Temephos concentration mg/kg (range of values)**	**Temephos in fleece (mg)**	**Fleece weight (kg)***	**Temephos concentration $mg.kg^{-1}$ (range of values)**	**Temephos in fleece (mg)**
0	3.70	123**	455	4.4	159**	700
7	3.80	52 (40-65)	197	4.50	106 (75-125)	477
30	4.12	46 (40-70)	190	4.82	70 (55-85)	337
60	4.54	19 (15-30)	86	5.24	45 (30-70)	236
90	4.96	18 (10-30)	89	NA	NA	NA

* Based on wool growth rate of 14 g per day (Burman *et al*, 1997)
** Theoretical value calculated by Burman *et al* (1997)

Since no initial samples were taken, the researchers used wool growth measurements to calculate theoretical fleece concentrations at treatment based on the volume of jetting fluid retained by the sheep. The values calculated were 123 and 159 mg/kg for 9 and 10 months of wool growth, respectively. These estimated values are much higher than those actually recorded 7 days after treatment. The researchers suggested that temephos may not be retained on fleece after treatment to the same extent as other organophosphate products used for sheep jetting. The evidence, while only

circumstantial, is consistent with the relatively poor hexane solubility of temephos compared with other organophosphate ectoparasiticides, resulting in less temephos being retained on the fleece.

3.4.4.3 Half-life

DEH has used the wool growth rates and temephos concentrations measured by Burman *et al* (1997) to estimate the values in the above table for the amount of temephos contained in each fleece. As the temephos concentration immediately after treatment was not recorded, it was not possible to accurately calculate a half-life value from these data. However, the loss of temephos from day 7 to day 90 after treatment, from the sheep with 9 months wool, would suggest a half life in the order of two to three months. Later the registrant provided in an appendix to the submission the half-lives of degradation for each sheep by manipulating the fleece residue results in individual sheep, and has clarified that the equation used was as follows:

$T_{1/2} = -7XLn2/\beta XLn10$

Where –7 converts to days, Ln2 = 0.693, β is the slope of the regression line for the plotted degradation data, and Ln10 = 2.303.

The results are shown in Table 3.3.

Table 3.3: Half-lives of depletion of temephos on sheep treated at 9 or 10 months wool growth

Treatment	Sheep No.	Half-life (days)
Sheep treated at 9 months wool growth and wool sampled on days 7, 30, 60 and 90 after treatment	0131 0140 0148 0155 0162	30 40 62 62 46
	Mean	48
Sheep treated at 10 months wool growth and wool sampled on days 7, 30 and 60 after treatment	0121 0143 0149 0151 0173	34 26 128 39 36
	Mean	53

It appears that the degradation half-lives of temephos on wool are not significantly different between the treatments at 9 or 10 months wool growth. However, the limited sampling points (days 7, 30 and 60) used for the half-life calculation for the latter treatment may incur significant error. It is noted that for sheep No. 0149, the half-life of 128 days is significantly different (greater) from those of other animals treated at 10 months wool growth, which the registrant notes may be related to the method of application or sampling method. However, despite the lack of an initial value, the data for the 9 months wool growth give a clear indication of the wool residue degradation with time.

3.4.4.4 Core Sampling of Wool from Efficacy Trials

The registrant also provided temephos residue data from two efficacy trials conducted for the registration process (Nunn and Russell, 1998). In the first trial at Tambar Springs 1280 merino wethers with nine months wool were treated with *Assassin* at 350 mg/L by hand jetting three months before shearing. After shearing the 32 bale clip produced from these sheep was machine sampled, one sample per bale taken with an 18 mm tip, and the samples were analysed for temephos residues by the CSIRO Division of Wool Technology. It appears that the samples from the 32 bales were blended and then sub-sampled and two analyses were conducted.

The temephos residues measured were 6.7 and 5.9 mg/kg. These values are lower than the mean value of 18 mg/kg (range 10-30) measured by Burman *et al.* (1997) where sheep with nine months wool were also treated three months before shearing. The lower values measured by core sampling of bales support the hypothesis presented by the registrant that band sampling, the method of sampling used by Burman *et al.* (1997), tends to overestimate residue values with backline applications as it does not sample untreated areas of the fleece such as the neck.

In the second efficacy trial reported 1087 merino wethers were again treated with *Assassin* at 350 mg/L by hand jetting at 88 days before shearing. No information is available on the number of bales produced at shearing but five bales were manually sampled using an 18 mm core tip taking four samples from the base and cap of each bale. Samples from each bale were blended and sub-sampled to provide samples for analysis. Two samples were analysed from four of the bales and five samples were analysed from the fifth bale giving a total of thirteen samples for analysis.

The concentrations of temephos measured ranged from 0.9 to 9.6 mg/kg with a mean value of 3.9 (± 2.49) mg/kg. Again the mean value is lower than the value recorded by Burman *et al.* (1997) for the equivalent time of treatment before shearing. As stated above, these data also support the hypothesis that band sampling tends to overestimate residue levels. Given that the bale samples are more appropriate than the band samples as input concentration for the hazard calculation, in the absence of wool clip residue data the maximum temephos concentration of 9.6 mg/kg will be used by DEH for the hazard calculations.

However, the wool residue data from these efficacy trials should be regarded with some caution as a full range of measurements was not made. For example, no attempt was made to record the volume of jetting fluid applied to each sheep or the volume retained on the fleece by measuring a sample of the treated sheep. This would have provided data that may have given a more accurate picture of actual decline of residue levels in commercial practice.

Lipophilic pesticides such as temephos generally follow the wool grease during scouring. The implications for environmental exposure will be discussed below, under environmental hazard.

3.4.4.5 Summary

The registrant has provided data on the half-lives of degradation of temephos on sheep treated at 9 or 10 months wool growth. The results indicate that, with a half-life of

around 50 days, the degradation of temephos on wool is relatively fast. The results for the efficacy trials based on the core sampling of wool clearly indicate that under the registered use pattern the fleece residues analysed from core sampling are significantly lower than those for band sampling. While there are no data on the amount applied per sheep etc, the registrant has pointed out the core samples were taken according to Australian Standard and AWTA procedures and should therefore be an accurate reflection of likely temephos levels following long wool treatment under commercial conditions.

3.5 ENVIRONMENTAL TOXICOLOGY

3.5.1 Existing data

Temephos has low mammalian toxicity but is moderately to highly toxic to birds and fish, and very highly toxic to invertebrates, particularly aquatic invertebrates. Aquatic toxicity is summarised in the figure overleaf which is taken from the publicly available environmental assessment report of July 1994 produced by the then Environment Protection Agency. Note that since the 1994 assessment the US EPA has published a Re-registration Eligibility Document (RED) dated 29 September and an Environment Fate and Effects Document (EFED) dated 4 October 1999 (US EPA 1999a,b). Apart from field studies more relevant to the mosquito application, this does not contain any relevant additional toxicity data.

Crustaceans are particularly sensitive to temephos. As noted in our public environmental assessment report, the following end-points for local marine species are available from published sources.

The results (LC50 = 2.3-3.1 µg/L) of toxicity testing on mud crab larvae *(Scylla serrata)* indicate very high toxicity to juvenile crustacea (Mortimer, 1990). This contrasts with end-points for adult crabs, which fall in the low mg/L range, some three orders of magnitude higher than concentrations which kill juveniles.

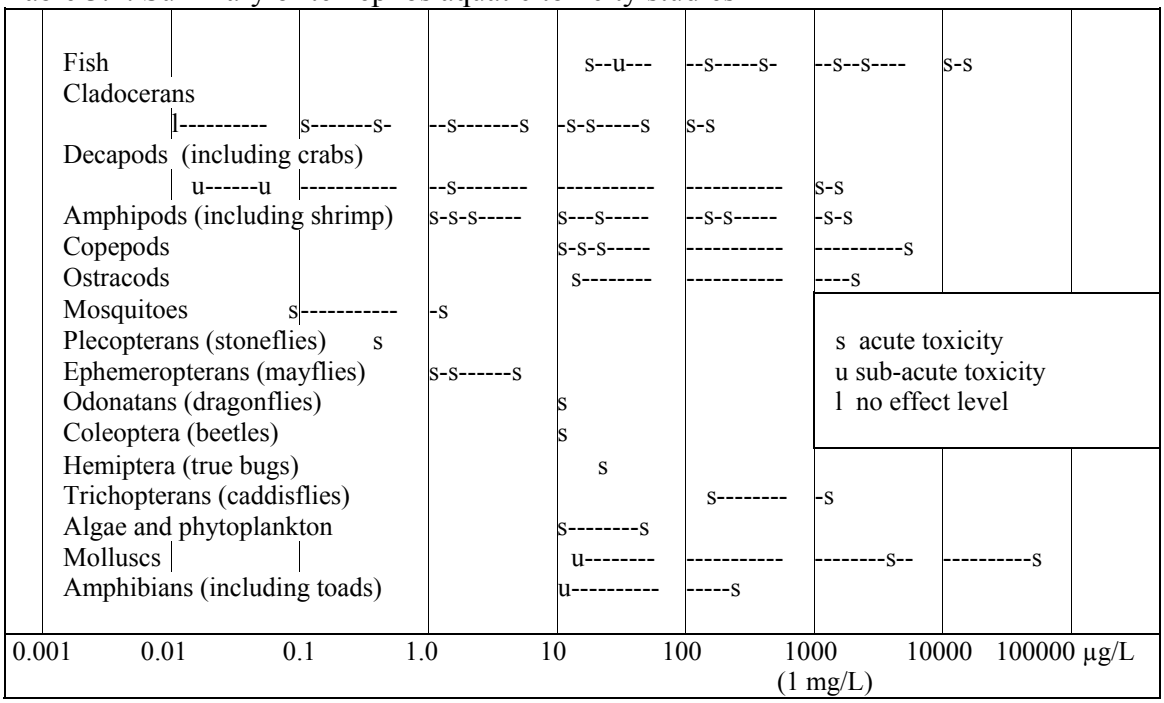
More recently (Chapman, 1993) end-points of 0.2 µg/L have been recorded in 48 hour static tests on yabby larvae *(Trypaea australiensis)*. Even adults were sensitive, with a 96 hour LC50 below 1 µg/L.

As reported in the DEH's publicly available environmental assessment report of July 1994, overseas results are available for mangrove tree crab larvae, indicating that the stress of moulting may exacerbate the toxic effects of temephos exposure. Measured concentrations (initially ranging between 2 and 70 µg/L) were observed to decline by at least 50%, and generally considerably more, during 48 hours of static laboratory testing. The critical concentration below which exposed larvae did not experience statistically significant reductions in survival through 72 hours was 7 µg/L. In the field, significant reductions in survival (typically 50-70% compared with 80-90% survival in controls) were observed by 12 days after application in larvae exposed to spray applications of temephos that left residues of 4 µg/L one hour after application (Pierce *et al*, 1993).

Summaries of some further studies, which provide additional data on the toxicity of temephos, are consistent with previous results. In laboratory studies temephos had a median LC50 of 10 µg/L for the shrimp *Leander tenuicornis,* which is a native of south eastern Queensland (Brown *et al*, 1996). In other laboratory studies with larvae of the mosquito species *Mansonia uniformis*, the LC50 of temephos was 7.69 µg/L (Yap *et al*, 1996). Static toxicity testing of temephos on the mouth brooder cichlid fish (*Tilapia melanopleura*) and dragonfly larvae (*Neurocordulia virginiensis*) found 96 hour LC50 values of 30.2 mg/L and 2.0 mg/L for the fish and dragonfly larvae respectively (Anadu *et al*, 1996).

The above results are summarised in Table 3.4 below.

Table 3.4: Summary of temephos aquatic toxicity studies



3.5.2 Conclusions based on existing data

Temephos is categorised as being very highly toxic to aquatic invertebrates on an acute basis. On the basis of the ecotoxicological data available, the freshwater organism most sensitive to acute toxicity of temephos is *Daphnia magna*, with a 48 h LC50 of 11 ng/L. This is from the static test using the Abate 4E formulation by Forbis and Frazier (1986) included in our original report. Importantly, the US EPA RED (1999) notes that this was considered a core study meeting all regulatory requirements. The RED quotes a NOEC of 30 ng/L for *Daphnia magna,* but this would seem to be a typographical error for 3 ng/L (cf 3.2 ng/L in our original report). Note that it appears results for the sensitive marine organism, the mysid shrimp, were not available to the US EPA, and that no acceptable studies on chronic toxicity were available as the US EPA guidelines were not fulfilled.

3.5.3 New Data

The registrant has provided data on the acute toxicity testing of temephos to *Daphnia magna* (Rhodes, 1999) performed in accordance with the US EPA FIFRA Guideline 72-2 and OECD Guideline 202.

First-instar *Daphnia magna* neonates (<24 h old) were obtained from an in-house culture. A total of 10 range-finding exposures were conducted. Five of these tests consisted of static exposures and five consisted of flow-through exposures. Three of the flow-through tests were conducted using an organic solvent and two were conducted without the organic solvent.

The data indicate that the range-finding tests conducted without an organic solvent resulted in variable mortality patterns, suggesting temephos was not always totally available in solution. Three attempts conducted for definitive testing without using an organic solvent and under flow-through conditions resulted in a similar pattern. The definitive tests were initiated with the addition of five neonate *Daphnia magna* to each test chamber, a total of 20 organisms per treatment. Analysis of the test solutions for temephos was performed using HPLC based on a validated method prior to the initiation of the study.

On the basis of the definitive testing, a nominal concentration range of 0.0 (control), 0.0 (0.10 mL/L DMF control), 0.0025, 0.0050, 0.010, 0.020, and 0.040 μg/L was selected. After 48 h of exposure, immobility/mortality and sublethal effects were observed at concentrations of 0.0050 μg/L and above. All test solutions appeared clear with no visible precipitate or surface film. Water quality measurements were within acceptable limits throughout the exposure. Although analysis of temephos in solution was unsuccessful, confirmation of the diluter stock solutions indicated appropriate dosing was carried out.

Based on the nominal test concentrations, the 48 h EC_{50} for *Daphnia magna* exposed to temephos was estimated to be 0.007 μg/L with 95% confidence limits of 0.006 and 0.009 μg/L based on nominal concentrations. This is slightly more toxic than the 48 h EC50 of 0.011 μg/L derived from the Forbis and Frazier (1986) study in DEH's original report. The No-Observed-Effect Concentration (NOEC) was 0.0025 μg/L based on the lack of immobilisation/mortality and sublethal effects.

3.5.4 Relevant environmental endpoint for Australian calculations

The most sensitive end-point is the above EC50 of 0.007 μg/L for *Daphnia magna.* Note this is based on a recent reliable test for which a full report has been provided by the registrant. While this was under flow-through conditions it is close to the static test result of 0.011 μg/L considered by the US EPA to be a core result.

However, we note that the ANZECC Water Quality Guidelines (ANZECC and ARMCANZ, 2000) contain a marine moderate reliability trigger value for temephos of 0.05 μg/L for 95% protection calculated using the statistical distribution method, with the 99% protection level being much lower at 0.0004 μg/L. The database for this

calculation included 8 fish species, 9 species of marine crustaceans (with 5 species of shrimps and prawns being most sensitive at 1-45 μg/L, not clear if this included a mysid shrimp result), 1 marine insect, 2 molluscs and 1 annelid. Further, only a freshwater low reliability trigger value of 0.05 μg/L based on adoption from the marine value could be derived. The guidelines rejected the alternative estimate obtained by applying an assessment factor of 100 to results for 21 species of fish (with the most sensitive value of 4.1 μg/L not accepted) but only 1 species of freshwater crustacean (*Gammarus* at 80-140 μg/L - note results for 8 species of freshwater insects were discarded as they included mosquitoes, the target species for temephos).

It is not clear why the ANZECC guidelines did not consider the published results of 0.2 μg/L and 2.3-3.1 μg/L respectively for the freshwater yabby larvae (Chapman, 1993) and the mud crab larvae (Mortimer, 1990). The latter is close to the most sensitive marine organism result.

The environmental end-point for temephos related to the release of the scouring effluent in Australia is based on the assessment factor (AF) approach. The volume of acute toxicity data available for temephos is considered to be adequate to enable an AF of 10, even though DEH has not necessarily fully assessed all the individual test reports. On this basis a predicted no effect concentration (PNEC) value of 0.7 ng/L has been set, which is significantly more sensitive than those previously used and much tighter than the ANZECC Water Quality Guideline value of 50 ng/L, derived using the statistical distribution approach.

However, as noted above the derived ANZECC Water Quality Guideline values do not include all the data available to DEH, importantly lacking some of the most sensitive data, and are of medium and low reliability for the marine and freshwater aquatic environments respectively. Crustaceans are clearly the most sensitive group, and in the absence of a mysid shrimp result (in DEH's experience usually even more sensitive than daphnids), a PNEC of 0.7 ng/L is used in our hazard assessment, considering the worst case will be discharge from a coastal outfall.

3.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

The risk that temephos would impact adversely on aquatic environments when scouring effluent is disposed of to land is low because of the low mobility of temephos in soils to which effluent would be applied. The main concerns arise in relation to discharge to sewer. Knowledge of sewage volumes, scouring rates and wool residues can be used to estimate concentrations leaving the outfall, which can then be compared with toxicity data to determine the environmental hazard.

3.7.1 Residue levels in the Australian wool clip

No monitoring data were provided or are available for temephos. However, during the 2001-2 AWI wool residue survey a mean fleece residue level of 1.4 mg/kg (Scott Williams AWI, personal communication) was found for total organophosphates (OPs). As diazinon is the main contributor to the total OP levels, it is apparent that the current temephos contribution in the mean wool clip would be considerably less. No results appear in the previous or more recent wool clip data available to DEH, suggesting either it hasn't been

tested for, or more likely residue levels are very low, ie well below 0.1 mg/kg.

3.7.2 Australian Model

As no monitoring data are available DEH has initially used a maximum residue level of 9.6 mg/kg from the bale samples at 88 days after treatment (see Section 6.3.4) as the worst case scenario for the hazard calculation. The results of the calculation performed by DEH take into consideration the following parameters as shown in Table 3.5.

Table 3.5: Determination of initial Q values by DEH

Parameters	**Worst case bale sampling results**	**30% long wool treatment****
Concentration of temephos in wool at harvest (mg/kg)	9.6	5.0
Mass of wool scoured in one day (tonnes)	50	50
Predicted market share of *Cooper Assassin Sheep Dip* (%)	1*	0.3***
Mass of temephos entering scouring plant on wool (g)	4.8	0.75
Percentage remaining on scoured wool (%)	4	4
Percentage removed with grease during scouring (%)	30	30
Percentage removed during sewage treatment (%)	50	50
Mass of temephos discharged (g)	1.6	0.25
Flow rate of sewage treatment plant (ML/d)	50	50
Predicted concentration in sewage outflow (ng/L)	32	5
Dilution in plume#	0.02	0.02
Potential Environmental Concentration (PEC) (ng/L)	**0.64**	**0.10**
Predicted No Effect Concentration (PNEC) (ng/L)	0.7	0.7
Quotient (PEC/PNEC)	**0.91**	**0.14**

* Based on the registrant's estimate of 1 million sheep treated in a flock size of 100 million – assumes all long wool treatment.

** Assumes only 30% of treatment is on long wool, with much treatment before 9 months growth, and that the contribution from short wool treatment is minor, ie less than 1 mg/kg.

*** Assumed amount of long wool treatment .

A plume dilution factor of 0.02 was derived from the study by Grundy et al. (2000)

While the worst case hazard calculations for Australian scouring conditions indicate an acceptable EEC/PNEC (Q) value of <1, the safety margin is very narrow, and it also relies on the low market share. However, it must be emphasised that this a very worst case estimate as it assumes that all treatments are on long wool sheep at 9 months, ie on the last legally available time when treatment can occur, and that the highest residues found in any tested bale will always occur. Clearly this is highly unlikely.

For a more realistic calculation, if we assume that only 30% is used for long wool treatment (as estimated by the registrant), and use a residue value of 5 mg/kg for long wool treatment[8], then the Q is lowered to below 0.2 (see Table 3.4). Alternatively this calculation assumes a mean residue level of about 4 mg/kg from the 5 long wool treatment bales and that many sheep will be treated prior to 9 months wool growth. It

[8] The worst case 9.6 mg/kg from 1 of 5 bales was employed, whereas the mean for these was 3.9 mg/kg and the range 0.9 to 9.6 mg/kg. In a separate trial, two other bales had residues of 6.7 and 5.9 mg/kg respectively (see Section 6.3.4).

also assumes only a limited contribution in the fleece from off shears treatment, as noted above residues may be expected to be below 1 mg/kg in this case (see also below).

Under the latter scenario, should use on long wool actually be 70% as in the registrant's previous estimates, then the Q rises to 0.34, indicative of how sensitive the potential hazard is to relatively small changes in market share and to the short/long wool split.

3.7.3 Discussion of potential Australian hazard and calculation of further scenarios

There is a great deal of uncertainty in the above hazard estimations, due to the lack of hard data. There is no certainty in the registrant's prediction that 1% of the flock will be treated with the product at maturity, or for the estimated 70:30 short/long wool split. Importantly there are no mechanisms available to regulate changes in market share.

The lack of any data on levels in the Australian wool clip, as determined by the AWI, is a further drawback, as it means that residue levels from experimental bales of treated long wool have to be used, either the worst case 9.6 mg/kg or the mean from 7 bales of about 5 mg/kg (and assuming a minor contribution for wool treated off shears).

The level of use of OP sheep ectoparasiticides is declining. Savage (1998) estimated 76% of the national flock was treated with OPs in 1997-1998, which at the time resulted in a mean wool clip residue of 5.8 mg/kg. Since that time OP levels have fallen significantly, with the mean OP levels on Australian fleece wool being 1.4 mg/kg in 2001-2002 (see above). Despite this, 54% of the samples tested had residues, which suggests that at least 50% of the flock is still being treated with OPs.

The percentage of the OP market that temephos may gain is very difficult to forecast. This market is currently dominated by diazinon, which made up about 90% of detected residues in 2001-2002, while chlorfenvinphos and propetamphos made up about 7.7 and 2.6% respectively. This suggests that while they are disappearing off the market, these two OPs were still being used to treat about 4.4 and 1.5 % of the national flock, which casts some doubt on the registrant's claim that at market maturity temephos will only treat about 1% of the flock. An estimate of at least 5% might be more accurate.

To cover this uncertainty several other scenarios are modelled in Table 3.6. These include a 5% market share based on 30 or 70% long wool use. Alternatively a mean clip level of 0.1 mg/kg is assumed, similar to that of the other OPs (chlorfenvinphos and propetamphos) currently available, apart from diazinon.

Table 3.6: Determination of further Q values covering various scenarios by DEH

Parameters	**5% market share- 30% long wool treatment***	**5% market share- 70% long wool treatment****	**0.1 mg/kg residues in total clip**
Concentration of temephos in long wool at harvest (mg/kg)	5.0	5.0	0.1
Mass of wool scoured in one day (tonnes)	50	50	50
Predicted market share of *Cooper Assassin Sheep Dip* (%)	1.5***	3.5***	NA
Mass of temephos entering scouring plant on wool (g)	3.75	8.75	5
Percentage remaining on scoured wool (%)	4	4	4
Percentage removed with grease during scouring (%)	30	30	30
Percentage removed during sewage treatment (%)	50	50	50
Mass of temephos discharged (g)	1.26	2.94	1.68
Flow rate of sewage treatment plant (ML/d)	50	50	50
Predicted concentration in sewage outflow (ng/L)	25.2	58.8	33.6
Dilution in plume#	0.02	0.02	0.02
Predicted Environmental Concentration (PEC) (ng/L)	**0.504**	**1.176**	**0.672**
Predicted No Effect Concentration (PNEC) (ng/L)	0.7	0.7	0.7
Quotient (PEC/PNEC)	**0.72**	**1.68**	**0.96**

* Assumes only 30% of treatment is on long wool, with much treatment before 9 months growth.
** Assumes 70% of treatment is on long wool, with much treatment before 9 months growth.
*** Of long wool treatment (assumes that the contribution from short wool treatment is minor, ie less than 1 mg/kg).
# A plume dilution factor of 0.02 was derived from the study by Grundy et al. (2000)
NA = Not applicable

The above calculations show either a hazard exists or at best there is only a very small safety margin. Clearly if the market share reaches 5% of the national flock, with more than about 40 % (or 2% of the national flock) used on long wool, a potential hazard to aquatic invertebrates inhabiting waters close to the ocean outfall could arise. There could be a similar hazard if temephos residues in the national clip rise above 0.1 mg/kg. This very low acceptable level in the clip compared with other OPs (see above) reflects the much higher aquatic toxicity of temephos to daphnia.

The latter calculation assumes complete mixing of wool after shearing and before scouring takes place. Clearly if this does not occur, and a "hot spot" arises, for example with 10% of a single daily scour lot containing temephos residues close to the maximum level of 9.6 mg/kg (ie all treated with 9 months wool), resulting in a residue of 0.96 mg/kg when combined with clean wool, a hazard clearly exists (Q ~10). This would still be the case if the "hot spot" is in the order of the mean value of around 5 mg/kg (Q ~ 5).

3.7.4 Conclusions regarding retention of long wool use

Table 3.4 indicates a local hazard will exist if the scour lot contains more than 1% of wool contaminated with the maximum expected temephos residues. DEH has no information on the likelihood/probability of such a scenario occurring. However, from the total calculations it is clear that if much above 1% of the sheep flock is to receive late long wool treatment with temephos, or more than 2% of sheep receive long wool treatment at any time, scouring of wool could pose an unacceptable hazard to aquatic invertebrates inhabiting waters close to the ocean outfall.

Given that there are no mechanisms available to regulate changes in market share, including the short/long wool split, DEH concludes that continued use of the product on long wooled sheep according to current label directions at the current 3 month WWP would be likely to have an unintended effect that is harmful to animals, plants or things or to the environment, ie to aquatic invertebrates inhabiting waters close to the ocean outfall. This is the direct outcome of the much higher aquatic toxicity of temephos to daphnia, which has been demonstrated since our original assessment of long wool use.

It follows then, that DEH recommends a variation to the approved label that is the removal of all instructions pertaining to long wool sheep. This variation would realise use that would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

3.7.5 DEH's Conceptual Model under Australian Conditions

The maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall, ie the PNEC of 0.7 ng/L to *Daphnia magna*. The result of this calculation is shown in Table 3.7.

Table 3.7: Calculated concentration of temephos (ng/L) in raw greasy wool based on the target concentration of 0.7 ng/L at the Black Rock ocean outfall for temephos

Parameters	**DEH's estimates**
Target concentration (ng/L)	0.7
Load entering the ocean which takes into account the plume dilution factor of 50 (ENV) (g)	50 ML X 0.7 ng/L X 50 = 1.75
Load entering sewage treatment plant (STP) (g)	100/50 X 1.75 = 3.5
Load entering wax recovery (WAX) (g)	100/70 X 3.5 = 5.0
Load entering scour (SCR) (g)	100/96 X 5.0 = 5.2
Concentration of residues on wool (mg/kg)	5.2/50 = 0.10

The above calculation confirms that the maximum acceptable mean residue in the wool clip is 0.1 mg/kg and confirms that the maximum market share for long wool treatment before a potential hazard arises to aquatic invertebrates inhabiting waters close to the ocean outfall is not much above 1%. This is also the case if a "hot spot" were to arise.

3.8 TRADE

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours.

3.8.1 UK/EU EQS/MAC Requirements

In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry to meet environmental standards. The former website[9] (http://www.basicweb.fsnet.co.uk/index.htm) includes the recently proposed values for total organophophates (OPs) of an AA of 30 ng/L and an MA of 100 ng/L, respectively. These are confirmed as values for freshwater in Annex G of of the Scottish Environmental Protection Agency web site[10]. While there are no specific values for temephos, values of 30 ng/L and 100 ng/L for AA and MAC, respectively, for total OPs are assumed for temephos.

The calculated wool residue levels on the basis of the EU/UK total OP requirements are shown in Table 3.8.

Table 3.8: Predicted concentration of temephos (ng/L) in river based on the EU/UK model by DEH

Parameters	Bale data	
	AA (chronic)	MAC (acute)
Concentration of temephos in wool at harvest (mg/kg)	9.6	9.6
Mass of wool scoured in one day (tonnes)	27.6	27.6
Predicted market share for *Assassin* (%)	1	1
Mass of temephos entering scouring plant on wool (g)	2.65	2.65
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	50	50
Mass of temephos discharged (g)	0.25	0.25
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	1.7	3.5
UK/EU expected requirement (ng/L)	10	100

On the basis of wool residue level from the bale samples and the estimated 1% market share, the predicted environmental concentrations for both AA and MAC would meet the expected UK/EU requirements. Calculations suggest a market share of close to 6% could be achieved before a hazard arises. It should also be remembered that this is a very worst case estimate as it assumes that all treatments are on long wool sheep at 9 months, ie on the last legally available time when treatment can occur, and that the highest residues found in any bale will always occur. Clearly this is highly unlikely.

Due to the much less sensitive end point used there is also a much lower hazard if a "hot spot" were to occur, as this would have to constitute about 6% of the processing lot and contain the maximum residue levels of about 10 mg/kg. Therefore, use of

[9] Available from 2001 but removed in mid 2003.
[10] Available on 6 march 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf

Assassin as labelled on both long and short wool is unlikely to unduly prejudice Australia's export trade.

3.8.2 DEH's Conceptual Model for EU/UK requirements

Using the conceptual model, the maximum mean concentration in raw wool can be estimated from the target concentration at the river outfall as shown in Table 3.8.

Table 3.8: Calculated concentration of temephos (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 30 (AA) and 100 (MAC) ng/L for temephos.

DEH based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MA (Acute)**
Target concentration (ng/L)*	30	100
Load entering the river (ENV) (g)	149 ML X 30 ng/L = 4.47	71 ML X 100 ng/L = 7.1
Load entering sewage treatment plant (STP) (g)	100/50 X 4.47 = 8.94	100/50 X 7.1 = 14.2
Load entering on-site treatment plant (OST) (g)	100/20 X 8.94 = 44.7	100/20 X 14.2 = 71
Load entering scour (SCR) (g)	100/96 X 44.7 = 46.563	100/96 X 71 = 74
Concentration of residues on wool (mg/kg)	46.563/27.6 = 1.69	74/27.6 = 2.68

* UK is the 'worst case scenario' for the EU and has EQS AA and MAC of 30 and 100 (ng/L) for individual organophosphates (see footnote 13), which do not include temephos, as well as total organophosphates. Hence these AA and MAC values are assumed for temephos.

On the basis of the maximum residue level of 9.6 mg/kg from bale samples and the predicted market share of 1%, it is estimated that the residue concentration in the wool clip would be 1% X 9.6 mg/kg = 0.096 mg/kg which is well below the AA and MAC of 1.69 and 2.68 mg/kg (see above table), respectively. Thus there is a low likelihood of undue prejudice to Australia's export trade under the current WHI of 3 months for temephos as long as its market share stays below 6% (this is based on a more likely level of 5 mg/kg, which takes into account that not all sheep would be treated with 9 months wool growth).

3.9 CONCLUSIONS

The registrant has provided additional data on the toxicity testing of temephos to *Daphnia magna*. The results indicate that the very sensitive result for *Daphnia magna* should be used as the environmental end-point for aquatic organisms arising from wool scouring under Australian conditions.

The registrant has also provided the calculated half-lives for the depletion of temephos in wool in sheep treated at 9 or 10 months wool growth indicating no significant difference between the two treatments and mean half-lives of 48 and 53 days for the 9 or 10 months wool treatment, respectively. In particular, the data for the 9 months wool growth give a clear indication of the wool residue degradation with time.

DEH calculations indicate that with the current wool withholding period (WWP) of 3 months, if much above 1% of the sheep flock is to receive late long wool treatment with temephos, or more than 2% of sheep receive long wool treatment at any time, scouring of wool could pose an unacceptable hazard to aquatic invertebrates inhabiting waters close to the ocean outfall. DEH has no information on the likelihood/probability of

such a scenario occurring. Given that there are no mechanisms available to regulate changes in market share, including the short/long wool split, DEH is not satisfied that that continued use of the product according to its label instructions on long wooled sheep including the current 3 month WWP would not be likely to be harmful to aquatic invertebrates inhabiting waters close to the ocean outfall. This is the direct outcome of the much higher aquatic toxicity of temephos to daphnia, which has been demonstrated since our original assessment of long wool use.

Regarding export trade, on the basis of wool residue level from the bale samples and the estimated 1% market share, the predicted environmental concentrations for both AA and MAC would readily meet the expected UK/EU requirements. Calculations suggest a market share of close to 6% could be achieved before a hazard arises. It should also be remembered that this is a very worst case estimate as it assumes that all treatments are on long wool sheep at 9 months, ie on the last legally available time when treatment can occur, and that the highest residues found in any bale will always occur. Clearly this is highly unlikely. Calculations also show an acceptable hazard if a "hot spot" were to occur, as this would have to constitute about 20% of the scour lot and contain the maximum residue levels of about 10 mg/kg. Therefore, the DEH concludes that the use of temephos on both long and short wool according to currently approved labels is unlikely to prejudice Australia's export trade. However, note that the WWP currently stated on labels is applicable to wool scouring in Australia, so an overseas WWP statement would be required.

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CHAPTER 4 - CHLORFENVINPHOS

Four products containing chlorfenvinphos were included in the Sheep Ectoparasiticides Review in accordance with the APVMA Gazette of 7 September 1999. However, since that time the registration of *Cooper's Suprex 100 Jetting Fluid* (Product No 33428, Schering-Plough Animal Health Ltd) and *WSD Jetting Fluid 100 Jetting Fluid for the Control of Flystrike on Sheep* (Product No 39576, Western Stock Distributors) have been cancelled. *Barricade 'S' Cattle Dip and Spray* (Product No 45211, Fort Dodge Australia Pty Ltd) and *Cooper's Blockade 'S' Cattle Dip and Spray* (Product No 46815, Schering-Plough Animal Health Ltd) remain on the market. However, instructions for use on sheep have been removed from the label for the former, and only treatment of sheep for ticks and buffalo fly (a very minor use) remains on the label for the latter.

On the basis that sheep ectoparasiticide products containing chlorfenvinphos are approved for use on sheep to treat ticks and buffalo fly only, there is expected to be very little if any use of sheep ectoparasiticide products containing chlorfenvinphos on sheep in accordance with existing approved label instructions. Therefore an environment assessment and comparative trade analysis on future exports of Australian raw wool has not been completed at this stage.

CHAPTER 5 - DICYCLANIL

5.1 INTRODUCTION

Dicyclanil was selected for review in accordance with the APVMA Gazette of 7 September 1999. A single product is registered containing this active constituent.

In 1998 the Department of the Environment and Heritage (DEH) conducted a detailed environmental assessment report for dicyclanil prior to registration of the product *Clik Spray-on Sheep Blowfly Treatment*, for the control of blowfly (*Lucilia cuprina*) strike in sheep.

Dicyclanil is an ectoparasiticide, its mode of action being as an insect growth regulator, preventing fly larvae from developing into pupae or adults. Tomlin (1997) indicates that it has high specificity to Diptera (flies) and Siphonaptera (fleas).

This report is based on the data submitted by Novertis Animal Health Australasia Pty Ltd for the Review, and the data contained in DEH's previous detailed environmental assessment report for dicyclanil.

5.2 CHEMICAL IDENTITY

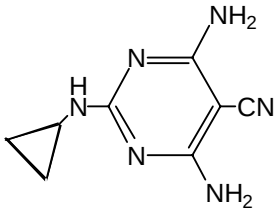
Chemical Name: 4,6-diamino-2-cyclopropylaminopyrimidine-5-carbonitrile (IUPAC)
4,6-diamino-2-(cyclopropylamino)-5-pyrimidinecarbonitrile (CAS)
5-cyano-2-cyclopropylaminopyrimidine-4, 6-diamine (ALTERNATIVE EXPRESSION OF NAME USED IN FATE STUDIES)

Common name: dicyclanil (ISO draft)

Manufacturer's Code Numbers: CGA-183893

CAS number: 112636-83-6

Structural formula:



Empirical formula: $C_8H_{10}N_6$

Molecular weight: 190.2

Purity of active constituent: Manufacturer's standard 98-102% w/w dicyclanil (range = 98.3-99.7%, av = 99.1% pure in five representative batches).

Impurities:	The active constituent may contain a maximum total of 2% of various organic and inorganic by-products and solvent residues, with maximum concentrations of individual substances ranging from 0.2-0.5% w/w.

5.3 PHYSICO-CHEMICAL PROPERTIES

Appearance:	*Pure substance:* Fine white powder *Active constituent:* White to beige powder
Odour:	*Pure substance & Active constituent:* Slight to acetic acid
Melting Point:	*Pure substance:* 250.5-252.4°C with thermal decomposition
Vapour Pressure:	*Pure substance:* 3.2 X 10^{-8} Pa @ 25°C (extrapolated) (< 0.0001 Pa - very slightly volatile, Mensink *et al*., 1995)
Henry's Law Constant[11]:	K = 1.65 X 10^{-8} Pa.m^3.mol^{-1} @ 25°C and pH 9 (minimum solubility) H = 6.64 X 10^{-12} @ 25ºC and pH 9 (H < 1 X 10^{-5} - very slightly volatile from water, Mensink *et al*., 1995)
Water Solubility:	*Pure substance (25°C):* pH 5.0 = 610 mg/L (buffer solution) pH 7.0 = 440 mg/L (buffer solution) pH 9.0 = 370 mg/L (buffer solution) pH 7.0 = 350 mg/L (pure water) (10-1000 mg/L - moderately soluble, Mensink *et al*., 1995)

Solubility in Organic Solvents: *Pure substance (mg/L solvent @ 20°C):*

hexane	<1	acetone	1200
toluene	19	ethyl acetate	1400
n-octanol	320	methanol	4900
dichloromethane	170		

n-Octanol/Water Partition Coefficient	log K_{OW} @ 25°C = 0.51 (pH 5.0), 0.69 (pH 7.1), 0.68 (pH 9.0)
Dissociation Constant:	pKa = 4.58 (weak base - calculations by DEH indicate that at low ionic strength, the proportion of the substance present as the neutral molecule is 72.5% at pH 5, 96.3% at pH 6 and ≥ 99.6% at pH 7 and above)
pH value	8.4 at 25°C

5.4 ENVIRONMENTAL EXPOSURE

5.4.1 Volume

Based on the actual 2001 and 2002 market volumes, the registrant expects the product will plateau at less than 12.5 tonnes active constituent per annum, with less than 7.5% of the total national flock treated.

[11] Calculated by the Department of the Environment and Heritage.

5.4.2 Application and use pattern

Clik Spray-on Sheep Blowfly Treatment is recommended for topical application by manual and automatic dosing guns along the backline and crutch area (the label stipulates "use only a Vetrazin Spray-On applicator gun"). It is administered once per year, before or at the beginning of fly activity, at rates according to the sheep's weight (Table 5.1), and may be used off-shears or on long wool sheep. According to the label's front panel, dicyclanil provides protection against flystrike for 18-24 weeks, and the registrant indicates that the product is particularly appropriate for areas where a long period of fly-strike protection is required.

Table 5.1: Dose recommendations for *Clik*.

Bodyweight of treated sheep (kg)	2 band treatment (body strike)		3 band treatment (body and crutch strike)	
	CLIK® (mL)	Dicyclanil (mg)	CLIK® (mL)	Dicyclanil (mg)
10-20	14	700	20	1000
21-30	16	800	25	1250
31-50	20	1000	30	1500
>50	24	1200	35	1750

Based on the label dose rate a mature sheep weighing between 31-50 kg would receive approximately 1.5 g for treatment or prevention of body and crutch strike. The registrant has confirmed that the length of the blowfly seasons, the length of protection offered by *Clik* and the relatively high cost per dose all combine to ensure that multiple treatment during a (wool) growing season does not occur in practice. Market analysis by the registrant is said to have indicated that >70% of *Clik* use is preventative, ie applied approximately 4-8 weeks after shearing, or 44-48 weeks prior to the next shearing.

General instructions on the label stipulate that the product should not be diluted, but applied directly using a *Vetrazin Spray-On* applicator gun, with the nozzle of the gun passing approximately 25 cm above the fleece, to provide a 15 cm band at each pass. The label recommends that the product should be applied in 2 bands along the back (overlapping at the midline), and if protection from crutch strike is also desired, a third band in the crutch area.

The label also stipulates that the product should not be applied in gusty or windy weather as spray drift will reduce the period of protection, and indicates that heavy rain following application could diminish the period of protection. Withholding periods of 28 days before slaughter for human consumption of meat in Australia and a wool withholding period (WWP) of 3 months before shearing are stipulated on the approved label.

5.5 ENVIRONMENTAL CHEMISTRY AND FATE

5.5.1 Environmental Fate

The following is the summary of the environmental fate of dicyclanil, as taken from DEH's original assessment report (July 1998, File No. 95/7060)

5.5.1.1 Hydrolysis

A hydrolysis study with radio-labelled dicyclanil was reported, with incubation in the dark under generally sterile conditions at pH 1, 3, 5, 7, 9 and 13 at ~50°C for 14 days. The studies showed that except under very alkaline conditions (pH 13), dicyclanil was hydrolytically stable, with a calculated hydrolysis half-life in excess of 1 year at 20-40°C.

5.5.1.2 Photolysis

A study of the photodegradation of dicyclanil in water (~10 ppm in pH 7 buffer) was conducted using cyclic illumination (12 hour light/12 hour dark) with an artificial light source (filtered Xenon arc lamp). Little degradation occurred in dark control samples (half-life ≥ 144 days) and degradation was also slow in irradiated samples under non-sensitised conditions (half-life = 61.2 days), but photodegradation occurred relatively rapidly in the presence of sensitisers (half-life 2.5 days with 1% acetone and 5.1 days with 10 ppm humic acids). Thus the study indicated that under aqueous conditions, dicyclanil is only slightly photodegradable (DT50 > 720 hours continuous illumination) in the absence of sensitisers, but fairly to readily photodegradable in the presence of sensitisers such as acetone or naturally occurring humic acids (DT50 = 96-240 or 24-96 hours continuous illumination, respectively). The main photoproduct was the dealkylation metabolite CGA 297107 (peak concentration 25-46% of applied radioactivity), with CGA 297106, produced by hydrolysis of CGA 297107, also present at up to 9% of applied radioactivity in the acetone study.

5.5.1.3 Degradation in soil and water

A study was provided of the degradation of ^{14}C-dicyclanil (labelled at the 2-pyrimidine position) in a loam soil under moist (75% of field capacity), aerobic conditions at ~20°C, with incubation continuing for up to 273 days. Dicyclanil was found to degrade rapidly, predominantly by dealkylation (loss of the cyclopropane ring) to form the metabolite CGA 297107 (peak concentration ~78% of applied radioactivity on the seventh day of incubation, declining to ~28% of applied radioactivity at the end of the incubation period). Calculated half-lives for dicyclanil and the metabolite CGA 297107 in the study were ~1.5 days and ~157-173 days, respectively.

A second identified metabolite was dicyclanil hydroxylated in the cyclopropane ring (peak concentration on day 21 of incubation at ~4-5% of applied radioactivity), and various other unidentified metabolites were detected at lower peak concentrations. Non-extractable radioactivity increased over the first 168 days of incubation to a peak of ~38% of applied radioactivity, before falling slightly to ~35% of applied radioactivity at 273 days. Cumulative evolution of ^{14}C-carbon dioxide at the end of the study had reached 24% of applied radioactivity, indicating significant mineralisation of the dicyclanil molecule. Thus dicyclanil is readily degradable (DT50 < 20 days - Mensink *et al.*, 1995) in soil under moist, aerobic conditions, but the principal metabolite formed, CGA 297107, is only slightly degradable (DT50 in the range 60-180 days - Mensink *et al.*, 1995) under the same conditions.

5.5.1.4 Mobility

Dicyclanil is very slightly volatile [vapour pressure < 1 X 10^{-3} Pa, H (Henry's Law Constant) < 1 X 10^{-5}] and unlikely to evaporate significantly from soil or water. A

batch equilibrium study of adsorption and desorption of dicyclanil on 5 soils indicated K_{OC} values for adsorption ranging from 89 to 273 (average 136) and desorption ranging from 108 to 403 (mean 186) for the first desorption cycle and 131 to 667 (mean 286) for the second desorption cycle. These data indicate that dicyclanil is likely to have medium to high mobility in soil (K_{OC} in the range 150-500 or 50-150, respectively). The results are consistent with the moderate water solubility (≥ 350 mg/L) and lack of lipophilicity of the substance (indicated by its log K_{OW} value of 0.51-0.69).

Some mobility in soil of dicyclanil and its metabolites was indicated in an aged soil leaching study, where a loam soil was incubated with ^{14}C-labelled dicyclanil for 73 hours and applied to columns of the same loam soil or a loamy sand soil, followed by leaching with the equivalent of 200 mm water over ≤ 48 hours. The aged soil contained 19.3% of applied radioactivity (AR) as dicyclanil, 70.0% as CGA 297107, 2.1% as U7.2, plus small amounts of various unknown metabolites. After leaching, the applied residues were largely restricted to the top 14 cm of the soil column with the loamy sand and the top 20 cm with the loam, with similar downward movement of dicyclanil and the principal metabolite CGA 297107. Very little radioactivity (< 0.2% of AR) was present in the leachate.

5.5.1.5 Field dissipation

A field dissipation study with dicyclanil was not provided, but the laboratory aerobic soil metabolism study indicates that dicyclanil reaching soil should degrade rapidly, largely to the metabolite CGA 297107, which should degrade more slowly. Some downward movement of the parent compound and metabolites may occur. No accumulation of dicyclanil in soil is expected.

5.5.1.6 Bioaccumulation

Based on its octanol/water partition coefficient (log K_{OW} = 0.51-0.69), dicyclanil is unlikely to bioconcentrate in fish, and has a predicted bioconcentration factor of ~2.

5.5.2 Existing Data for Fate of Residues Applied to Sheep

In the response to the September 1999 Gazette notice, the registrant again provided the wool residue studies (Kearney and Ochudzawa 1996; Smal and Chaophrasy 1996) that had already been reviewed in DEH's assessment report (File No. 95/7060). A summary taken from this report follows.

5.5.2.1 Fate in the period immediately following application

Two studies examined the fate of dicyclanil in the period immediately following application to sheep by either a pour-on method (using a formulation similar, but not identical, to *Clik*®) or jetting (using a different formulation). Retention of the applied spray was 90.0-98.2% (mean 94.7%) of the applied amount with the pour-on, but only 39-59% (mean 49.4%) with jetting (where the main loss was to run-off - mean of 37% of the dose to be administered). The data suggested that a small amount of the dried dose was lost by rub-off in the first 7 days after application (≤ 3.9% with pour-on application and ≤ 1.4% with jetting). Absorption was estimated at 4% of the applied dose with pour-on application and 2% of the retained dose with jetting, most of the

absorbed dose being recovered in urine and faeces. Residues in fleece were concentrated in the area where the substance was applied, but with low levels in untreated areas, indicating some spread of the material within the fleece.

5.5.2.2 Fate in wool between application and shearing

Three studies examined the fate of dicyclanil in wool, two studies with pour-on application (monitored for 20 and 46 weeks, respectively) and one with jetting (monitored for 24 weeks), again with different formulations for pour-on and jetting. Sheep were kept dry or exposed to simulated rain treatments, in both cases being kept under cover (hence significant photodegradation of dicyclanil is unlikely to have occurred, whereas this may be a possibility in practice due to sensitisation by humic acids). The concentration of dicyclanil remaining in wool was potentially affected by growth dilution (increase in staple length) as well as dissipation by degradation, absorption and movement within and from the fleece.

In the 20 week pour-on study, mean residues in whole staples from the treated backline area of sheep kept dry or exposed to a rain treatment declined from 10.9 g/kg and 13.7 g/kg, respectively, one week after application to 1.45 g/kg and <0.04 g/kg, respectively, after 20 weeks (half-lives calculated by DEH 53.2 and 6.5 days, respectively, in sheep kept dry or exposed to 500 mm rain). In the 46 week pour-on study, mean residues in whole staples from the treated backline area of sheep kept dry or exposed to a rain treatment declined from 8.58 g/kg and 4.92 g/kg, respectively, 2 weeks after application to 1.88 g/kg and 0.026 g/kg, respectively, after 23 weeks, and were 0.37 g/kg after 46 weeks in sheep kept dry (half-lives calculated by DEH 70.7 and 19.9 days, respectively, in sheep kept dry or exposed to 1000 mm rain).

In both studies, mean whole staple residues in wool from the flanks, which had not been directly treated, were much lower (0.37-0.39 g/kg at one week in the 20 week study and 0.29-0.34 g/kg in the 46 week study, falling to ≤0.10 g/kg by 20-23 weeks - half-lives calculated by DEH for sheep kept dry were 68.4 and 22.1 days, respectively, in the 20 week and 46 week study).

In the jetting study, mean residues in whole staples from the treated area of sheep were much lower, falling from 0.94-1.80 g/kg 2 days after application to 0.20-0.33 g/kg after 24 weeks, final residues with a rain treatment differing little from those in sheep kept dry, despite more rapid initial dissipation (half-lives calculated by DEH = 67.4-82.6 days). DEH notes that none of these sheep were regularly exposed to sunlight, and the rate of degradation is potentially faster where there is opportunity for photodegradation to occur. Nonetheless, depending on the interval between application and shearing and the amount of exposure of the sheep to rain, a significant proportion of the applied substance may remain in wool at shearing, albeit at lower concentrations due to growth dilution as well as other means of dissipation.

In all cases, dicyclanil residues were largely concentrated in the portion of the staple that had originally been treated (i.e. the tip). Residues of the metabolite CGA 297107 were measured in the pour-on studies and found to be present at only low peak concentrations (mean whole staple concentration in backline wool <0.10 g/kg). It is also noted that these applications were not performed at the worst case scenario where

treated wool were harvested at 12 weeks after a long wool sheep treatment. Instead sheep were shorn at 8 weeks before treatment and monitored for 20 and 46 weeks after treatment for the two pour-on applications. These trials were akin to a short wool treatment. Therefore, it was difficult to derive the maximum wool residue concentration from both trials for use as input concentrations for hazard calculation in wool scouring.

Also, for the jetting application it was not clear at what stage of the wool growth sheep were treated but the wool residues were monitored for 25 weeks after treatment. Again it appeared this wool residue trial resembled a short wool treatment, and in total the data resulted in the need to be conservative when recommending the WWP at registration.

5.5.3 New Data for Fate of Residues Applied to Sheep

The applicant has provided new wool residue data based on the label recommendations for *Clik* on lambs and sheep with 6 weeks, 6 months and 9 months wool growth.

5.5.3.1 Report No. TR 02/03/1790: Depletion of dicyclanil residues from wool.

Two hundred and eight Merino sheep of mixed sex and age were selected for the study (Hosking and George 2002). These sheep were grazed on three properties; site one had 104 sheep consisting of unshorn 3 month old lambs and mature sheep with 6 weeks, 6 and 9 months wool growth respectively. Sites 2 and 3 had 52 mature sheep each, with 6 weeks and 9 months wool growth, respectively. Each treatment group consisted of 26 animals. Sheep were administered with *Clik* by spray-on application at the recommended label rate for body and crutch strike. The sheep that were treated with 6 weeks, 6 or 9 months wool growth were shorn about one year after their previous shearing ie about 10-11, 6 and 3 months after treatment, respectively. Lambs were shorn about 6 months after treatment. While detailed rainfall and temperature data are available for all sites, there is no indication whether these were over or under the long time averages to allow an understanding of the possible weather effects on the residue profile.

Dicyclanil and its metabolite residues in wool were determined by both the band and core sampling methods. Six sheep were band sampled for each treatment group. Wool staple length was measured immediately prior to band sampling. Backline and flank sites were measured and recorded as these sites formed part of the sample that was taken from a narrow band around the circumference of the sheep, excluding the belly. The remaining animals (n=20) were retained for full shearing as the core sampling group. At the final shearing, fleece wool from the core sampling groups of sheep were skirted and sorted into fleeces and pieces for each of the treatment groups (n = 20). The wool was baled in a manner that replicated commercial farming practices. Baled wool was core sampled using a wool corer attached to a cordless drill that cut the wool specimens into 15 mm lengths. The samples were stored below –20°C until preparation and analysis occurred.

Wool samples were analysed by HPLC to determine the concentration of dicyclanil and its metabolite CGA 297107 using the Analytical Procedure 239C.03 (George

2002). Control and fortified samples were included with every set of samples analysed. The core samples were analysed in duplicate except for the 6 weeks group at site 3 where they were analysed in triplicate.

The dicyclanil wool residue results for the band and core samples for lambs and sheep with 6 weeks, 6 and 9 months wool growth at sites 1, 2 and 3 are summarised in Tables 5.2 and 5.3.

Table 5.2: Mean dicyclanil level in wool (mg/kg) derived from the band samples at sites 1, 2 and 3.

Site	**Wool growth on shearing group**	**Approximate weeks after treatment**						
		Day 1	**4**	**8**	**12**	**16**	**24**	**46**
1	lambs	3040	471.0	18.0		3.0	1.5	
1	6 weeks	3340	265.0	35.2		15.1	6.3	1.0
2	6 weeks		634.0	75.3		12.5	5.1	2.5
3	6 weeks		813.0	148.0		25.5	8.0	2.6
1	6 months	638	170.0	43.7		20.0	7.5	
1	9 month	571	218.0	53.7	22.6			
2	9 month		123.0	69.5	20.5			
3	9 month		326.0	140.0	**22.9**			

Table 5.3: Mean dicyclanil level in wool (mg/kg) derived from the core samples at sites 1, 2 and 3.

Site	**Shearing group**	**Approximate weeks after treatment**					
		Fleece			**Pieces/bellies**		
		12	**24**	**46**	**12**	**24**	**46**
1	lambs		1.44			3.4	
1	6 weeks			<1.0			1.94
2	6 weeks			1.6			1.64
3	6 weeks			3.1			2.61
1	6 months		4.76			3.5	
1	9 month	16.1			6.3		
2	9 month	**20.6**			6.4		
3	9 month	4.5			3.1		

The results clearly indicate that in band samples the dicyclanil wool residues depleted with time for treated sheep at different wool growths, with treated sheep with 9 months wool growth having the highest residues remaining in wool at harvest. It is noted that wool residues in band samples and core (fleece) samples at shearing are surprisingly similar for sheep with the same period of wool growth, except that there is more variation in the fleece samples (where it ranges from 4.5 to 20.6 mg/kg for sheep with 9 months wool growth, and <1.0 to 3.1 mg/kg for sheep with 6 weeks wool growth). Normally band sample residues are higher than those in the core samples due to the effect of dilution by untreated wool.

Half-lives for the depletion of dicyclanil residues in wool calculated from the above trial were not included in the report. However, these are contained in the separate report by Horton (2002) provided at the same time. They ranged from 23 (for unshorn 3 month old lambs) to 50 days (treatment 6 weeks after shearing), with treatments

applied closer to the next shearing resulting in the shorter half-lives (26-33 days for 9 months wool compared with 42-50 days for 6 weeks wool, respectively).

5.5.4 Conclusions

On the basis of these results, it is apparent that the highest mean dicyclanil residues in wool are 22.9 mg/kg derived from the band sampling for sheep with 9 months wool growth. However, based on the more realistic core sampling results, this would correspond to a maximum wool residue level of 20.6 mg/kg. This value will be used in the hazard calculation as a comparison to that using the wool clip data.

5.6 ENVIRONMENTAL EFFECTS

5.6.1 Existing Ecotoxicity data

The following is the summary of the environmental toxicity of dicyclanil taken from the original July 1998 assessment report.

5.6.1.1 Birds

A study of the acute oral toxicity of dicyclanil found that the LD50 from a single oral dose was in the range 500-1620 mg ai/kg bodyweight to Japanese quail (*Coturnix coturnix japonica*), indicating that the substance is slightly toxic to this bird species (500< LD50 ≤2000 mg/kg bw). The no observed effects level (NOEL) for this test was much lower than the LD50, at 50 mg/kg bw, because while mortalities occurred only at the highest dose (1620 mg ai/kg), various other (usually temporary) effects were observed at lower doses (lethargy at 50-1620 mg ai/kg, lower food consumption for a period at 154-1620 mg ai/kg and more serious effects at 500 and 1620 mg ai/kg). A subacute dietary toxicity study with dicyclanil and the same species indicated an LC50 with dicyclanil of >5000 ppm, i.e. practically non-toxic. Based on a very minor effect of dicyclanil on initial food consumption at 490 ppm, the NOEL was <490 ppm, with more practically significant effects on food consumption and bodyweight gain evident at 1565 ppm.

5.6.1.2 Aquatic Organisms

Acute toxicity tests (96 hour exposure, static test conditions) with dicyclanil indicated a LC50 value in the range 32-68.3 mg/L (nominal concentrations; No Observed Effect Concentration (NOEC) = 32 mg/L) to rainbow trout (*Onchorynchus mykiss*) and a LC50 of >67.8 mg/L (mean measured concentrations; NOEC = 37.8 mg/L) to bluegill sunfish (*Lepomis macrochirus*). A limit test of the toxicity of the metabolite CGA 297107 to rainbow trout indicated a LC50 >86.5 mg/L and NOEC <86.5 mg/L. Hence both substances are at most slightly toxic (10< LC50 ≤100 mg/L) to these fish species.

Acute toxicity tests (24 or 48 hours exposure under static test conditions) with dicyclanil and the daphnid *Daphnia magna* indicated that with acute exposure, dicyclanil was moderately toxic to daphnids (24 hour EC50 = 17 mg/L nominal concentration in one test, 48 hour EC50 = 8.3 mg/L nominal concentration in a second test and 48 hour EC50 = 1.1 mg/L in a third test with measured concentrations). In each case, the NOEC was much lower than the EC50 for immobilisation (0.58 mg/L, <0.58 mg/L and 0.08 mg/L, respectively). An acute toxicity test with the metabolite

CGA 297107 and *D. magna* indicated a 48 hour EC50 of >100 mg/L (NOEC = 100 mg/L), i.e. practically non-toxic.

A test of the chronic exposure (21 days) and reproductive toxicity of dicyclanil indicated greater toxicity to adult daphnids (21 day EC50 in the range 0.060-0.19 mg/L nominal concentrations) and much greater toxicity to reproduction (EC50 could not be calculated, but the NOEC was < 0.0019 mg/L based on statistical comparison with the control, though the practical effect of this difference appeared minor). Measured concentration data were not obtained in this test and the test was judged deficient by DEH, and therefore not able to be used in the hazard/risk assessment.

72 hour growth inhibition tests indicate that dicyclanil and the metabolite CGA 297107 are both slightly toxic to freshwater green algae (EbC50 of dicyclanil to *Scenedesmus subspicatus* = 19.5 mg/L and EbC50 of CGA 297107 to *Selenastrum capricornutum* = 74.8 mg/L, both based on mean measured concentrations).

5.6.1.3 Terrestrial invertebrates

Two studies of the toxicity of dicyclanil to the earthworm species *Eisenia foetida* were reported, one indicating a 14 day exposure LC50 >1000 mg/kg dry soil (NOEC <62.5 mg/kg), and the other a 14 day LC50 of 510 mg/kg (NOEC = 37 mg/kg - all nominal concentrations). Thus dicyclanil is slightly toxic to earthworms exposed to it in soil (LC50 in the range 100-1000 mg ai/kg dry soil).

5.6.1.4 Phytotoxicity

Phytotoxicity from dicyclanil appears unlikely following use of the substance directly on sheep.

5.6.1.5 Micro-organisms

An activated sludge respiration inhibition test indicated no significant inhibitory effect of dicyclanil in the concentration range tested (up to 105.5 mg/L), thus dicyclanil has low toxicity to sludge micro-organisms.

5.6.2 New Ecotoxicity Data

The registrant has now submitted a report on the chronic toxicity study of dicyclanil to *Chironomus riparius* to address the deficiency in the ecotoxicity data identified in the original environmental assessment of *Clik Spray-on Sheep Blowfly Treatment*.

5.6.2.1 ECT Study Number: RIME (Leweke et al. 2001)

The study was performed in accordance with the proposed OECD guideline 218 for the testing of chemicals: “Sediment-water chironomid toxicity test using spiked sediment”, February 2000.

First instar chironomid larvae were exposed to a concentration range of the test chemical and controls in a static sediment-water system in glass vessels. The artificial sediment consisted of 4-5% dry weight sphagnum moss peat (particle size ≤ 1 mm), 20% kaolin clay (dry weight) and 75-76% quartz sand. The test substance was spiked into the sediment and first instar larvae were subsequently introduced into the test vessels in which the sediments and water concentrations had been equilibrating for 48

h. The test organisms were exposed to these concentrations and controls for a period of 28 days. The larvae were fed during the period of the test. The effects to be determined were reduced emergence rate and development rate as compared to the control.

The temperature, pH, dissolved oxygen content and water hardness of the overlying water were measured in all test vessels. The tests were conducted at 20 ± 2°C. During each measurement, the water temperature remained in the range of ± 1°C in all test vessels. The light regime was 16/8 h light/dark with an intensity of 500 to 1000 lux. The lethal and sublethal effects values were compared with control values to determine the Lowest Observed Effect Concentration (LOEC) and hence the NOEC.

To define the concentrations of the definitive test, two range finding tests were performed. This was done in sediment-water systems consisting of 34.25 g sediment and 170 mL overlying water. At the beginning of the test, 10 larvae per vessel were inserted. The first range finding test was performed as a 10-day growth test. The end points were mortality and dry weight of the larvae in comparison to the control. The second range finding test was performed as a combination of a 10-day growth test and a 28-day test with mortality and emergence as the end points. The range finding tests indicated a NOEC and LOEC of 0.01 and 0.1 mg/kg sediment (dry weight [dw]), respectively.

Definitive tests were performed to determine the development rate and emergence rate based on the nominal concentrations of 0.045, 0.137, 0.412, 1.235, 3.704, 11.11, 33.33 and 100 µg/kg sediment (dw). The results indicated that dead pupae and incompletely hatched larvae were observed at the test concentration of 100 µg/kg. The NOEC based on observations concerning the test organisms was 33.33 µg/kg (dw) and the corresponding LOEC was 100 µg/kg (dw).

In analytical samples without test organisms, dicyclanil and its metabolite were spiked into sediment specimens, pore water and overlying water to determine the % recovery for the test chemicals. The average recovery for dicyclanil in water samples (pore water and overlying water) was 91.1% and the corresponding metabolite (CGA 297107) was 88.9%. The average recoveries for dicyclanil and its metabolite in sediment were 86.0% and 92.3%, respectively. The Limit of Detection (LOD) was estimated at 2.5 µg/kg for sediment samples and 0.25 µg/L for water samples. The Limit of Quantitation (LOQ) was found to be 25 µg/kg sediment (dw) for sediment samples and 1 µg/L for water samples. The applicant indicated that no corrections were performed for recoveries as the values were within the required 70-110% range.

In actual testing using test organisms, the concentration of dicyclanil and its metabolite were analysed in centrifuged sediment, overlying water and pore water of the test specimen after a cartridge clean-up. The mobile phase eluate was injected onto the HPLC system. Dicyclanil and its metabolite were analysed from sediment samples by

Table 5.4: Determinations of concentrations of dicyclanil and its metabolite for the Chironomid toxicity studies in sediment, pore water and overlying water samples

Compartment	Sample No.	Nominal concentration of dicyclanil (µg/kg sediment [dw])	Total amount of dicyclanil (µg)	Test period (days)	Concentration dicyclanil (µg/kg sediment[ww])	Metabolite concentration (µg/kg sediment [ww]	Total residues expressed in dicyclanil* (µg)
Sediment	SN 40	33.33	8.61	0	<LOQ (21.3)	<LOQ	6.9
	SN 40	33.33	8.61	0	<LOQ (24.5)	<LOQ (12.2)	12.9
	SN 44	100	25.88	0	97.3	<LOQ	31.5
	SN 44	100	25.88	0	59.1	<LOQ (8.1)	22.5
	SN 44	100	25.88	0	72.4	<LOQ	23.4
	SN 71	33.3	9.0	28	<LOQ (18.7)	<LOQ (15.5)	12.9
	SN 67	100	26.32	28	<LOQ (47.8)	<LOQ (10.4)	20.1
	SN 12	0	0	0	<LOQ	<LOQ	0
	SN 63	0	0	28	<LOQ	<LOQ	0
Pore water			Volume (mL)				
	SN 2	20,000	NA	0	19,750		
	SN 41	33.3	51	0	<1	<1	0
	SN 41	33.3	51	0	1.0	<1	0.05
	SN 45	100	51	0	<1	<1	0
	SN 45	100	51	0	4.0	<1	0.21
	SN 84	33.3	54	28	<1	<1	0
	SN 80	100	54	28	3.0	<1	0.16
	SN 13	0	51	0	<1	<1	0
	SN 76	0	59	28	<1	<1	0
Overlying water	SN 19	0.137	200	0	<1	<1	0
	SN 23	0.412	200	0	<1	<1	0
	SN 27	1.235	200	0	<1	<1	0
	SN 31	3.704	200	0	<1	<1	0
	SN 35	11.1	200	0	<1	<1	0
	SN 39	33.3	200	0	<1	<1	0
	SN 39	33.3	200	0	<1	<1	0
	SN 43	100.0	200	0	<1	<1	0
	SN 43	100.0	200	0	<1	1.0	0.51
	SN 81	33.3	400	28	<1	<1	0
	SN 77	100	400	28	<1	<1	0
	SN 11	0	200	0	<1	<1	0
	SN 74	0	200	28	<1	<1	0

LOQ = 25 and 1 µg/kg sediment (dw) for sediments and water samples, respectively
LOD = 2.5 and 0.25 µg/kg sediment (dw) for sediments and water samples, respectively
Values in brackets were determined below the LOQ and were used in the determination of total residues
* Denotes total residues expressed as dicyclanil calculated as follow:
([dicyclanil](ww) + [metabolite](ww) X 1.2669) X humidity (%) X amount of sediment specimen (dw)
where 1.2669 is the conversion factor for the difference in molecular weight between metabolite and dicyclanil (Note that the applicant did not provide the % humanity but has provided the specimens wet and dry weights to the table and an alternative total residue calculation).

using a soxhlet extraction with methanol. The pore water samples were prepared by centrifugation of the sediment. The results for the determination of the concentrations of dicyclanil and its metabolite in sediment, pore water and overlying water on the basis of the NOEC and LOEC determined from the definitive tests are shown in Table 5.4.

The data indicate that the concentrations of dicyclanil and its metabolite were below or close to the non-detectable level in pore water and overlying water. It is noted that concentrations of dicyclanil and its metabolite were measured as wet weight in sediments (refer to Table 4). The registrant has applied a formulae to calculate the total residues expressed as dicyclanil in the sediments which take into account the % moisture and conversion factor of 1.2669 for the metabolite.

On the basis of the total residues determined in sediments and water samples, the registrant has calculated the % recoveries of dicyclanil and its metabolite performed in sediment, pore water and overlying water. The results are shown in Table 5.5.

Table 5.5: Percentage of measured concentrations compared to the nominal concentrations of samples in the different compartments at the beginning and the end the 28 days test period.

Sample No.	**Nominal concentration dicyclanil (µg/kg sediment [dw])**	**Compartments**	**Test period (day)**	**Recovery dicyclanil %**	**Recovery CGA 297107 %**	**Total recovery %**
SN 2	**20 mg/L**		-2	98.7	-	98.7
SN 40	33.33	Sediment	0	80.1	*	80.1
SN 41	33.33	Pore water	0	0.6	*	0.6
SN 39	33.33	Overlying water	0	*	*	*
SN 40	33.33	Sediment	0	92.1	**58.1**	150.2
SN 41	33.33	Pore water	0	*	*	*
SN 39	33.33	Overlying water	0	*	*	*
SN 44	100.00	Sediment	0	121.7	*	121.7
SN 45	100.00	Pore water	0	*	*	*
SN 43	100.00	Overlying water	0	*	*	*
SN 44	100.00	Sediment	0	73.9	**12.8**	86.7
SN 45	100.00	Pore water	0	0.8	*	0.8
SN 43	100.00	Overlying water	0	1.9	*	1.9
SN 44	100.00	Sediment	0	90.5	*	90.5
SN 45	100.00	Pore water	0	*	*	*
SN 43	100.00	Overlying water	0	*	*	*
SN 71	33.33	Sediment	28	70.1	**73.7**	143.8
SN 84	33.33	Pore water	28	*	*	*
SN 81	33.33	Overlying water	28	*	*	*
SN 67	100.00	Sediment	28	60	16.6	76.6
SN 80	100.00	Pore water	28	*	0.6	0.6
SN 77	100.00	Overlying water	28	*	*	*

* Denotes measurements were <LOD
Note that there are two SN 71 samples and the SN 2 sample has a concentration of 20,000 mg/L reported in the submission

The % recoveries of dicyclanil and its metabolite in pore water and overlying water were consistent with their concentrations determined in Table 5.5 at the nominal concentrations of 33.33 and 100 µg/kg sediment (dw). It is observed that dicyclanil was recovered mostly in the sediments with reduced concentrations at the end of the test period (day 28). However, recovery of its metabolite increased from non-detectable level to 73.7% in sediment from day 0 to day 28 at the nominal concentration of 33.33 µg/kg sediment. This may be explained by the fact there was microbial activity in the sediments resulting in the formation of the metabolite.

It is noted that at a nominal concentration of 33.33 μg/kg sediment and day 0 sampling, there is a significant increase in the metabolite recovery (58.1%) in one of the samples reported in the sediment compartment. This anomaly was also observed at the nominal concentration of 100 μg/kg and day 0 sampling where the metabolite recovery of 12.8% was obtained in the sediment sample in one of the similar test systems. The registrant concludes that the metabolite is formed to an extent, that within reasonable variation, exceeds the level of detection. Replicated analyses on SN 40 and SN 44 were performed to assure the quality of the results. However, the registrant did not clarify the absence of metabolites in similar test systems.

It is also noted that the % recovery of dicyclanil in sediment from day 0 to day 28 appears to have decreased from 92.1 to 70.1% and from 121.7 to 60% at the nominal concentrations of 33.33 μg/kg and 100 μg/kg sediment, respectively. The results in the recovery studies clearly indicate that dicyclanil was adsorbed strongly to sediments. This is in strong contrast to the earlier adsorption and desorption studies (Plücken 1997) indicating dicyclanil is likely to have medium to high mobility in soil, consistent with the moderate water solubility (350 mg/L) and lack of lipophilicity of the substance (M^{c}Call 1980). Furthermore, on the basis of the Gustafson Ubiquity Score (GUS) calculation, the metabolite is likely to be a better leacher than dicyclanil (see DEH 1998 report) and thus the high recovery (73.7%) observed for the metabolite in sediment on day 28 at the nominal concentration of 33.33 μg/kg is surprising.

The author indicated that the study reported moderate adsorption and moderate to low mobility for dicyclanil. The author also indicated, on the basis of the cited literature, that dicyclanil's aniline like structure is likely to bind strongly to soil and sediment. As explained above DEH does not agree with the author's statement that dicyclanil has moderate adsorption and moderate to low mobility. DEH also considers it inappropriate to extrapolate the soil binding effects of aniline to dicyclanil. The registrant should note that if dicyclanil binds moderately to soil or sediment, there would be little dicyclanil remaining for ocean discharge after sewage treatment in the scouring process since dicyclanil would be retained in the sludge. Therefore, dicyclanil in the aqueous phase, rather than in the sediments, is more appropriate for determining the hazard when dicyclanil is discharged into ocean.

5.6.3.2 Conclusions

The registrant has provided a report for a chronic toxicity study of dicyclanil to *Chironomus riparius* in accordance with the proposed OECD Test Guideline 218. DEH concludes that the results of this chironomid test are not acceptable to modify the previously used chronic environmental end point of 0.2 μg/L for dicyclanil. Our view remains that a result from a test where spiked water rather than spiked sediment is used is more appropriate for this relatively soluble pesticide.

5.6.4 End points used in the Hazard Assessment

The *Clik Spray-on Sheep Blowfly Treatment* label includes a WWP of 12 weeks on the basis of NOEC of 6 μg/L established for dicyclanil against *Daphnia magna*. In the hazard assessment at registration, the NOEC was reduced by 30 fold (6/30 = 0.2 μg/L) based on the observation that cyromazine, being structurally similar to dicyclanil, was

30 times more toxic to Chironomids than it was to *Daphnia*. This assumption was made in the absence of acceptable toxicity data of dicyclanil to Chironomids.

Dicyclanil has high specificity to Diptera and Siphonaptera and its mode of action is as an insect growth regulator, preventing fly larvae from developing into pupae or adults. There is a paper in the scientific literature (i.e. not a GLP study) on the related cyromazine toxicity to the chironomid (non-biting midge) species *Chironomus zealandicus*, an important fish food in various freshwater situations (Robinson and Scott, 1995). As this is a species of Diptera and cyromazine is also claimed to have a large degree of specificity to Diptera, it is not surprising that the highest toxicity was found in sensitive stages of this species (eggs or early instars). However, the most toxic 96 h LC50 was still only 100-400 mg/L for 2nd- and 3rd-instars, compared with a daphnia 48 h LC50 of >92.8 mg/L using measured concentrations. As is the case with dicyclanil and daphnia, the chronic toxicity is much higher and Robinson and Scott (1995) reported a maximum acceptable toxicant concentration (MATC) with chronic exposure of this species to cyromazine of 0.0175 mg/L.

There is therefore some uncertainty as to what endpoint to use for the Australian situation. Normally we would apply an assessment factor (AF) of 10 or 100 to the most sensitive acute result. While daphnids are the most acutely sensitive of the usual aquatic test species (48 h EC50 = 1.1 mg/L), they are not a very sensitive species due to dicyclanil's specificity and mode of action. A diptera species such as a chironomid would be preferred, but there are no acceptable results available (nor for the mysid shrimp which is usually a very sensitive marine invertebrate, though possibly less so in this case). Further, the 48 h NOEC for daphnia is much lower at 0.08 mg/L, indicating that dicyclanil's toxicity is chronic rather than acute, underlined by its much lower 21 day chronic toxicity to daphnia (see below).

On the understanding that there are no marine diptera in Australia, the acute daphnia result is used but with an AF of 1000 to derive the predicted no effect concentration (PNEC), ie 1.1 µg/L. This allows for the uncertainty as to which may be the most sensitive species, and the chronic mode of action, with the relatively high solubility of dicyclanil ensuring good dispersion once discharged.

For the overseas situation, in the absence of published EQS data, DEH would normally use the results of the study that clearly indicated chronic exposure to daphnids as the greatest hazard to any of the species tested, but this study was considered deficient, particularly as measured concentration data were not available. A NOEC of <2 µg/L (nominal) was indicated based on statistical significance, but the data were non-monotonic and a more reasonable NOEC, based on a decrease in the cumulative number of live young produced per female per day together with the occurrence of dead young, may be 6 µg/L (LOEC 20 µg/L – nominal concentrations). As noted above, in the hazard assessment in the July 1998 report, the NOEC was reduced by 30 fold (6/30 = 0.2 µg/L or 200 ng/L) on the basis that the related cyromazine was 30 times more toxic to Chironomids than it was to *Daphnia*.

It is noted that Shaw may have also considered the relative toxicity of cyromazine to daphnids and chironomids in deriving a value of 0.2 µg/L (= 200 ng/L) for the hazard

assessment of dicyclanil in British rivers (Russell 1998). Chironomids are likely to be exposed to these substances in British rivers downstream of scours, hence this is the appropriate value to use for hazard assessment for the EQS in that situation in the absence of an acceptable chironomid study (see above).

For the MAC, Savage (1998) used a figure of 11 μg/L, which appears to be derived from use of an assessment factor of 100 based on the daphnia acute 48 h EC50 of 1.1 mg/L. For the reasons outlined above this may not be sufficiently protective, and in this assessment we will use the value of 1.1 μg/L, as for the Australian situation.

5.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

The risk that dicyclanil would impact adversely on aquatic environments when scouring effluent is disposed of to land is low because of its low mobility in soils to which effluent would be applied. The main concerns arise in relation to discharge to sewer. Knowledge of sewage volumes, scouring rates and wool residues can be used to estimate concentrations leaving the outfall, which can then be compared with toxicity data to determine the environmental hazard.

5.7.1 Residue levels in the Australian wool clip

Each year since 1992-3 the Australian wool industry has undertaken a survey of the pesticide residues in national wool clip, but dicyclanil has only recently been registered and was first added to the list for the survey in the year 1999-2000.

Recent Australian Wool Innovations data (Scott Williams, AWI, personal communication, March 2003) indicate mean values for dicyclanil in Australian fleece wool of 0.1 and 0.4 mg/kg for 1999-2000 and 2000-2001, respectively. However, in 2001-2002 the mean residues in all wool sampled rose sharply to 1.8 mg/kg. This rose further to 2.1 mg/kg in 2002-2003, but dropped to 1.5 mg/kg in 2003-2004 (I Russell, 2004). In the latest figures 9.4% of samples had residues greater than the limit of resolution (LoR), and with the mean residue when treated at 16.2 mg/kg (compared with 20.6 and 23.0 mg/kg for 2001-2002 and 2002-2003, respectively), with the highest residue level in the survey at 80 mg/kg (note 140 mg/kg in 2002-2003). Residues at >50 mg/kg, which constituted only 0.5% of the sales lots, contributed 22% of the residue load, with a further 33% contributed by residues in the range 29-49.5 mg/kg (1% of sales lots). In total, 4.5% of the sales lots, with residues >10.0 mg/kg, contributed 88% of the residue load.

The mean value of 1.8 mg/kg for the past 3 seasons will be used as the input concentration for the hazard calculation for dicyclanil. For comparison, the residue level of 20.6 mg/kg representing the 2001-2002 mean residue when treated (as noted above, also the maximum wool residue level found in cored bale analysis during the registrant's testing) has also been used. This represents a "hot spot" sales lot, but may not be truly representative as based on the 2001-2002 AWI Wool Residue Survey 2% of the sales lots had residues in the range of 10.0 to 24.9 mg/kg, with 3% above this value.

5.7.2 Australian Model

The Australian model (Savage 1998) is used by DEH to predict the worst case level of dicyclanil present in sewage effluent entering the Barwon waters from the Black Rock treatment plant. DEH has used both the mean residue level data of 1.8 mg/kg for the past 3 seasons and the mean residue level of 20.6 mg/kg (when detected in lots) as the input concentrations for the hazard calculation of dicyclanil. The results of the calculation performed by DEH take into consideration the following parameters as shown in Table 5.6.

Table 5.6: Determination of Q values by DEH

Parameter	Wool clip sample	Mean residue if treated
Concentration of dicyclanil in wool at harvest (mg/kg)*	1.8	20.6
Mass of wool scoured in one day (tonnes)	50	50
Mass of dicyclanil entering scouring plant on wool (g)	90	1030
Percentage remaining on scoured wool (%)	4	4
Percentage removed with grease during scouring (%)	0	0
Percentage removed during sewage treatment (%)	0	0
Mass of dicyclanil discharged (g)	86.4	988.8
Flow rate of sewage treatment plant (ML/d)	50	50
Predicted concentration in sewage outflow (ng/L)	1728	19776
Dilution in plume#	0.02	0.02
Effective Environmental Concentration (EEC) ng/L	**34.6**	**395.52**
Predicted No Effect Concentration (PNEC) (ng/L)	1100	1100
Quotient (EEC/PNEC)	**0.03**	**0.36**

* These are based on the monitoring data for 2001-2002 from treatment under the approved label for *Clik.*

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).

DEH's hazard calculations indicate that an environmental hazard is unlikely to arise based on the AWI mean residues level data for the past 3 seasons or if the mean residue when treated of 20.6 mg/kg (representing a potential "hot spot" sales lot – see comments above) is used, as the Q value is <1 (as is appropriate for the comparison of the EEC with the PNEC). However, the safety margin for the latter is relatively small.

5.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of DEH's conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall under Australian conditionsie, the PNEC of 1100 ng/L. The results are shown in Table 5.7.

Table 5.7: Calculated concentration of dicyclanil (ng/L) in raw greasy wool based on the target concentration of 1100 ng/L at the ocean outfall for dicyclanil

Parameters	DEH's estimates
Target concentration (ng/L)	1100
Load entering the ocean which takes into account the plume dilution factor of 50 (ENV) (g)	50 ML X 1100 ng/L X 50 = 2750
Load entering sewage treatment plant (STP) (g)	100/100 X 2750 = 2750
Load entering wax recovery (WAX) (g)	100/100 X 2750 = 2750
Load entering scour (SCR) (g)	100/96 X 2750 = 2864.6
Concentration of residues on wool (mg/kg)	2864.6/50 = 57.3

The calculation indicates that there is unlikely to be an environmental hazard based on the 2001-2002 monitoring data of 1.8 mg/kg mean residues on all wool for dicyclanil under Australian conditions. This is also the case for the scouring of "hot spots" as represented by the mean residue when wool was treated of 20.6 mg/kg.

The calculations suggest that for an unacceptable hazard to occur to aquatic organisms close to the ocean outfall, residue levels in wool need to be above 50 mg/kg. As residue levels above this constituted only 1% of the sales lots in the 2001-2002 AWI survey (or 0.5% in 2003-2004), for a processing lot to contain that level of residue it would have to result from a small pocket of grazing country where most farmers use dicyclanil and the wool grown is such that little if any mixing occurs prior to processing. The probability of this would appear very unlikely.

In conclusion, treatment of sheep according to the approved label (including a 3 month WWP) and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

5.8 TRADE

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours.

5.8.1 UK/EU EQS/MAC Requirements

In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry to meet environmental standards. However, there are no AA and MAC EQS values for dicyclanil in the EQualSTM database[12] or the former website[13] (http://www.basicweb.fsnet.co.uk/index.htm), or in Annex G of of the Scottish Environmental Protection Agency web site (accessed on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf), and therefore the values derived above (200 ng/L for AA and 1100 ng/L for MAC, see Section 5.6.4) have been used. The calculated river levels on the basis of the EU/UK model and possible AA and MAC values are shown in Table 5.8.

[12] The EqualS^{TM} database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[13] Available from 2001 but removed in mid 2003.

Table 5.8: Predicted concentration of dicyclanil (ng/L) in river based on the EU/UK model

Parameters	Wool clip sample		Hot spot	
	AA (chronic)	**MAC (acute)**	**AA (chronic)**	**MAC (acute)**
Concentration of dicyclanil in wool at harvest (mg/kg)	1.8	1.8	20.6	20.6
Mass of wool scoured in one day (tonnes)	27.6	27.6	27.6	27.6
Mass of dicyclanil entering scouring plant on wool (g)	49.7	49.7	568.6	568.6
Percentage remaining on wool (%)	4	4	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	0	0	0	0
Percentage removed during sewage treatment (%)	0	0	0	0
Mass of dicyclanil discharged (g)	47.7	47.7	545.8	545.8
Flow rate of river (ML/d)	149	71	149	71
Predicted Environmental concentration in river (ng/L)	**320.1**	**671.8**	**3683**	**7687**
UK/EU expected requirement (ng/L)*	200	1,100	200	1,100

* The AA and MAC values are as derived above (see Section 5.6.4) for dicyclanil. Both the AA and MAC values have no official standing.

Using the AWI mean residue level result for the past 3 seasons of 1.8 mg/kg on all wool for dicyclanil, the predicted environmental concentration estimates fails and just meets the possible UK/EU requirements of 200 and 1,100 ng/L for AA and MAC, respectively. However, based on the mean residues of 20.6 mg/kg when wool was treated, it is apparent that both the possible AA and MAC values are greatly exceeded.

5.8.2 DEH's Conceptual Model for EU/UK requirements

The maximum mean concentration in raw wool can be estimated from the target concentration at the river outfall as shown in Table 5.9.

Table 5.9: Calculated concentration of dicyclanil (ng/L) in raw greasy wool based on the EU/UK model with the possible target concentrations of 200 (AA) and 11,000 (MAC) ng/L.

Parameters	AA (Chronic)	MAC (Acute)
Target concentration (ng/L)	200	1,100
Load entering the river (ENV) (g)	149 ML X 200 ng/L = 29.8	71 ML X 1100 ng/L = 78.1
Load entering sewage treatment plant (STP) (g)	100/100 X 29.8 = 29.8	100/100 X 781 = 78.1
Load entering on-site treatment plant (OST) (g)	100/100 X 29.8 = 29.8	100/100 X 781 = 78.1
Load entering scour (SCR) (g)	100/96 X 29.8 = 31.0	100/96 X 78.1 = 81.4
Concentration of residues on wool (mg/kg)	31.0/27.6 = 1.12	81.4/27.6 = 2.95

The above model confirms that based on the mean residues level on all wool of 1.8 mg/kg for dicyclanil from the past 3 seasons AWI monitoring data, the possible AA will not be met and the safety margin for the possible MAC value is relatively narrow. Based on the mean residue when wool was treated of 20.6 mg/kg data, it is apparent that both the possible AA and MAC values are greatly exceeded.

Based on the above estimates, the current use of *Clik* might adversely prejudice Australia's export trade. Note, however, that both the AA and MAC values used have no official standing.

5.9 WOOL WITHHOLDING PERIOD (WWP)

In its original submission for the Sheep Ectoparasiticides Review dated March 2000, the registrant proposed a Nil WWP for the current Australian use pattern for the product, and a WWP of 16 weeks under the UK requirements. These were based on the modelling available at the time (brief details only were provided).

The registrant's proposed nil local WWP is the same as that published by Horton and Campbell (2001). However, the proposed WWPs of <54 days and <56 for AA and MAC, respectively, by Horton and Campbell (2001) are significantly less than the 16 weeks originally estimated by the registrant using similar but less refined older methodology. Note that the Horton and Campbell (2001) estimates were based on a 10-fold increase in use based on the then AWI monitoring levels.

More recently (August 2002), the registrant provided additional wool residue data as assessed above (Section 5.6.3), as well as a report by Horton (2002) proposing to revise the UK WWP to 5 weeks based on all the available data, and using the latest version of the Horton-Campbell model.

Using the latest version of the Withholding and Blending Model (Horton and Campbell, 2001), the total wool residue data and their derived half-lives from the trials described above (Sections 5.6.2 & 5.6.3), as well as assuming 1200 mg was retained on a >50 kg sheep for a body strike treatment, and 1800 mg for a body and crutch strike, Horton (2002) was able to predict the residues from the approved label treatment with *Clik* and derive recommended maximum processing lot concentrations of 1,146 mg/kg for Australia and 1.75 and 46 mg/kg in wool for UK EQS AA and MAC respectively. This in turn was converted into sales lot maxima of >500, 66 and 266 mg/kg in wool respectively.

Note that Horton's (2002) Australian calculations were based on the daphnia acute 48 h EC50 of 1.1 mg/L, rather than the estimated 1.1 μg/L PNEC for chironomids used above. The former is clearly not appropriate as 50% of daphnia, which are very unlikely to be the most sensitive organism, would die at this concentration. Based on this inappropriate end point Horton concluded that even if sheep with 12 months wool are treated on the day of shearing, the residue of 336 mg/kg (1800 mg/5.35 kg fleece) would be well within the limits and therefore no WWP for Australian wool processing is required.

For the UK, Horton (2002) assumed that *Clik* will be used on a maximum of 10% of the sheep flock, and modelling using the 2000-2001 AWI survey data showed that a WWP of 34 days would be adequate to avoid exceeding 1.75 mg dicyclanil per kg of wool. Note that at 0.4 mg/kg mean residues were significantly below the 2001-2002 level of 1.8 mg/kg. Further, even though the same 200 ng/L EQS AA was used, the calculations were performed for the less demanding Calder River system. For the MAC, it was

concluded a WWP of 2 weeks would be adequate, but again the end point of 1.1 mg/L rather than 1.1 μg/L and the less demanding Calder River system, were used.

5.9.1 Conclusions concerning WWP

While DEH concludes above that treatment of sheep with *Clik* and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment, this is based on the current 3 month WWP. DEH is unable to agree with the registrant's modelling that a nil WWP is appropriate as this is based on the daphnia acute 48 h EC50 end point of 1.1 mg/L. This is clearly not appropriate as 50% of daphnia, which are very unlikely to be the most sensitive organism, would die at this concentration, and use of a more sensitive end point, such as the estimated 1.1 μg/L PNEC for chironomids DEH has used, is required.

Likewise DEH is unable to conclude a reduction of the WWP for scouring under overseas conditions is supportable, as calculations indicate that the registered use of *Clik* may already adversely prejudice Australia's export trade.

5.10 CONCLUSIONS

Dicyclanil is a synthetic insect growth regulator with high specificity to Diptera and Siphonaptera. A reliable chronic exposure study is lacking, but it has a high chronic toxicity to aquatic invertebrates (*Daphnia magna*), though acute toxicity to daphnids is only moderate. The main environmental concern is that residues of dicyclanil on harvested wool may impact on aquatic biota when scouring effluents are discharged.

The registrant has now provided a report for a chronic toxicity study of dicyclanil to *Chironomus riparius* in accordance with the draft OECD test guideline 218. DEH concludes that the results of this Chironomid test are not sufficient to modify the previously used chronic environmental end point of 200 ng/L for dicyclanil. DEH's view remains that a result from a test where spiked water rather than spiked sediment is used is more appropriate for this relatively soluble pesticide.

DEH's calculations using both the 2001-2002 AWI dicyclanil mean clip residue and mean residue if treated (1.8 and 20.6 mg/kg respectively) enable it to conclude that under Australian scouring conditions with the current WWP of 3 months the continued use of products containing dicyclanil in accordance with current label instructions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the Australian environment.

However, the DEH concludes there is a potential prejudice to trade associated with the use of products containing dicyclanil, based on a comparative analysis of likely scour residues and their likely future impact on exports of Australian raw wool. Again, this contrasts with the registrant's modelling which showed that a WWP of 34 days would be adequate for the AA EQS, and a WWP of 2 weeks for the MAC. However, this used the 2000-2001 AWI survey data (at 0.4 mg/kg this is significantly below the 2001-2002 level of 1.8 mg/kg), an inappropriate end point for the MAC calculations, and was also performed for the less demanding Calder River system.

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CHAPTER 6 - CYROMAZINE

6.1 INTRODUCTION

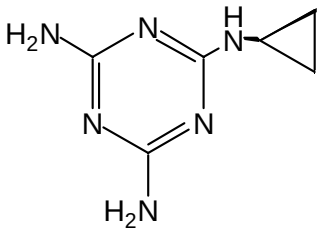
Cyromazine is the active constituent in two registered products included in the Sheep Ectoparasiticide Review. It is an insect growth regulator with contact action, interfering with moulting and pupation (Tomlin 1997).

Fleece residue data were provided for the nominated products, *Vetrazin Liquid Sheep Blowfly Treatment* and *Vetrazin Spray-On Sheep Blowfly Treatment*, both of which are used for the control of sheep blowfly. According to the APVMA's PUBCRIS database on 24 November 2003, 3 products under review are no longer registered, although a number of generic products with this use pattern have been registered since the start of this review.

Prior to this review, cyromazine wool residue data and wool scouring effects had not been evaluated for environmental effects by the Department of the Environment and Heritage (DEH). This review summarises the existing information including chemistry and environmental fate and toxicity data assessed previously for nuisance fly use and evaluates the wool residue data submitted by the registrant in March 2000 and March 2003.

6.2 CHEMICAL IDENTITY

Chemical Name:	N-cyclopropyl-1,3,5-triazine-2,4,6-triamine (IUPAC) 2-cyclopropylamino-4,6-di amino-s-triazine
Common name:	cyromazine
Manufacturer's Code Numbers/synonyms:	CGA-72662, OMS/WHO-2014
CAS number:	66215-27-8
Empirical formula:	$C_6H_{10}N_6$
Molecular weight:	166.2
Structural formula:	



Purity of Active:	Minimum purity of cyromazine active constituent = 95% w/w (range = 96.1-97.1%, average = 96.5% pure in three representative batches).

6.3 PHYSICO-CHEMICAL PROPERTIES

Appearance:	*Pure substance:* Colourless, crystalline. *Active:* White to beige powder
Melting Point:	*Pure substance:* 220-222°C
Vapour Pressure:	*Pure substance:* 1.8 X 10^{-7} Pa @ 20°C (< 0.0001 Pa - very slightly volatile, Mensink *et al*. 1995)
Henry's Law Constant[14]:	K = 2.72 X 10^{-6} Pa.m^3.mol^{-1} @ 20°C and pH 7.5 (minimum solubility) H = 1.17 X 10^{-9} @ 20°C and pH 7.5 (H < 1 X 10^{-5} - very slightly volatile from water, Mensink *et al*. 1995)
Water Solubility:	*Pure substance (20°C):* pH 7.5 = 11 g/L (buffer solution) (> 1000 mg/L - readily soluble, Mensink *et al*. 1995)

Solubility in Organic Solvents: *Pure substance (g/L solvent @ 20°C):*

hexane	(0.1)	acetone	(1.7)
toluene	(0.1)	n-octanol	(2.2)
methylene chloride	(0.3)	isopropanol	(2.5)
ethyl acetate	(1.3)	methanol	(22)

n-Octanol/Water Partition Coefficient	K_{OW} @ 20°C = 0.8
Dissociation Constant:	pKa = 5.3 and 1.7 (weak base - calculations by DEH indicate that at low ionic strength, the proportion of the substance present as the neutral molecule is approximately 50% at pH 5.3, 83% at pH 6 and ≥98% at pH 7 and above)

6.4 ENVIRONMENTAL EXPOSURE

6.4.1 Volume

No information was provided for the market share of cyromazine products, but it is noted Savage (1998) estimated 26% of the national flock was treated with products containing this active constituent.

6.4.2 Application and use pattern

Labels for both Vetrazin products contain instructions for long wool treatment/prevention of blowfly strike on sheep. The maximum dose rate for *Vetrazin Liquid Sheep Blowfly Treatment* is 4 g/sheep by jetting. It is noted that the maximum dose rate for *Vetrazin Spray-on Sheep Blowfly Treatment* would correspond to 5.04 g/sheep with 10 months wool growth. Therefore, *Vetrazin Spray-on Sheep Blowfly* application results in the highest dose of cyromazine for long wool treatment of sheep. Both products have a label wool withholding period (WWP) of 2 months.

[14] Calculated by the Department of the Environment and Heritage.

Table 6.1: The registered use patterns for the *Vetrazin* products

Product name	Treatment	Routes of administration	Maximum dose rate
Vetrazin Liquid Sheep Blowfly Treatment	Protect flystrike on long wool sheep (at least 6 weeks wool growth)	Jetting	4 L of jetting fluid at 2/1000 of 500 g/L (1 g/L). This corresponds to 4 g cyromazine per sheep
		Dipping	Dip sheep at concentration of 2/1000 dilution of 500 g/L (1 g/L)
Vetrazin Spray-on Sheep Blowfly Treatment	Protect long wool sheep from strike by blowfly (*Lucilia cuprina*)	Spray-on (for up to 10 months of wool growth)	84 mL at 60 g/L cyromazine (5.04 g cyromazine per sheep)

6.5.3 Amount of Residues Retained on Fleece

6.5.3.1 Dipping

It is assumed by the registrant that sheep dipped with the Vetrazin products would take up 3 L/sheep and 4 L/sheep allowing for run-off from sheep with up to 6 weeks and more than 12 weeks wool growth, respectively. This is equivalent to 3 or 4 g cyromazine/sheep, respectively, at the time of dipping.

6.5.3.2 Jetting

As cyromazine does not strip as effectively as organophosphates, the registrant assumes that half would be lost to run-off and 2/3 would be applied to the fleece (the other 1/3 to the breech). Therefore, the mass of cyromazine applied to the fleece as a result of the application of the Vetrazin product would be 4 L X 2/3 (to fleece) X 1/2 (after run-off) X 1 g/L = 1333 mg cyromazine for sheep with 9-10 months wool growth. This amount is consistent with those retained on sheep in the experimental studies by Campbell et al (1998), Levot and Sales (1997) and Hosking and George (2002).

6.5.3.3 Spray-on

The product is applied in concentrated form down the backline and thus limited run-off is expected. The mass of cyromazine that would be applied to fleece wool would be 17-28 mL X 3 bands X 60 g/L = 3060 or 5040 mg per sheep for 6 months or less and for 10 months wool growth, respectively. The three bands would consist of 2 bands for the body and 1 band for the crutch area.

6.5 ENVIRONMENTAL CHEMISTRY AND FATE

6.5.1 Summary of Environmental Fate

The following has been taken from the assessment undertaken for the nuisance fly application previously assessed by DEH.

Cyromazine is hydrolytically stable under normal environmental conditions, only hydrolysing significantly under very acid or alkaline conditions. The substance is stable to direct photolysis in aqueous solution and in soil, but may be rapidly

photodegraded in water in the presence of sensitisers such as humic acids. The rate of degradation of cyromazine under aerobic conditions found in soil, soil/manure mixtures and manure metabolism studies and in water/sediment systems varied widely, estimated half-life values for the substance ranging from as little as 2.7 days in one soil study to as long as 164 days in another, ~39 days in one manure study to ~493 days in a soil/manure mixture, and were 93-254 days in water/sediment systems.

In all cases, the predominant (if not only) extractable metabolite detected was melamine, which in several cases accumulated to significant concentrations relative to the initial cyromazine concentration, as it degrades more slowly than the parent substance, though mineralising slowly, presumably following deamination to ammelin, ammelid and cyanuric acid. Cyromazine and/or its degradation products partitioned very largely to the aqueous phase in water/sediment and activated sludge studies. Although neither cyromazine nor melamine adsorb strongly to soil (see below), non-extractable residues remaining in soil or manure in various metabolism studies sometimes reached a high percentage of the applied radioactivity and later declined from peak levels [e.g. peak non-extractable residues were ~60% of applied radioactivity by ~90 days incubation in an aerobic metabolism study with a muck (high organic matter content) soil, but had declined to ~50% applied radioactivity by 367 days incubation]. The nature of these residues is unknown, but the data suggest that non-extractable residues may still be somewhat susceptible to degradation or may be remobilised.

Cyromazine is unlikely to evaporate significantly from soil or water. A batch equilibrium study of adsorption and desorption of cyromazine indicated that cyromazine is likely to have medium to very high mobility in soil (K_{OC} for adsorption = 41-185), with adsorption lowest in the one soil tested with an alkaline pH (possibly due to the effect of pH on the molecular species present). A leaching study with freshly applied cyromazine indicated that it was highly mobile in an alkaline sand and somewhat mobile in three other soils with slightly acid pH. One aged soil leaching study also indicated greater leaching in an alkaline than an acid soil, but this was not evident in an aged soil study with the same soil types where less water was applied to the soil columns.

Based on its water solubility, melamine is also expected to be highly mobile in soil, and this metabolite was found to a greater extent than the parent substance in leachate from the first aged soil study. Calculations of the Gustafson Ubiquity Score (GUS) indicate that cyromazine ranges from an "improbable leacher" (GUS < 1.8) to a "probable leacher" (GUS > 2.8). Thus cyromazine and/or its metabolite melamine may potentially reach groundwater, depending on the degradation rate and soil characteristics affecting mobility.

Various field or semi-field studies, including soil residue, plant uptake, plant dissipation, and ground-water monitoring studies, indicate cyromazine dissipation half-lives of 75-284 days in soil, and suggest that the metabolite melamine may be more persistent. Both cyromazine and in particular melamine were shown to be somewhat mobile under field conditions, having been detected to a depth of 30-46 cm. Cyromazine was found to dissipate rapidly from pasture grass, with a half-life of 2.6-3.3 days. Water analyses from test wells in a small scale prospective ground water

monitoring study found no detectable residues of cyromazine, but melamine was detected in water at 0.10-0.21 µg/L in four samples from different sampling intervals.

Bioaccumulation studies with ^{14}C-cyromazine and bluegill sunfish (*Lepomis macrochirus*) and estimates based on water solubility or K_{OW} data indicate that cyromazine and its metabolite melamine are both unlikely to bioaccumulate (measured bioconcentration factor for cyromazine in bluegill sunfish generally <1.0).

6.5.2 Wool Residues Data (original submission)

In March 2000 the registrant provided the following wool residue data, which examined the residue dissipation in wool for long wool treatment by jetting and short wool treatment by dipping from the use of the Vetrazin products. The effects of rain on the residue levels in treated wool were also examined. The residue levels at different zones of the treated wool and at different parts of the staple were also investigated, including residue levels following application of the spray-on formulation.

6.5.2.1 Residue Depletion in Fleece

The registrant has summarised available data on the residues depletion studies derived from the literature including on the breakdown of cyromazine in wool using the model developed by Campbell et al. (1998). The average half-lives from treatment to shearing for cyromazine from experimental studies estimated by the Campbell model are shown in Table 6.2.

Table 6.2: Average half-life of cyromazine dissipation from treatment to shearing determined by the Campbell model

Method of treatment	Time of treatment after shearing	Range (days)	Mean half-life (days)	Reference
Plunge dip	6 weeks	34-44	39	Avcare taskforce report (1994)
Hand jet	10 weeks	45-53	49	Bull (1978)
Hand jet	6 months	77-127	96	Campbell et al (1998)
Hand jet	8 months	59-120	79	Campbell et al (1998)*
Modified Harrington AJR**	8 months	37-266	66	Campbell et al (1998)*
Harrington AJR	8 months	27-72	39	Campbell et al (1998)*
Hand jet	8 months	78-225	116	Levot and Sales (1997)
Hand jet	9 months	76-284	120	Avcare taskforce report (1994)

* Modified from Levot and Sales (1997)

** Automatic Jetting Race

Except for jetting, there are insufficient data to make a comparison between the methods of application. It appears that the breakdown rate after application by jetting races may be faster than after application by hand jetting. According to the registrant the use of a jetting race applies less chemical than hand jetting and the chemical is more exposed on the surface of the wool. Hence, the residues would break down and wash out more easily. Note that while the modified Harrington AJR initially delivered a much higher dose than hand jetting in the Levot and Sales (1997) study reviewed below, there was no significant difference in mean residues on the fleece 1 day later.

6.5.2.2 Fleece Residue Trial

This trial (Avcare 1994) was performed in accordance with the procedure outlined in the propetamphos trial (Chapter 2 of this report). The results are shown in Tables 6.3 and 6.4.

Table 6.3: Cyromazine residues in wool (mg/kg greasy wool) from sheep with 6 weeks wool growth dipped with the *Vetrazin* product at the label dose rate of 1 g/L

Weeks post-treatment	**Cyromazine residues in wool (mg/kg wool)**		**Mean cyromazine residues in wool ± SD (mg/kg wool)**	
	Backline	**Flank**	**Backline**	**Flank**
1	781, 653, 431, 742, 588	1385, 745, 856, 1046, 1160	639 ± 139	1038 ± 252
6	18, 41, 31, 100, 58	111, 188, 134, 111, 105	50 ± 32	130 ± 34
12	29, 103, 8, 25, 13	193, 59, 55, 59, 32	36 ± 39	80 ± 64
26	5, 12, 7, 2, 5.6	1, 1, 4, 9, 44	6.3 ± 3.7	12 ± 18
46	0.7, ND, ND, 1, 0.4	1, 1, ND, 1, 2	0.4 ± 0.4	1 ± 0.7

Limit of detection = 2 mg/kg for weeks 1, 6 and 12, and 0.1 mg/kg for weeks 26 and 46
ND – Non-detectable level
Cyromazine residues in wool of untreated controls were at non-detectable level

Table 6.4: Cyromazine residues in wool (mg/kg) from sheep with 9 months wool growth jetted with the product *Vetrazin* at the maximum label dose rate of 1 g/L

Weeks post-treatment	**Cyromazine residues in wool (mg/kg wool)**		**Mean cyromazine residues in wool ± SD (mg/kg wool)**	
	Backline	Flank	Backline	Flank
1	438, 297, 1242, 1005, 612	413, 63, 187, 318, 560	719 ± 395	308 ± 193
6	422, 317, 400, 364, 414	187, 113, 16, 57, 217	383 ± 43	118 ± 85
12	141, 64, 340, 204, 202	254, 21, 17, 74, 215	190 ± 101	116 ± 111

Limit of detection = 2 mg/kg
Note that mean cyromazine residues in backline and flank of untreated controls were ND and 7 mg/kg, respectively. The latter is not significant when compared to the levels found in treated wool.

A similar residue depletion pattern is observed in cyromazine as is observed in propetamphos in the backline and flank regions (see Chapter 3 of this report).

6.5.2.3 Insecticide Residues in Wool from Sheep Jetted by Hand and via Automatic Jetting Races

Sheep with 8 months wool growth were randomly assigned to 7 groups of 14 or 15 (Levot and Sales 1997). Sheep were treated at the recommended dose rate of 1 g/L with the Vetrazin product. Fifteen sheep were left untreated as controls. The product was applied by hand-jetting or via a standard or modified Harrington AJR. About 275 g of wool was removed from the withers of five sheep in the untreated controls on day 1 pretreatment and from 5 sheep on 1 day, 8 weeks and 16 weeks after treatment. The day after the 16 weeks post-treatment, samples were collected, the sheep were shorn in their group and the fleece were bulked into bales. To ensure a representative sample of wool was collected from each bale, 20 core samples were removed from each bale. The core samples from each bale were combined and subsamples were taken for residue analysis by HPLC.

The results indicate that hand-jetting delivered 2.8-3.2 L/sheep, the standard Harrington AJR delivered 1.6-1.8 L/sheep and the modified Harrington AJR delivered 4.2-4.7 L/sheep. Mean cyromazine residues at 1 day after treatment showed that was no significant difference in the residues level left by the three application methods. Cyromazine residues in treated wool from individual sheep were about 300 mg/kg at 1 day after treatment and had dropped to 50-150 mg/kg by 120 days after treatment. At 50 and 120 days after treatment, residue levels on sheep jetted by hand are significantly higher than that the other two application methods. Between 1 and 56 days after treatment cyromazine residues declined markedly but there was very little difference in the residue levels measured 56 and 120 days after treatment. The half-life of cyromazine in wool is affected by the application method. The results are shown in Table 6.5.

Table 6.5: Calculated dissipation half-lives of cyromazine applied to sheep with Vetrazin (1 g/L) using three application methods

Method	**Half-lives (days)**	**95% confidence limit (days)**
Hand-jetting	75	60-190
Harrington AJR	28	9-56
Modified Harrington AJR	35	17-82

Degradation was faster on sheep jetted via the standard and modified Harrington AJRs. The results indicate that residues on individual sheep that had been hand-jetted decayed at a negligible rate between 56 and 120 days after treatment. This suggests that the breakdown of cyromazine exposed to sunlight and dust on the outside of the wool was complete by day 56 after treatment and the breakdown thereafter was slower because the remaining residue was protected from sunlight as it was predominatly located below the surface of the fleece.

In comparison with Table 6.2, the half-life of cyromazine in Table 6.5 is consistent with that performed by the Campbell model using hand jetting. However, half-lives were longer in the calculations performed by the Campbell model when compared with Levot and Sales (Table 6.5) using the standard and modified Harrington AJR. The overall results indicate that cyromazine applied by hand jetting to sheep with 6 or 8 months wool growth has a longer half-life than those applied by automatic jetting race. This may be explained by the fact that when the pesticide is applied deeper into the wool by hand jetting, it is protected from sunlight and thus the rate of breakdown is slower.

6.5.2.3 Technical Report No. 78/5/668

This trial consisted of 6 merino weaners treated at the dose rate of 1 g/L by jetting (Bull 1978). Each sheep was jetted for 20 seconds receiving approximately 2.3 L of spray. This was applied from the back of the poll to the tail. Wool samples were collected on days 1, 6, 14, 28, 42, 56, 84, 112 and 168 after treatment and analysed by GC. No details were provided on how the wool samples were taken (eg band sampling around the girth). The results are shown in Table 6.6.

Table 6.6: Cyromazine residues on wool of treated sheep (n = 5) jetted at a dose rate of 1 g/L

Days after treatment	**1**	**6**	**14**	**28**	**42**	**56**	**84**	**112**	**168**
Cyromazine residues in wool (mg/kg)	2037-3994	1833-2667	1171-1933	750-1350	500-967	367-617	167-402	42-251	12-47*
Mean ± SD (mg/kg)	3275 ± 726	2250 ± 307	1430 ± 286	1039 ± 241	744 ± 193	493 ± 101	292 ± 83	136 ± 78	27 ± 14

* One sheep was struck by blowfly 154 days after treatment

The initial dissipation of cyromazine from day 0-14 indicates that the half-life on wool is 10 days. A better estimate of the half-life of cyromazine in wool would be obtained from 14 days and onward and this was determined to be 28 days. The trial did not indicate the wool growth at the time of the treatment, the dilution factor as a result of the wool growth with time and the region where treated wool was sampled. Therefore, any results should be treated with caution as it is not clear whether it is a short or long wool treatment and the estimated half-life may not be accurate.

6.5.2.4 CGA 84/10/1012

This trial was conducted to investigate the effects of rain had upon the cyromazine residues in wool after sheep were exposed to artificial rain at varying periods after treatment (Strong and Adams 1984). Groups of merino sheep (each n = 6) with 3 months wool growth were treated with the product at the recommended dose rate of 1 g/L in a Sunbeam Sheep Shower. On the day of treatment one group was exposed to artificial rain at a rate of 25 mm in 6 h. Other groups were exposed to rain for the prescribed periods on days 1, 3, 14, 15, 28, 29, 98 and 99 after treatment. When the sheep were dry, wool was sampled from the shoulder, middle of the back and from the rump, and stored at –15ºC until analysed. No details were provided on the number of wool samples taken, or the quantity contained in each sample.

Fifty-six days (8 weeks) after treatment, some sheep from the two different rain exposure groups were sampled more extensively to examine the distribution of cyromazine in the fleece. Wool from the girth of the sheep and from the left and right of the backline were sampled. Samples were also taken from the middle of the side and from the edge of the belly. The staple from the remaining wool was cut to yield top and bottom halves of the staple and analysed. The results are shown in Tables 6.7, 6.8, 6.9, 6.10 and 6.11.

Table 6.7: Cyromazine residues found in wool when sheep (n = 5) were exposed to rain during the first 3 days following treatment. Rain was applied at a rate of 25 mm per 6 h period.

Time of rain exposure after treatment	Cyromazine residues (mg/kg) found in wool at times (weeks) after treatment				
	0	**1**	**4**	**8**	**12**
No artificial rain	630-1570	560-1020	680-1020	450-1120	560-770
Mean ± SD	980 ± 320	720 ± 160	790 ± 130	690 ± 230	650 ± 80
Rain applied on the day of treatment	NS	120-250	170 ± 320	120-260	80-230
Mean ± SD		170 ± 50	220 ± 60	190 ± 50	180 ± 60
Rain applied on the day after treatment	NS	140-410	200-320	220-440	210-440
Mean ± SD		260 ± 100	260 ± 46	320 ± 80	330 ± 90
Rain applied 3 days after treatment	NS	190-380	270-510	280-670	320-590
Mean ± SD		280 ± 80	380 ± 80	430 ± 170	470 ± 120

NS denotes no sample

Table 6.8: Rain applied to treated sheep (n = 6) either at 2 or 4 weeks after treatment at the rate of 25 mm per 6 h on 2 consecutive days

Rain exposure at times after treatment	Cyromazine residues (mg/kg) found in wool at times (weeks) after treatment			
	1	**4**	**8**	**12**
No artificial rain applied	560-1020	680-1020	450-1120	560-770
Mean ± SD	720 ± 160	790 ± 130	690 ± 230	650 ± 80
2 weeks	580-1280	320-900	460-960	390-640
Mean ± SD	980 ± 230	540 ± 200	620 ± 190	510 ± 90
4 weeks	750-1230	660-1280	330-800	310-680
Mean ± SD	1010 ± 190	1000 ± 270	470-175	500 ± 140

Table 6.9: Rain applied at a rate of 25 mm to sheep (n = 6) on two distinct occasions during the first 4 weeks after treatment

Rain exposure at times (day) after treatment	Cyromazine residues (mg/kg) found in wool at times (weeks) after treatment				
	1	**4**	**5**	**8**	**12**
No artificial rain applied	560-1020	680-1020	NS	450-1120	560 ± 770
Mean ± SD	720 ± 160	790 ± 130	NS	690 ± 230	650 ± 80
0 and 28, 29	260-510	320-480	170-420	250-570	190-360
Mean ± SD	380 ± 100	420 ± 60	250 ± 90	340 ± 120	280 ± 70
14, 15 and 28, 29	630-950	250-730	250-440	250-500	220-550
Mean ± SD	770 ± 110	450 ± 160	360 ± 70	360 ± 90	350 ± 110

NS denotes no sample

Table 6.10: Effects of pre-treatment wetting of sheep (n = 6) upon the cyromazine residues in wool of *Vetrazin* treated sheep

Treatment group	**Cyromazine residues (mg/kg) found in wool at times (weeks) after treatment**		
	5	**8**	**28**
No prior wetting	630-1570	560-1020	680-1020
Mean ± SD	980 ± 320	720 ± 160	790 ± 130
25 mm rain applied during period from 18-24 h before treatment	880-1420	480-1140	490-1190
Mean ± SD	1160 ± 186	900 ± 250	940 ± 280

Table 6.11: Effects of rain applied 14 weeks after treatment upon the cyromazine residue levels in wool of treated sheep (n = 12). Rain was applied at the rate of 25 mm per 6 h on consecutive days.

Treatment group	**Cyromazine residues (mg/kg) found in wool at times (weeks) after wetting**		
	-6	**-2**	**+2**
Rain applied 14 weeks after treatment	450-1290	560-1230	200-670
Mean ± SD	790 ± 280	800 ± 220	370 ± 150

The data clearly indicate that more cyromazine residues were removed by rain during the first three days after treatment than were removed when rain exposure occurs two or more weeks after treatment (see Tables 6.7 and 6.8). The data also indicate that cyromazine residues remain fairly constant at 1, 4, 8 and 12 weeks after treatment. Reduction in the residues when rain was applied 2, 4, or 14 weeks after treatment were less than when rain was applied within the first three days of treatment (see Tables 8 and 11). Pre-treatment wetting did not influence the magnitude of the cyromazine residues (see Table 10). It was claimed that the results on days 5 and 8 were caused by a leak in the glasshouse during a storm on day 6.

6.5.2.5 Trial No. 93/6/1411

Ten merino wethers with 14 weeks wool growth were selected for the trial (Strong and Bull 1993). The sheep were treated by applying along the backline from the base of the neck to the rump with the spray-on formulation at a dose rate of 2 g per sheep (compare with 5.04 g/sheep normally – see Section 6.5). Wool samples were collected from three sites (tip, mid and base) along the backline from the base of the neck to the rump. Five sheep were placed in an enclosure on day 3 and subjected to artificial rain at the rate of 50 mm over the period of 1-2 hours and later exposed to rain on day 45 and 87 after treatment. The remaining 5 sheep were exposed to rain on days 45 and 87 after treatment. Wool samples were collected from all sheep on day 7.

Six weeks after treatment, all sheep had wool samples collected from them and 3 days later exposed to rain. At weeks 7 and 12 wool samples were collected and at day 87, sheep were exposed to rain again and on week 13 final wool samples were collected. The staple of the sample was sectioned into top, middle and bottom for further analysis with respect to the distribution of the cyromazine residues in the fleece. The samples were analysed by HPLC and stored at -15ºC until analysed. The results are shown in Tables 6.12 and 6.13.

Table 6.12: Distribution of cyromazine residues in fleece treated by spray-on formulation at a dose rate of 2 g per sheep. The formulation was applied along the backline and exposed to artificial rain at the times (days) after treatment.

Time of rain exposure after treatment	**Cyromazine residues (mg/kg) on wool on days after treatment**					
	Day 1	**Day 7**	**Day 42**	**Day 49**	**Day 84**	**Day 91**
Days 45 and 87	6930-26700	7780-16700	16200-21700	1180-2930	613-1500	135-369
Mean ± SD	17270 ± 7700	12160 ± 3710	17140 ± 4150	1710 ± 700	980 ± 324	250 ± 85
Days 3, 45 and 87	6910-18600	410-1720	132-1650	193-370	64-187	25-78
Mean ± SD	12320 ± 5130	1094 ± 500	690 ± 581	244 ± 73	125 ± 52	54 ± 24

* Only the tip results are shown as the cyromazine residues in other sites are significantly lower (see Table 6.13)

Table 6.13: Relative concentration of cyromazine in the fleece assuming concentration at the tip as the reference position and expressing the results at other regions as % at the tip.

Rain exposure pattern	**Position of staple**	**Relative concentration of cyromazine in the fleece**					
		Day 1	**Day 7**	**Day 42**	**Day 49**	**Day 84**	**Day 91**
Days 45 and 87	Mid	2.6	2.0	2.5	3.6	3.6	12
	Base	0.9	0.8	ND	2.3	ND	ND
Days 3, 45, 87	Mid	6.9	15.4	10.6	7.9	26	52
	Base	2.2	4.9	ND	8.6	ND	ND

ND denotes not determined

Cyromazine residues clearly remain at the tip of the fleece without appreciable dissipation until exposure to rain occurs, after which they are greatly reduced. Multiple exposure to rain resulted in continued reduction in the concentration of cyromazine at the tip of the fleece (see Table 6.12). As a result, the proportion of cyromazine at the base and mid of the staple compared with that found at the tip increased appreciably after rain (see Table 6.13). These data suggest that there is little binding between cyromazine and the constituents in the fleece. The action of the rain also allows some distribution of cyromazine from the treated wool zone to other zones on the sheep.

The data indicate that cyromazine is relatively mobile on wool compared with the other more lipophilic actives. However, the levels tabulated above need to be treated with caution as sheep were treated with 14 weeks wool and sampled only for up to 13 weeks after.

6.5.3 Wool Residues Data (later submission)

In March 2003 the registrant provided two additional wool residues depletion studies.

6.5.3.1 Report No. TR 02/12/1828: Depletion of cyromazine residues from wool after treatment with Vetrazin Liquid

One hundred and thirty six Merino sheep of mixed sex and age were selected for the study (Hosking and George 2002). Sheep were grazed on three properties; site 1 had

84 sheep consisting of unshorn 3 months old lambs and mature sheep with 6 weeks and 6 months wool growth, respectively. Sites 2 and 3 had 26 mature sheep each, with 6 weeks wool growth. Each treatment group consisted of 26 animals, except for the 6 months treatment group on site 1, which comprised of 32 animals, as two groups of six were used for band sampling.

Sheep were treated with the product by hand-jetting with a Dutjet wand at the recommended label rate according to the time since last shearing and taking surface area into consideration. Except for lambs, treatment focussed on the poll, body and crutch areas, ensuring saturation to the skin. Lambs were only treated on the body and crutch. Based on the "rule of thumb" to apply about 0.5 L of jetting fluid for every month of wool growth (minimum 1.5 L and maximum about 4 L) lambs received ~2 L (2 g), sheep with 6 weeks wool ~1.5 L (1.5 g) and sheep with 6 months wool ~3 L (3 g). The second lot of 6 sheep treated with 6 months wool growth (used for band sampling) was treated again 3 months later, resulting in over double the dose being applied (total ~7.5 L or 7.5 g).

At site 1, run-off was captured after treatment by allowing excess jetting fluid to drain (until it stopped) into a metal drip tray placed on the floor of the race (5 minutes for lambs, 10 minutes for sheep). In this way the volume retained on lambs/sheep could be calculated, this ranged from 0.85 L for lambs to 1.77 L for 6 months wool (2.5 L for those treated the second time at 9 months wool growth), or 42.5 to 59 % of applied. At sites 2 and 3 sheep were weighed before and after treatment (following a 10 minute drainage period), and the differences in weight used to estimate the amount retained. Comparison, including also weighing the sheep on site 1, showed that the volumetric method was by far the more accurate.

Sheep that were treated with 6 weeks, 6 or 9 months wool growth were shorn about one year after their previous shearing ie about 10-11, 6 and 3 months after treatment, respectively. Lambs were shorn about 6 months after treatment. Detailed rainfall and temperature data are available for all sites, mean maximum tempertature ranged between 20.1 and 25.8^{o}C, and between 535 and 890 mm of rain fell over the year's study.

Cyromazine residues in wool were determined by both the band and core sampling methods. Six sheep were band sampled from each treatment group (two lots for the 6 month treatment group on site 1), with the same sheep sampled at each time. Wool staple length was measured immediately prior to band sampling. Backline and flank sites were measured and recorded as these sites formed part of the sample that was taken from a narrow band around the circumference of the sheep, excluding the belly. The remaining animals (n=20) were retained for full shearing as the core sampling group. At the final shearing, fleece wool from the core sampling groups of sheep were skirted and sorted into fleeces and pieces for each of the treatment groups (n = 20). The wool was baled in a manner that replicated commercial farming practices. Baled wool was core sampled using a wool corer attached to a cordless drill that cut the wool specimens into 15 mm lengths. The samples were stored below –20°C until preparation and analysis occurred.

Wool samples were analysed by HPLC to determine the concentration of cyromazine. Control and fortified samples were included with every set of samples analysed. The

core samples were analysed in duplicate except for the 6 weeks group at site 3 where they were analysed in triplicate. The cyromazine wool residue results for the band and core samples for lambs and sheep with 6 weeks and 6 months wool growth at sites 1, 2 and 3 are summarised in Tables 6.14 and 6.15:

Table 6.14: Mean cyromazine level in wool (mg/kg) derived from the band samples at sites 1, 2 and 3.

Site	**Wool growth on shearing group**	**Approximate months after treatment**						
		Day 1	**1**	**2**	**3**	**4**	**6**	**11**
1	lambs	932	582	136		79.6	32.4	
1	6 weeks	1430	261	36.9		19.4	6.00	1.51
2	6 weeks		203	61.5		29.0	31.5	14.8
3	6 weeks		467	176		121	74.2	20.1
1	6 months (T1)	416	186	135		72.7	**51.6**	
1	6 months (T2)*	578	325	267	210			

* Residues after the second application

Table 6.15: Mean cyromazine level in wool (mg/kg) derived from the core samples at sites 1, 2 and 3.

Site	**Shearing group**	**Approximate months after treatment**					
		Fleece			**Pieces/bellies**		
		3	**6**	**11**	**3**	**6**	**11**
1	lambs		20.2			7.88	
1	6 weeks			1.48			1.42
2	6 weeks			6.10			1.51
3	6 weeks			10.0			5.28
1	6 months (T1)		**52.4**			20.0	

The results indicate that in band samples the cyromazine wool residues depleted with time for treated sheep with different wool growths, with treated sheep with 6 months wool growth having the highest residues remaining in wool at shearing. Sheep treated twice (6 and 9 months after shearing) had higher levels for the three months after the second dose (up to double) compared to those treated only once, based on band sampling. The wool residues in band samples and core (fleece) samples for sheep with 6 weeks wool growth indicate lower residues from the latter as expected, though there was considerable variation between sites for band sampling (levels range from 1.51 to 20.1 mg/kg). Band sampling also indicates a relatively steady decline in levels over time. However, the band or core sampling results for sheep treated with 6 months wool are almost identical.

Half-lives for the depletion of cyromazine residues in wool calculated from the above trial were not included in the report. However, these are contained in the separate report by Campbell and Horton (2003), and range from 56 (treatment 6 weeks after shearing) to 90 days (for 9 months wool treatment), with treatments further from the next shearing having the shorter half-lives. This contrasts with the data reported below, and obviously reflects the greater protection from degradation that jetting

treatment deeper into 6 months wool affords. Note that the sheep treated twice were excluded from these calculations.

On the basis of these results, the highest mean cyromazine residues in wool are 51.6 mg/kg derived from the band sample for sheep with 6 months wool growth. However, based on the more realistic core sampling results, this would correspond to a surprisingly similar maximum wool residue level of 51.6 mg/kg.

6.5.3.2 Report No. TR 03/01/1831: Depletion of cyromazine residues from wool after treatment with Vetrazin Spray-On (field evaluation).

Two hundred and fourteen Merino sheep of mixed sex and age were selected for the study (Hosking and George 2003). Sheep were grazed on three properties; site 1 had 110 sheep consisting of unshorn 3 months old lambs and mature sheep with 6 weeks, 6 and 9 months wool growth respectively. Sites 2 and 3 had 52 mature sheep each, with 6 weeks and 9 months wool growth, respectively. Each treatment group consisted of 26 animals, except for the 6 months treatment group on site 1, which comprised 32 animals, as two groups of six were used for band sampling.

Sheep were treated with the product at the recommended label rate for body and crutch strike using a manual dosing gun fitted with a spray (fan) nozzle. The second lot of 6 sheep treated after 6 months wool growth (used for band sampling) was treated again 3 months later, resulting in more than double the dose being applied. The sheep that were treated with 6 weeks, 6 or 9 months wool growth were shorn about one year after their previous shearing ie about 10-11, 6 and 3 months after treatment, respectively. Lambs were shorn about 6 months after treatment. Detailed rainfall and temperature data are available for all sites, and were as above.

Cyromazine residues in wool were determined by both the band and core sampling methods, using identical numbers and procedures (including the assay method) as for the trial reported above. The cyromazine wool residue results for the band and core samples for lambs and sheep with 6 weeks, 6 and 9 months wool growth at sites 1, 2 and 3 are summarised in Tables 6.16 and 6.17.

Table 6.16: Mean cyromazine level in wool (mg/kg) derived from the band samples at sites 1, 2 and 3.

Site	Wool growth on shearing group	Approximate months after treatment						
		Day 1	1	2	3	4	6	11
1	Lambs	7280	762	19.8		4.34	3.1	
1	6 weeks	4530	256	27.6		21.0	7.38	1.97
2	6 weeks		306	24.3		5.04	1.38	1.62
3	6 weeks		810	145		44.6	15.7	6.97
1	6 months (T1)	656	37.2	42.8		26.4	53.7	
1	6 months (T2)*	801	35.2	46.3	37.7			
1	9 month	712	4090	223	**91.1**			
2	9 month		95.8	46.7	40.9			
3	9 month		403	109	84.8			

* Residues after the second application

Table 6.17: Mean cyromazine level in wool (mg/kg) derived from the core samples at sites 1, 2 and 3.

Site	Shearing group	Approximate months after treatment					
		Fleece			Pieces/bellies		
		3	6	11	3	6	11
1	lambs		4.00			22.8	
1	6 weeks			<1.0			<1.00
2	6 weeks			1.06			1.98
3	6 weeks			3.13			4.58
1	6 months (T1)		20.8			7.38	
1	9 month	**47.6**			26.6		
2	9 month	25.9			9.51		
3	9 month	3.15			2.67		

The results indicate that in band samples the cyromazine wool residues depleted with time for treated sheep at different wool growths, with treated sheep with 9 months wool growth having the highest residues remaining in wool at shearing. Surprisingly, based on band sampling, residues for the sheep treated twice (6 and 9 months after shearing) had very similar levels for the first three months after the second dose compared to those treated only once, and from band sampling results these were lower than sheep treated only once with 9 months wool growth. The wool residues in band samples and core (fleece) samples indicate lower residues from the latter as expected, though there was considerable variation between sites (ranging from 3.15 to 47.6 mg/kg for sheep with 9 months wool growth, and <1.0 to 3.13 mg/kg for sheep with 6 weeks wool growth). Band sampling also indicates an initial fast depletion followed by a considerable slowing, with in one case [6-month (T1)] levels being twice as high after 6 compared with 4 months.

Half-lives for the depletion of cyromazine residues in wool calculated from the above trial were not included in the report. However, these are contained in the separate report by Campbell and Horton (2003), and range from 24 (for 9 months wool treatment) to 39 days (treatment 6 weeks after shearing), with treatments closer to the next shearing having the shorter half-lives. Note that the sheep treated twice were excluded from the calculations.

On the basis of these results, the highest mean cyromazine residues in wool are 91.9 mg/kg derived from the band sample for sheep with 9 months wool growth. However, based on the more realistic core sampling results, this would correspond to a maximum wool residue level of 47.6 mg/kg.

6.5.4 Summary of Wool Residue Depletion Studies

Several wool residue depletion studies at the registered use rates have been conducted. These include studies on the distribution of the residue levels on the different regions of the fleece and the staple. Calculated half-lives ranged between 39-120 days.

Several trials were performed to investigate the effects of rain on the fleece residue levels on treated sheep. The data indicate that reduction in the cyromazine residues

when rain was applied 2, 4, or 14 weeks after treatment were less than when rain was applied within the first three days of treatment. Pre-treatment wetting did not influence the magnitude of the cyromazine residues on fleece.

The definite studies for the depletion of cyromazine residues from wool after treatment of both types of formulation were conducted under typical wool growing conditions after the Sheep Ectoparasiticides review was announced. These indicate that cyromazine residues in wool deplete over time for treated sheep with different wool growths. For the jetting product the half-lives ranged from 56 to 90 days, with treatment further from the next shearing having the shorter half-lives. This contrasts with spray-on treatment where the half-lives were both shorter (range 24 to 39 days) and with the shorter half-lives coming from treatments closer to the next shearing. This would appear to reflect the greater protection afforded by jetting treatment deeper into longer wool.

6.6 SUMMARY OF ENVIRONMENTAL TOXICITY

The following information was obtained from DEH's assessment report for nuisance fly uses of cyromazine.

6.6.1 Birds

Acute oral and dietary toxicity studies indicate that cyromazine and a very similar formulation to the registered nuisance fly product were slightly toxic (500< LD50 ≤2000 mg/kg bodyweight) to practically non-toxic (LD50 >2000 mg/kg) to the four bird species tested, though sometimes having an antifeedant and/or emetic effect at the higher rates tested. The active ingredient and product also have only slight acute toxicity to mammals.

6.6.2 Aquatic organisms

Cyromazine was found to be practically non-toxic (96 h LC50 >100 mg/L) or at most slightly acutely toxic (10< 96 h LC50 ≤100 mg/L) to five fish species tested. A reported 32 d LOEC value of 36 mg/L from an early life-stage test with fathead minnow (*Pimephales promelas*) indicates that cyromazine is very slightly toxic to this fish species with chronic exposure. The substance has been found to be at most slightly acutely toxic to the daphnid *Daphnia magna* (48 h EC50 = >92.8 mg/L using measured concentrations, but is more than 150 X as toxic to this species with chronic exposure (21 day life cycle test adult size (length) LOEC = 0.64 mg/L).

Cyromazine was found to be at worst slightly toxic to the turbellarian flatworm species *Dugesia dorotocephala* and *D. tigrina.* Cyromazine and a sheep flystrike formulation were practically non-toxic via acute exposure to second to fourth instars of the chironomid *Chironomus zealandicus* and to larvae of the mayfly *Deleatidium* sp., with the most toxic 96 h LC50 still being only 100-400 mg/L for 2nd- & 3rd-instars of chironomids. However, there was greater chronic toxicity from cyromazine to eggs or early-instar larvae of *Chironomus zealandicus*. The chronic LC50 for larval mortality estimated from the data (after correction for control mortality) was 64 µg/L and the maximum acceptable toxicant concentration (MATC) calculated by the authors from

the data was 30 µg/L (arithmetic mean of 10 and 50 µg/L), or 17.5 µg/L based on two whole-of-life chronic toxicity tests.

Cyromazine was practically non-toxic to the green algal species *Scenedesmus pannonicus*. The metabolite melamine has been found to be practically non-toxic to fish, *Daphnia magna* and to *Scenedesmus pannonicus*.

6.6.3 Terrestrial invertebrates

Cyromazine is as an insect growth regulator with contact action, interfering with moulting and pupation. The substance appears to have relatively low toxicity to adult bees and bee larvae, and its harmful effects as an insect growth regulator to insect and mite predators and parasites varies with species and the degree of exposure they experience, e.g. cyromazine was found to be harmful to predatory mites in a glasshouse study and to pupal parasitoids of the *Lyriomyza* leafminer. The substance was found to be safe with predatory beetles and mites in manure (evidently with exposure to both juvenile and adult stages) and was found to be very slightly toxic (>1000 mg/kg dry soil) to the earthworm species *Eisenia foetida*, while the metabolite melamine was found to be at most moderately toxic (LC50 = 10-100 mg/kg).

6.6.4 Phytotoxicity

Cyromazine is closely related to other triazines used as herbicides, but appears to have relatively little useful herbicidal activity, as in plants it is generally rapidly metabolised to melamine. The most sensitive species tested exhibit serious damage at rates of 1-2 kg ai/ha. Cyromazine is generally not harmful to microbial activity, in some cases stimulating soil nitrification, respiration or nitrification, and with no harmful effects on activated sludge metabolism, and melamine is evidently not inhibitory to microbial activity, but is very slow to degrade.

6.6.5 End points used in hazard assessments of this report

For the Australian situation DEH would normally apply an assessment factor (AF) of 10 or 100 to the most sensitive acute result. While daphnids are the most sensitive of the usual aquatic test species (48 h EC50 >92.8 mg/L), they are not likely to be a very sensitive species due to cyromazine's specificity and mode of action. However, the available results for the preferred diptera species (96 h LC50 = 100-400 mg/L for 2nd- & 3rd-stage chironomid instars) surprisingly indicate this is equally insensitive on an acute basis, though it should be noted this result is derived from a non-standard test performed on a non-standard species.

Therefore the acute daphnia result will be used but with an AF of 100 to derive the Predicted No Effect Concentration (PNEC), ie <928 µg/L. This allows for the uncertainty as to which may be the most sensitive species, and the chronic mode of action, which are offset by the high solubility of cyromazine ensuring good dispersion once discharged. Published data by Robinson and Scott (1995) indicate the dangers of basing environmental exposure limits, especially for IGRs, solely on short term acute toxicity studies.

For the overseas situation, in the absence of published UK EQS data DEH would normally use the MATC of 17.5 µg/L based on two whole of life chronic toxicity tests

on *Chironomids* as the aquatic environmental end point for cyromazine. Chironomids are likely to be exposed to cyromazine in British rivers downstream of scours, hence it would be an appropriate value to use for EQS in hazard assessments for that situation in the absence of a chironomid study performed to international guidelines.

Savage (1998) used figures of 5 and 930 μg/L for the UK EQS and MAC respectively, noting these were based on estimates that "have no official standing", with the latter derived from Russell's estimate of the LC0 acute toxicity value. This is essentially the same as proposed above for use for the Australian situation. However, the EQS value is tighter than proposed, and will therefore be used in the absence of a NOEC in the available literature.

6.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

The main hazard that may arise from the registered use of the products is likely to derive from wool scouring effects of the treated sheep and the run-off onto soil from jetting and dipping of treated sheep. However, only the wool scouring effects are assessed in this report.

6.7.1 Residue levels on Australian wool

According to the Australian Wool Innovations' (AWI) annual survey for pesticide residues on fleece wool (Scott Williams, personal communication, March 2003), mean cyromazine residues have fluctuated in a band from 5.1 to 10.2 mg/kg greasy wool from 1994-1995 until 2000-2001, depending on seasonal conditions and susceptibility to flystrike.

The mean cyromazine residues on Australian fleece wool for 2001-2002 was 8.6 mg/kg, with 35.6% of samples having residues greater than the limit of resolution (LoR), and with the mean residue when treated 24.3 mg/kg, with the highest residue level in the survey a surprisingly high 220 mg/kg. Interestingly while residues at >50 mg/kg constituted only 5% of the sales lots, they contributed to 49% of the residue load, with a further 27% contributed by residues in the range 29-49.5 mg/kg (7% of sales lots). In total 21% of the sales lots with residues >10.0 mg/kg contributed 93% of the residue load.

The mean cyromazine residues on Australian fleece wool for 2002-2003 fell slightly to 6.0 mg/kg, with 30.2% of samples having residues greater than the LoR and the mean residue when treated was 19.8 mg/kg. However, the mean cyromazine residues on Australian fleece wool rose again in 2003-2004 to 7.5 mg/kg, with 29.0% of samples having residues greater than the LoR and the mean residue when treated was 26.0 mg/kg (Russell, 2004).

The value of 8.6 mg/kg, representing the highest mean value on Australian fleece wool over the past 3 seasons will be used as the input concentration for the hazard calculation for cyromazine. For comparison the residue level of 52.4 mg/kg,

representing the mean residue from cored bale analysis when treated with the jetting product 6 months before shearing, has also been used. This is very similar to the level of 47.6 mg/kg found when sheep were treated 9 months after shearing with the spray-on product and represents a "hot spot" sales lot. Note that in the 2001-2002 AWI Wool Residue Survey 5% of the sales lots had residues >50 mg/kg.

6.7.2 Australian Model

The Australian model (Savage 1998) has been used by DEH to predict the worst case level of cyromazine present in sewage effluent entering the Barwon waters from the Black Rock treatment plant. The results of the calculations performed by DEH takes into consideration the following parameters as shown in Table 6.18.

Table 6.18: Determination of Q values by DEH

Parameter	Cored bale analysis	AWI annual survey data
Concentration of cyromazine in wool at harvest (mg/kg)	52.4	8.6
Mass of wool scoured in one day (tonnes)	50	50
Mass of cyromazine entering scouring plant on wool (g)	2620	430
Percentage remaining on scoured wool (%)	4	4
Percentage removed with grease during scouring (%)	0	0
Percentage removed during sewage treatment (%)	0	0
Mass of cyromazine discharged (g)	2515.2	412.8
Flow rate of sewage treatment plant (ML/d)	50	50
Predicted concentration in sewage outflow (ng/L)	5.03×10^4	8.256×10^3
Plume dilution factor#	0.02	0.02
Predicted Environmental Concentration (PEC) ng/L	1006	165.12
Predicted No Effect Concentration (PNEC) (ng/L)	9.3×10^5	9.3×10^5
Quotient (PEC/PNEC)	**1.1×10^{-3}**	**1.8×10^{-4}**

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000)

The Q value derived based on the AWI monitoring and wool residue depletion data is <<1 even when the value of 52.4 mg/kg based on a cored bale following treatment with the jetting product 6 months prior to shearing (or the spray-on 3 months prior) is used. Even taking the extreme worst case of a processing lot containing the highest residue of 220 mg/kg in a sales lot during the 2001-2002 AWI survey, the Quotient is 4×10^{-3}. If the maximum 600 mg/kg residue in the 2003-2004 clip is used the Q is 1.3×10^{-2}. Since the Q is <<1, this indicates that there is not likely be a hazard to aquatic life under any situation following wool scouring Australian conditions under the current 2 month WWP.

6.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of the model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall under Australian conditions, ie the PNEC. The result is shown in Table 6.19.

Table 6.19: Calculated concentration of cyromazine (ng/L) in raw greasy wool based on the target concentration of 930 ug/L at the ocean outfall for cyromazine

Parameters	**DEH's estimates**
Target concentration (ng/L)	9.3×10^5
Load entering the ocean which takes into account the plume dilution factor (ENV) (g)	50 ML X 930,000 ng/L X 50 = 2.325×10^6
Load entering sewage treatment plant (STP) (g)	$100/100 \times 2.3 \times 10^6 = 2.325 \times 10^6$
Load entering wax recovery (WAX) (g)	$100/100 \times 2.3 \times 10^6 = 2.325 \times 10^6$
Load entering scour (SCR) (g)	$100/96 \times 2.3 \times 10^6 = 2.422 \times 10^6$
Concentration of residues on wool (mg/kg)	$2.2 \times 10^6/50 = 48,436$

The calculations confirm that there is unlikely to be an environmental hazard based on the 2001-2002 AWI monitoring data of 8.6 mg/kg for cyromazine under Australian conditions, or from the mean residue of 52.4 mg/kg from cored bale analysis when treated with the jetting product 6 months before shearing (or the spray-on 3 months prior). Likewise there is no hazard using the maximum residue level found in a 2003-2004 sales lot of 600 mg/kg. Therefore it may be concluded that treatment of sheep according to the approved label (with a 2 month WWP) and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

6.8 TRADE

6.8.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, environmental quality standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry. However, the EqualS™ database[15], the former website[16] (http://www.basicweb.fsnet.co.uk/index.htm), or Annex G of of the Scottish Environmental Protection Agency web site (accessed on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf), reveal there are no EQS AA and MAC values for cyromazine. Therefore the calculated wool residue levels on the basis of EU/UK requirements and the AA and MAC values adopted above (Section 6.6.5) are used in Table 6.20.

[15] The EqualS™ database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[16] Available from 2001 but removed in mid 2003.

Table 6.20: Predicted concentration of cyromazine (ng/L) in river based on the EU/UK model by DEH

Parameters	DEH's estimate	
	AA (chronic)	MAC (acute)
Concentration of cyromazine in wool at harvest (mg/kg)	8.6	8.6
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of cyromazine entering scouring plant on wool (g)	237.36	237.36
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	0	0
Percentage removed during sewage treatment (%)	0	0
Mass of cyromazine discharged (g)	227.87	227.87
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	**1529.3**	**3209.4**
UK/EU expected requirement (ng/L)*	5000	930,000

* These values are derived above. Both the AA and MAC values have no official standing.

On the basis of the 2001-2002 AWI monitoring data of 8.6 mg/kg for cyromazine, the predicted environmental concentration for AA and MAC meet the possible UK/EU requirements of 5000 and 930,000 ng/L, respectively. This would still be the case using the mean residue value when treated of 24.3 mg/kg, and for MAC (but not for AA) if the core bale sampling level of 52.4 mg/kg is used. This is assumed as a "hot spot" sales lot, noting that 5% of these in the 2001-2002 AWI monitoring results had cyromazine levels >50 mg/kg. As cyromazine is widely used there is some possibility that there would be insufficient dilution during processing. However, as the Q = ~1.95, only limited dilution in wool processing lots before scouring would need to occur. Further, the AA is a mean annual average that can be exceeded at least for some of the time.

6.8.2 Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the river outfall as shown in Table 6.21.

Table 6.21: Calculated concentration of cyromazine (ng/L) in raw greasy wool based on the proposed EU/UK model.

DEH estimates based on UK/EU proposed EQS (AA/MA) Requirements		
Parameters	**AA (Chronic)**	**MA (Acute)**
Target concentration (ng/L)	5000	930,000
Load entering the river (ENV) (g)	149 ML X 5000 ng/L = 745	71 ML X 930,000 ng/L = 66,030
Load entering sewage treatment plant (STP) (g)	100/100 X 745 = 745	100/100 X 66,030= 66,030
Load entering on-site treatment plant (OST) (g)	100/100 X 745 = 745	100/100 X 66,030= 66,030
Load entering scour (SCR) (g)	100/96 X 745 = 776	100/96 X 66,030= 68,781
Concentration of residues on wool (mg/kg)	776/27.6 = 28.1	68,781/27.6 = 2,492

On the basis of the above model, the 2001-2002 AWI monitoring data of mean residues of 8.6 mg/kg for cyromazine would comfortably meet the calculated AA and MAC values of 28.1 and 2,492 mg/kg, respectively. Again this would still be the case using the mean residue value when treated of 24.3 mg/kg, and for MA if the core bale sampling level of 52.4 mg/kg is used, assuming a "hot spot" sales lot, but not for the

AA. Since this level is a possible considering the widespread use of cyromazine, there is the potential for use of cyromazine according to label instructions to unduly prejudice Australia's export trade, though as noted above this possibility would not seem to be high.

6.9 WOOL WITHHOLDING PERIOD (WWP)

In its original March 2000 submission, the registrant proposed a *Nil* WWP for the current use pattern for the Vetrazin products. This was based on the residue data and modelling available at the time (relatively brief details only were provided).

Proposed WWPs for cyromazine were reported by Horton and Campbell (2001) based on the wool residue breakdown model and using the 1999-2000 AWI wool residues data (since there was some concern whether the most recent data represented the "average" residues), but allowing for a four fold increase in the use of cyromazine. The results are shown in Table 6.22.

Table 6.22: Suggested days from treatment to shearing using the Horton-Campbell Model

Cyromazine	**UK AA EQS (days)**	**UK MAC EQS (days)**	**Australia (days)**
Jetting	0	0	0
Spray-on	<23	0	0
Dip	<193	0	0

In March 2003 the registrant provided the additional wool residue data assessed in Section 6.5.3, as well as a report by Campbell and Horton (2003), which used the latest version of the Horton-Campbell model.

Using the total wool residue data and their derived half-lives from the trials described above, as well as making assumptions about the amount of cyromazine retained for the various treatments, and allowing for the growth of wool at the time of treatment, Campbell and Horton (2003) were able to predict the residues from the treatments with cyromazine and derive recommended maximum processing lot concentrations of 97,000 mg/kg wool for Australia and 43 and 3890 mg/kg in wool for the UK EQS AA and MAC respectively. This in turn was converted into sales lot maxima of >97,500 mg/kg in wool for Australia, or >1050 and >4000 mg/kg in wool for the UK AA and MAC, respectively.

Based on this Campbell and Horton (2003) concluded that even if sheep with 6 weeks wool growth are dipped, jetted or sprayed on the day of shearing, the residue of about 3,200 mg/kg (3000 mg/0.93 kg fleece), 1,100 mg/kg (1000 mg/0.93 kg fleece) and 3,300 mg/kg (3060 mg/0.93 kg fleece), respectively would be well within the limits, and therefore no WWP for Australian wool processing is required.

For the UK AA, Campbell and Horton (2003) note that the maximum levels for UK processing lots of 43 mg/kg is an annual average value that must not be exceeded on average over the full course of the year. This was derived for the less demanding Calder River system or 28 mg/kg for the more stringent Spenborough used by Savage (1998). The authors note that the average cyromazine levels in wool when detected in sales lots

was 23 mg/kg over 1999-2001, which confirms that even if use of cyromazine were to increase 3-4 times, then the UK AA EQS still would not be exceeded (based on the expected dilution when converted into processing lots). They also note that while premature shearing of lambs is more common than with adult sheep, the breakdown rate is 1.4 times faster. They conclude that because premature shearing does not require a WWP for adult sheep, it is also not necessary for lambs.

For the UK MAC Campbell and Horton (2003) note that application of the spray-on product (5040 mg in the worst case) to sheep immediately before normal shearing (approximately 5 kg wool) would leave a maximium concentration of 1008 mg/kg on wool which is less than their processing lot maximum of 3,890 mg/kg. Similarly treatment and shearing with only 6 weeks wool also leaves residues below this level (see calculations above). Therefore they conclude no WWP is needed to ensure that the MAC is not exceeded.

The authors also take into account repeat treatments, noting that the sheep treated at 6 and 9 months wool growth with the spray-on product had lower residues than those treated once only with 9 months wool growth. While this was not the case for sheep treated by hand jetting, the level of 210 mg/kg wool is well below their estimated sales lot maximum concentrations, the lowest being >1050 mg/kg for the UK EQS MAC. Therefore again no WWP is required.

6.10 CONCLUSIONS

Products containing cyromazine are in wide use in Australia, including several generic cyromazine products that have been recently registered. These products are claimed to prevent/treat sheep blow fly strike.

The hazard calculations based on the AWI monitoring data indicate that there is unlikely to be an environmental hazard both locally and overseas under the registered use of cyromazine (ie 2 month WWP). The DEH is therefore able to conclude that the use of selected sheep ectoparasiticide products containing cyromazine in accordance with approved label instructions and the current WWP would not be likely to have an effect that is harmful to animals, plants, or things or to the Australian environment under Australian scouring conditions.

However, there may be a potential hazard from “hot spots” based on the EQS. The DEH therefore concludes that there is a marginal potential prejudice to trade associated with the use of products containing cyromazine, based on a comparative analysis of likely scour residues and their likely future impact on exports of Australian raw wool.

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CHAPTER 7 - IVERMECTIN

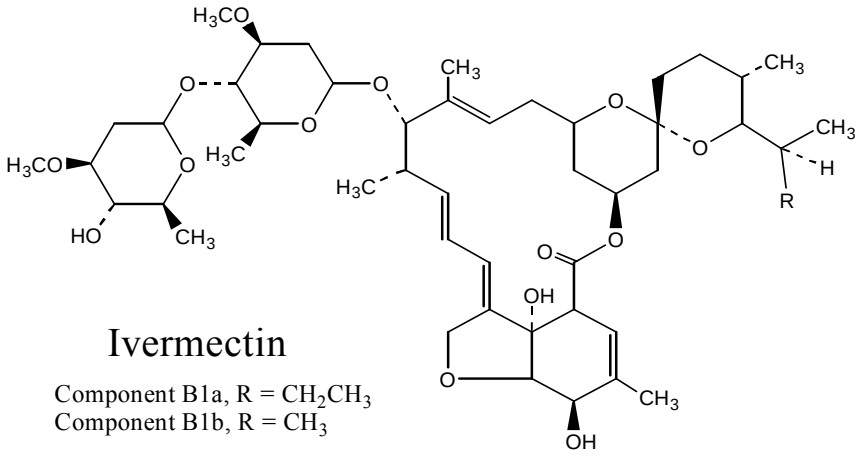
7.1 INTRODUCTION

This report is based on published data and the data provided by the registrant for the sheep ectoparasiticide review. There are currently 108 registered products containing ivermectin of which *Jetamec Jetting Fluid Concentrate* was selected for the review in accordance with the APVMA Gazette of 7 September 1999. The product is registered for use in treating and preventing blowfly strike in sheep and in treating biting lice in long wooled sheep by jetting.

7.2 CHEMICAL IDENTITY

Name:	22,23-dihydroavermectin B_{1a} and 22,23-dihydroavermectin B_{1b}
Common name:	Ivermectin
Manufacturer's code numbers & synonyms:	22,23-dihydroavermectin B_1 22,23-dihydro C-076B_1 MK-933
CAS number:	22,23-dihydroavermectin B_{1a} : 70161-11-4 22,23-dihydroavermectin B_{1b}: 70209-81-3 Ivermectin:70288-86-7
Molecular formula:	22,23-dihydroavermectin B_{1a}: $C_{48}H_{74}O_{14}$ 22,23-dihydroavermectin B_{1b}: $C_{47}H_{72}O_{14}$
Molecular weight:	22,23-dihydroavermectin B_{1a}: 874 22,23-dihydroavermectin B_{1b}: 860
Purity of TGAC:	22,23-dihydroavermectin B_{1a}: 80% minimum 22,23-dihydroavermectin B_{1b}: 20% maximum Overall purity > 95%

Structural formula:



Ivermectin

Component B1a, R = CH_2CH_3
Component B1b, R = CH_3

7.3 PHYSICAL AND CHEMICAL PROPERTIES

These have been obtained from CVM (1996) and Campbell (1989).

Appearance:	white to yellowish white crystalline powder
Melting point:	150°C (ill-defined)
Partition coefficient K_{ow}:	1651
Vapour pressure	$<1.5 \times 10^{-9}$ mm Hg
Water solubility (mg/L):	5 ppm in saturated solution
Solubility in other solvents:	Freely soluble in methanol, p-dioxane, dimethylformamide and ethyl acetate; soluble in 95% ethanol, diethyl ether, methylene chloride acetone and aromatic hydrocarbons; and very slightly soluble in aliphatic hydrocarbons.

7.4 ENVIRONMENTAL EXPOSURE

7.4.1 Volume

The registrant has indicated that the product has a maximum of 10% market share for long-wool jetting. As the market for jetting products is about half the Australian sheep flock, such a market share implies a maximum of 5% of all Australian wool is treated with ivermectin. This value will be used in the hazard calculation for wool scouring.

7.4.2 Application and use pattern

The recommended dose rate applied by jetting for the control of blowflies (*Lucilia cuprina*, *L. sericata*, *Chrysomya rufilacies*, and *Calliphora nociva*) is 1/2500 X 75 mg/mL = 0.03 mg/mL and the minimum rate of jetting fluid is 2.5 L per animal. Therefore, the total amount of ivermectin administered per animal is at least 0.03 mg/mL X 2500 mL = 75 mg.

The recommended dose rate for the treatment of lice on adult sheep with long wool is 0.5 L per month of wool growth. Hence, for 9 months wool growth, the amount of ivermectin administered is 9 X 0.5 L = 4.5 L of the diluted concentration of 0.03 mg/mL ie 4500 mL X 0.03 mg = 135 mg per animal.

For the treatment of blowfly strike, wool must be thoroughly saturated to skin level along the backline and breech. The pizzle area of wethers and the poll (particularly in horned sheep) is also treated. For the treatment of lice in long wool sheep, the skin and fleece must be thoroughly wet to skin level from poll to tail in a band along the back about 25 cm wide. Wool and skin on the sides of the neck in front of the shoulders should also be wet to skin level.

The label indicates “DO NOT apply later than 12 weeks before shearing”.

7.5 ENVIRONMENTAL CHEMISTRY AND FATE

7.5.1 Residue depletion on Australian wool

7.5.1.1 Report No. ASR 12507: Levels of Ivermectin (MK933) present in wool and wool byproducts at proposed withholding periods

Three hundred and ninety 16-month old Merino ewes and wethers weighing 30.5-52 kg with 12 months wool growth were allocated to three groups (each group = 130 animals - Scott et al. 1990). One group was administered with the registered product by jetting at the label recommended dose rate (approximately 3 L of 0.03 mg/mL or 90 g per sheep) and shorn 56 days after treatment and the other group was treated in a similar fashion and shorn 84 days after treatment. The remaining group was used as the untreated control and shorn on day 55. Note this represents about 14 or 15 months wool growth prior to shearing.

Following shearing of the treated animals and untreated animals, fleeces from each treatment group were packed in four bales. 95 days after treatment, core samples were collected from each bale of greasy wool and fleeces were scoured at the wool scouring plant at CSIRO Division of Wool Technology, Geelong, Victoria. Wool from each group was scoured separately and samples (about 100 g each) were collected for ivermectin measurement in unscoured greasy wool, scoured wool, wool grease and scour wastes. Ivermectin residues were analysed using HPLC with fluorescence detection. The results are shown in Tables 7.1, 7.2 and 7.3.

Table 7.1: Ivermectin concentrations in unscoured greasy wool from bale cored samples

Wool shorn after treatment (days)	**Ivermectin concentration (mg/kg)**	**Mean ivermectin concentration (mg/kg)**
56	1.03, 1.19	1.11
	1.12, 1.29	1.21
	1.26, 1.28	1.27
	1.19, 1.03	1.11
Total Mean		**1.17**
85	1.63, 1.73	1.68
	1.72, 1.47	1.59
	1.45, 1.52	1.48
	1.39, 1.28	1.34
Total Mean		**1.52**

Ivermectin residues for untreated controls were at non-detectable levels

Table 7.2: Ivermectin concentrations remaining in scoured wool from bale core samples

Wool shorn after treatment (days)	Ivermectin concentration (ppb)	Mean ivermectin concentration (ppb)
56	0.28, 0.29	0.29
	0.14, 0.15	0.15
	0.29, 0.27	0.28
	0.31, 0.30	0.31
	0.27, 0.26	0.27
	0.24, 0.24	0.24
	0.25, 0.24	0.26
	0.25, 0.27	0.27
Total Mean		**0.26**
85	0.20, 0.20	0.20
	0.16, 0.14	0.15
	0.24, 0.23	0.24
	0.21, 0.23	0.22
	0.32, 0.34	0.33
	0.26, 0.22	0.33
	0.29, 0.27	0.24
	0.27, 0.27	0.28
Total Mean		**0.24**

Ivermectin residues for untreated controls were at non-detectable levels

Table 7.3: Summary of mean ivermectin quantities in unscoured wool and wool scouring by-products

Components (by-products) of wool scouring	Day 56 after treatment			Day 85 after treatment		
	Mean ivermectin concentration ± SD (mg/kg)	Mass of components (kg)	Total ivermectin (mg)	Mean ivermectin concentration ± SD (mg/kg)	Mass of components (kg)	Total ivermectin (mg)
Unscoured wool	1.17 ± 0.08	677	792	**1.52 ± 0.15**	743	**1130**
Heavy solid tank sludge	0.20 ± 0.03	>5	>1	0.024	7.6	0.2
Decanter centrifuge sludge	0.44 ± 0.07	13.8	6.1	0.40 ± 0.03	8.5	3.4
Primary centrifuge sludge	0.34 ± 0.03	31.6	10.7	0.38 ± 0.05	21.9	8.3
Primary centrifuge middle phase	0.092 ± 0.068	1460	134	0.071 ± 0.062	1990	141
Primary centrifuge cream phase	3.55 ± 2.0	54.6	194	1.35 ± 0.90	47.2	63.7
Rinse water	0.0012 ± 0.0003	4183	5.0	0.0010 ± 0.0004	5123	5.1
Anhydrous grease	9.2 ± 0.99	4.2*	38.6	8.1 ± 0.13	2.1**	17.0
Scoured wool	0.26 ± 0.05	474	123	0.24 ± 0.05	498	**120**
Total in components			474			342

* 2.0 kg of approx 60% grease remained in the centrifuge

** Centrifuge failed – recovery of cream resulted in low yield

The results indicate that under the recommended use pattern where the wool withholding period (WWP) of 12 weeks on the label is observed, the mean ivermectin

concentration in the unscoured wool sampled by baled cores was found to be 1.52 mg/kg (see Table 7.1). This value is lower than the mean ivermectin concentration of 4.25 mg/kg derived from the band sampling of the backline treatment area of 10 sheep from each treatment measured concurrently. The lower value is to be expected since the coring technique would have sampled a combination of the treated and untreated parts of the fleece. This value will be used as the input concentration for the hazard calculation.

Table 7.3 summarises the mean concentration of ivermectin in the unscoured wool on days 56 and 84 after treatment and in the scoured wool and scour effluent by-products in the scouring process. The primary centrifuge cream phase and the resultant anhydrous wool grease have the highest mean concentration of ivermectin. The mass of ivermectin in scoured wool was approximately 10.6% of ivermectin mass found in the unscoured greasy wool at 85 days after treatment (see Table 7.3).

The registrant did not calculate the degradation rate of ivermectin residues on wool, an estimation is not possible as only the residue results at shearing are available.

7.5.2 Summary of environmental fate

The registrant has provided summaries of the findings of the 1991 submission and has indicated that comprehensive data on the environmental chemistry and fate and toxicology of ivermectin have been previously reviewed. Published data since this submission are also incorporated into this aspect of the review. The relevant data are summarised below.

No data on hydrolysis were provided. The photolytic data indicate that photodegradation to less active compounds occurs near the surface of open, flat bodies of water. The half-life was affected by the season, being 12 h in summer and 39 h in winter (Bloom and Matheson 1993). Ivermectin underwent photodegradation on a thin dry film on glass with an estimated half-life of about 3 h in summer sunlight (Halley et al. 1989). When sprayed onto the surface of soil outdoors in summer avermectin B1 had a half-life of approximately 5 hours.

The degradation half-life of ivermectin in soil varies greatly depending on conditions from 7-14 days outdoors in summer to 93-240 days in soil kept in the laboratory in the dark. Temperature is considered an important factor in the degradation process, which increases with increase in temperature (Halley et al. 1989). The half-life of ivermectin in marine sediments is approximately 100 days (Davies et al. 1998).

Ivermectin is rather insoluble in water and has a high octanol-water partition coefficient. Soil-binding studies with ^{3}H-labelled ivermectin confirmed that is tightly bound to soil as is evident from the high partition coefficient of K_D = 227-333 and high organic carbon binding constant of K_{oc} = 12600 to 15,700 (Halley et al. 1989). K_{oc} values are a good index of the leaching ability of the compound. Run-off in surface water and leaching into ground water should be minimal.

No field dissipation studies were provided, but exposure will be limited from use for the control of blowfly and lice control. Therefore, the potential for accumulation in soil is considered unlikely.

Ivermectin was shown to bioaccumulate in mussels (*Mytilus edulis*) by a factor of 750. Depuration studies of ivermectin from mussels had a calculated half-life of 22 days. However, bioconcentration for trout and bluegill sunfish indicate that ivermectin does not bioaccumulate in these species (Davies et al. 1997).

7.6 ENVIRONMENTAL EFFECTS

7.6.1 Avian/mammal toxicity

Ivermectin is not very toxic to birds, chickens, ducks and mammals. Considering the method of application, either as a drench or jetting fluid, toxicity to these species is considered unlikely (Halley et al. 1989).

7.6.2 Aquatic toxicity

The relevant results for the selected aquatic organisms and other species provided by the registrant or based on more recently published data are summarised in the following tables:

Marine species

Species	**LC_{50} (ng/L)**	**LOEC or LC_{10} (ng/L)**	**Reference**
Crustaceans *Neomysis integer* (mysid shrimp)	26 (48 h)	3.6	Grant and Briggs 1998
	70 (96 h)	-	Davies et al. 1997
Gammarus spp	33	3.3	Grant and Briggs 1998
Amphipod *Corophium volutator*	180 000	50 000	Davies et al. 1998
Star fish *Asteria rubens*	23 600 000	5 000 000	Davies et al. 1998

Freshwater species

Species	**LC_{50} (ng/L)**	**LOEC or LC_{10} (ng/L)**	**Reference**
Invertebrates *Daphnia magna* (water flea)	25 (48 h)	10.0	Bloom and Matheson 1993; Halley et al. 1989
Fish *Salmo gairdneri* Rainbow trout	3300 (96 h)	900	Halley et al. 1989
Lepomis macrochirus Bluegill sunfish	5300 (96 h)	-	Halley et al. 1989
Alga *Chlorella pyrenoidosa*	>10000000 (14 days)	-	Halley et al. 1989

Other species

Species	LC_{50} (mg/kg)	LOEC or LC_{10} (mg/kg)	Reference
Earthworm *Eisenia foetida*	315 (28 days)	12.0	Halley et al. 1989
Soil Micro-organisms Bacteria, Fungi	-	No effect at up to 2000 ppm	Halley et al. 1989
Phytotoxicity	-	No effect at 10 kg/ha	Bloom and Matheson 1993

7.6.3 End point to be used for hazard assessment

As scouring effluent will be discharged to ocean, the results that the most sensitive marine species to ivermectin is the mysid shrimp (*Neomysis integer*) with an LC50 of 26 ng/L (48 h exposure) are most relevant. To estimate an acute no effect concentration is difficult as NOECs for sensitive species are not available. Based on the Lowest Observable Effect Concentration (LOEC) of 3.6 ng/L for mysid shrimp available from the literature, it is apparent that the acute NOEC value can be any value below 3.6 ng/L. Applying an Assessment Factor of 10 to the LC50 of 26 ng/L would yield a value of 2.6 ng/L, which is not sufficiently protective. Therefore, the acute Predicted No Effect Concentration (PNEC) of 1 ng/L is proposed based on the tentative MAC derived from the UK EQualS^{TM} database (see Section 7.9.1).

7.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

7.7.1 Residue levels in the Australian wool clip

There are no AWI monitoring data available for ivermectin. Therefore ivermectin concentrations of 1.52 mg/kg obtained from core bale sampling of wool treated with the product will be used as the input concentration (refer to Table 7.1) for the hazard calculation.

7.7.2 Australian model

The Australian model is used based on scouring at Geelong, where primary treated effluent from scouring of wool is discharged daily through the Geelong sewerage system to the Black Rock ocean outfall.

The Department of the Environment and Heritage's (DEH) calculations are shown in Table 7.4. A default value of 80% derived from the Woolmark report (Savage 1998) as the ivermectin percentage removed during sewage treatment is used, as is the 4% generally applied to lipophilic chemicals which remain on wool after scouring. Due to the problems encountered by Scott et al (1990) the default value of 30% removed with grease during scouring has also been retained.

Table 7.4: Determination of Q value for ivermectin by DEH

Parameters	**DEH estimate**
Concentration of ivermectin in wool at harvest (mg/kg)	1.52
Mass of wool scoured in one day (tonnes)	50
Predicted market share of *Jetamec#*	5
Mass of ivermectin entering scouring plant on wool (g)	3.8
Percentage remaining on scoured wool (%)	4
Percentage removed with grease during scouring	30
Percentage removed during sewage treatment (%)	80
Mass of ivermectin discharged (g)	0.51
Flow rate of sewage treatment plant (ML/day)	50
Dilution in plume*	0.02
Potential Environmental Concentration (PEC) (ng/L)	**0.2**
Predicted No Effect Concentration (PNEC) (ng/L)	1
Quotient (PEC/PNEC)	**0.2**

DEH has used a market share of 5% for *Jetamec* as estimated by the registrant.

*A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).

DEH's calculations yield a Q value of <1 indicating that there is unlikely to be an environmental hazard. The safety margin is greater if 10% is assumed to remain on scoured wool (Q = 0.08), but this may be offset by a lesser amount than assumed being removed with the wool grease.

The calculations suggest that if the market share increases to about 25%, there is a potential for an environmental hazard to occur. However, this is unlikely under present conditions.

7.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall as shown in Table 7.5.

Table 7.5: Calculated concentration of ivermectin (ng/L) in raw greasy wool based on the target concentration of 1 ng/L at the outfall for ivermectin

Parameters	**DEH's estimates**
Target concentration (ng/L)	1
Load entering the ocean (ENV) (g)	50 ML X 50 X 1 ng/L = 2.5
Load entering sewage treatment plant (STP) (g)	100/20 X 2.5 = 12.5
Load entering wax recovery (WAX) (g)	100/70 X 12.5 = 17.86
Load entering scour (SCR) (g)	100/96 X 17.9 = 18.6
Concentration of residues on wool (mg/kg)	18.6/50 = 0.37

It is apparent that on the basis of the wool residue data of 1.52 mg/kg and a market share of 5% for ivermectin, (1.52 X 0.05 = 0.076) there is unlikely to be an environmental hazard when ivermectin is used according to the currently approved label instructions as long as it is below its maximum allowable mean concentration of 0.37 mg/kg any scour lot. Since the market share would need to rise to about 25% before a potential hazard exists (unlikely under present circumstances) it may be concluded that treatment of sheep according to the approved label (including a 3 months WWP) and scouring of wool under Australian conditions would not be likely

to have an unintended effect that is harmful to animals, plants or things or to the environment.

7.8 TRADE

7.8.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, environmental quality standards (EQS) for Annual Average (AA) and Maximum Allowable Concentration (MAC) are in place for the textile industry to meet environmental standards. The EQualS^{TM} Version 3.0 database[17] indicates that the proposed AA and MAC values for ivermectin are 0.1 and 1 ng/L, respectively. These tentative values and subject to review, which remained the same on the former website[18] (http://www.basicweb.fsnet.co.uk/index.htm), and are listed as tentative in Annex G of of the Scottish Environmental Protection Agency web site (available at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf, accessed on 6 March 2006). The predicted environmental concentrations in rivers on the basis of the tentative EU/UK requirements are shown in Tables 7.6.

Table 7.6: Predicted concentrations of ivermectin (ng/L) in river based on the EU/UK model by DEH

DEH EU/UK models estimate		
Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of ivermectin in wool at harvest (mg/kg)	1.52	1.52
Mass of wool scoured in one day (tonnes)	27.6	27.6
Predicted market share of the *Jetamec* product (%)	5	5
Mass of ivermectin entering scouring plant on wool (g)	2.1	2.1
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	80	80
Mass of ivermectin discharged (g)	0.08	0.08
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	**0.5**	**1.1**
UK/EU expected requirement (ng/L)	0.1	1

On the basis of the DEH calculations, the predicted environmental concentrations are higher than the tentative UK/EU requirements for both EQS AA and MAC, particularly for AA, indicating a significant environmental hazard. Therefore there is a high potential for adverse effects on trade from the use of ivermectin for treatment of lice on sheep.

[17] The EqualS^{TM} database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[18] Available from 2001 but removed in mid 2003.

7.8.2 DEH's Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the outfall as shown in Table 7.7.

Table 7.7: Calculated concentration of ivermectin (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 0.1 (AA) and 1 (MAC) ng/L for ivermectin

DEH calculations based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)*	0.1	1
Load entering the river (ENV) (g)	149 ML X 0.1 ng/L = 0.0149	71 ML X 1 ng/L = 0.071
Load entering sewage treatment plant (STP) (g)	100/20 X 0.0149 = 0.0745	100/20 X 0.071 = 0.355
Load entering on-site treatment plant (OST) (g)	100/20 X 0.0745 = 0.3725	100/20 X 0.355 = 1.775
Load entering scour (SCR) (g)	100/96 X 0.3725 = 0.39	100/96 X 1.775 = 1.85
Concentration of residues on wool (mg/kg)	0.39/27.6 = 0.014	1.85/27.6 = 0.067

* UK is 'worst case scenario' for the EU and has tentative EQS values for AA and MAC of 0.1 and 1 (ng/L) for ivermectin.

On the basis of the above model, given the worst case scenario, the wool residue data of 1.52 mg/kg for *Jetamec* (even taking market share into account 0.05 X 1.52 = 0.076 mg/kg), would not meet the UK/EU requirements, particularly for AA, under the currently labelled use pattern. Therefore there is a high potential for adverse effects on trade from the use of ivermectin for treatment of lice on sheep according to label instructions with the current 3 months WWP.

7.9 CONCLUSIONS

Two registered ivermectin products are used on sheep by jetting for treatment of ectoparasiticdes on sheep, one of which is covered by this review. The concern that arises is the environmental exposure of water to ivermectin through release of scouring effluent.

DEH calculations indicate that there is unlikely to be an environmental hazard from scouring of wool under Australian conditions, even if the market share increases significantly. Therefore it may be concluded that treatment of sheep according to the approved label (including a 3 months WWP) and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

DEH estimates for overseas requirements indicate that there are potential trade implications with the current WWP of 3 months. In the absence of residue data and an accurate current market share for ivermectin products, DEH is unable to establish an appropriate WWP based on the data available. However, a simple calculation suggests the amount of sheep treated with ivermectin should not exceed 1% of the Australian sheep flock to meet the tentative EQS at the current 3 months WWP.

It must be noted that the current assessment is based on a market share of 5% of one product. The actual amount of ivermectin in wool will be affected by overall usage, which in turn depends on number of products on the market and the market share of each product. An increase or decrease in either could result in an increase or decrease in the predicted concentration of ivermectin in the sewerage outflow. Thus, the predicted concentration of ivermectin in sewage outflow could conceivably be higher when all currently registered products are considered.

7.10 REFERENCES

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CHAPTER 8 - TRIFLUMURON

8.1 INTRODUCTION

Zapp Pour-on Lousicide for Sheep was included in the review in accordance with the APVMA Gazette of 7 September 1999. There are a number of other veterinary products containing triflumuron that have been recently registered for use as lousicides on sheep, all of which appear to be image products.

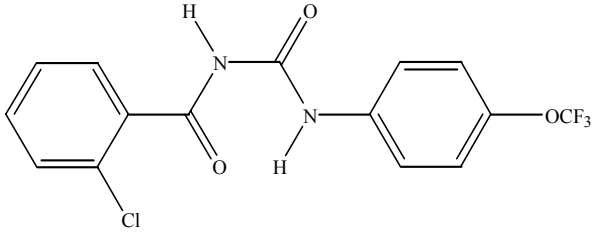
Zapp is registered for use in the control of body lice *Bovicola ovis* on shorn sheep up to 7 days off-shears and lambs at foot. As no WWP was set for *Zapp*, it has a default WWP of 2 months, though as an off-shears treatment wool is unlikely to be shorn at 2 months after treatment due to limited wool growth.

Products containing triflumuron are currently registered for use on sheep in New Zealand. Products containing triflumuron are also registered for use by jetting on sheep in South Africa.

Although the product is an off-shears treatment on sheep, for the purposes of the review it is considered a short and long wool treatment due to the persistence of triflumuron after application. This report will focus on the wool scouring effects of triflumuron from veterinary use on sheep and update as appropriate the previously available assessment report drafted as part of the registration evaluation.

8.2 CHEMICAL IDENTITY

Chemical Name:	1-(2-chlorobenzoyl)-3-(4-trifluoromethoxyphenyl)urea (IUPAC) 2-Chloro-[[[4-(trifluoromethoxy)phenyl]amino]carbonyl]benzamide (CAS)
Common name:	triflumuron
Manufacturer's Code Numbers/synonyms:	SIR-8514; BAY SIR - 8514
CAS number:	64628-44-0
Empirical formula:	$C_{15}H_{10}ClF_3N_2O_3$
Molecular weight:	358.7
Structural formula:	



Purity of active: >95%

Impurities:	Identity	Max (%)
	2-chlorobenzamide	<4.0
	N,N'-bis[4-trifluoromthoxy) phenyl]urea	<0.1
	4-chloro-N-[[[4-trifluoromethoxyl] phenyl]amino]carbonyl]benzamide	<0.1
	4-trifluoromethoxybenzamine	<0.5

8.3 PHYSICO-CHEMICAL PROPERTIES

Appearance:	Approved active - colourless, odourless solid Product - yellow powder, specific odour
Melting Point:	195°C
Vapour Pressure:	4 X 10^{-7} Pa (at 20°C)
Henry's Law Constant[19]:	K = 2.72 X 10^{-6} Pa.m^3/mol[1] @ 20°C and pH 7.5 (minimum solubility) H = 1.17 X 10^{-9} @ 20°C and pH 7.5 (H < 1 X 10^{-5} - very slightly volatile from water, Mensink *et al*. 1995)
Water Solubility:	25 µg/L (at 20°C)
Solubility in Organic Solvents:	hexane (<100 mg/L) toluene (2-5 g/L) dichloromethane (20-50 g/L)
n-Octanol/Water Partition Coefficient:	Log P = 4.91
Dissociation Constant:	No acidic protons as basic nitrogens present.

8.4 ENVIRONMENTAL EXPOSURE

8.4.1 Volume

Based on usage volumes for the product for the years 1997-1999 the applicant expects that <20 tonnes per annum will be used at full market penetration. Sales information from 1996 indicated the market share to be 13.4% of all sheep shorn. The estimated maximum market share was only 16% as the registrant expected increasing competition from new insect growth regulator pour-on products. The sales volume climbed steadily prior to 1998 but reached a plateau and the registrant expects little further growth.

8.4.2 Application and use pattern

The product is applied as a single strip along the backline from poll to the butt of the tail using the dedicated gun and nozzle. It can be used on all sheep up to 7 days off-shears and on unshorn lambs up to 2 months of age. Application rates range from 10 mL (0.25 g triflumuron) for lambs less than 10 kg to 35 mL (0.875 g triflumuron) for sheep

[19] Calculated by the Department of the Environment and Heritage.

weighing between 85-95 kg. Application rates are to be increased by 5 mL for every 10 kg above 95 kg body weight. Dose rates are based on the heaviest sheep in the mob.

To avoid cross infection, treated sheep are not to be mixed with untreated for at least 4 weeks, with the exception of ewes with lambs. According to the registered label, lambs will either be treated according to body weight with the ewes if at foot when shearing, or up to 2 months of age if born after ewes are shorn.

8.5 ENVIRONMENTAL CHEMISTRY AND FATE

8.5.1 Summary of previous studies

As indicated in previous assessments, triflumuron is hydrolytically stable, except under alkaline conditions, and moderately persistent in soils (half life of 52 days for a single soil under laboratory conditions). Degradation involves hydrolysis to *o*-chlorobenzoic acid, which is mobile and labile, and the corresponding urea, which sorbs strongly to soil and is more persistent. Aerobic aquatic metabolism proceeds at a similar rate to soil metabolism in the laboratory with a slower rate under anaerobic conditions. Triflumuron has a very strong affinity for organic matter, and residues introduced to soil can be expected to remain immobile until they degrade.

8.5.2 New environmetal fate studies

The registrant has provided additional studies on the environmental chemistry and fate for the sheep ectoparasiticide review. The studies are relatively old and mostly have little bearing on the environmental assessment for wool residues. The results are briefly summarised below.

8.5.2.1 Photodecomposition of ^{14}C-Alsystin on soil

Coody (1986) investigated the light-induced decomposition of ^{14}C-material on a soil surface, which indicated that triflumuron is equally stable on illuminated and non-illuminated soil surfaces with respect to the direct effect of the UV radiation. An earlier report indicated volatile losses from an illuminated soil, which is in contrast to the current study where neither parent compound nor its metabolites volatilised from either system (light or dark) during the 41 day study period. It is concluded that the earlier study utilised an artificial light source that emitted higher energy (thus allowing photodecomposition reactions to occur) than in the current study, which demonstrates triflumuron is likely to exhibit limited photodecomposition under natural conditions.

8.5.2.2 Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of triflumuron in water.

Hellpointner (1991) determined the quantum yield of the direct photodegradation of triflumuron in aqueous solution according to the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) method on polychromatic light. From the UV absorption data and the kinetic results of two previous photodegradation experiments, the quantum yield was calculated to be 0.0095. Using the quantum yield and the UV absorption data two different simulation models were employed to estimate the environmental half-life of triflumuron by direct photodegradation in water.

There was good agreement between the environmental half-lives obtained from these two arithmetic models. The data indicate that direct photodegradation in aqueous medium is not the main degradation pathway of triflumuron in the environment, and that the half-life concerning the direct photodegradation may range from two months to more than one year depending on the environmental conditions.

Indirect photodegradation mechanisms may, however, contribute to the degradation in the environment, as Wilmes and Wünsche (1979) found accelerated degradation in methanol, ethyl acetate and acetone. These authors tested photodegradation of triflumuron on silica gel, which indicated no degradation after 10 weeks exposure.

8.5.2.3 Calculation of the chemical lifetime of triflumuron in the troposphere

Calculations based on those by Atkinson indicate the chemical lifetime of triflumuron in the air averages in the range of 0.15-1.5 days, with respect to the OH-radical reaction only (Hellpointner, 1993). Based on this relatively short lifetime in air, and as it is not volatile, it is unlikely that triflumuron will accumulate or be transported in the air over long distances.

8.5 2 4 Analyses of the insecticide triflumuron in Spanish soils

Samples of Spanish soils were obtained from two layers (0-5 cm and 5-20 cm) following treatment with Alsystin 25 OF (an experimental triflumuron formulation) at 180 mL/ha (Bachlechner, 1988). Ten studies were performed over one year and included 9 sampling days per study in the case of the GC method, the results of which compared reasonably well with parallel HPLC analysis. Based on the analyses of the 0-5 cm layer, the half-life of triflumuron ranged from 20-83 days. No active ingredient could be found in the 5-20 cm layer. Soil residues were low at the beginning of the trial and by day 90 the active constituent had degraded to the limit of determination of 0.01 mg/kg.

8.5.2.5 Adsorption of triflumuron to soil

In this study (Bachlechner, 1989), the adsorption of triflumuron to three standard soils [slightly humus sand (a), strongly humus loamy sand (b) and slightly humus sandy loam (c)] was investigated in accordance with the OECD Test Guideline 106. The aqueous samples of triflumuron were analysed by HPLC (UV detection).

The results indicate that triflumuron was adsorbed at an initial concentration of 0.0125 mg/L at 85.6% (a), at 92.4% (b) and at 83.1% (c). The adsorption coefficients (K_d, with the K_{oc} calculated relative to the organic carbon content in parentheses) were 33.3 (2510), 71.1 (2940) and 27.9 (2450) for (a), (b) and (c), respectively. A comparison of the adsorption coefficients shows a close correlation between the adsorption of triflumuron and the humus content of the soil, accounting for the higher adsorption coefficient for (b) than the other soil types as its humus content is the highest.

8.5.2.6 Summary of additional studies

Most of the "new" studies add limited additional information, except that triflumuron is confirmed to be relatively stable to photodegradation on the soil surface, in contrast to an earlier study that indicated volatile losses from an illuminated soil. Direct photodegradation studies in water indicate that the environmental half-lives may range from two months to more than one year. Indirect photodegradation mechanisms may, however, contribute to degradation in the environment. Degradation and adsorption

studies in soils indicate that triflumuron has a half-life in the 0-5 cm layer of Spanish soils ranging from 20-83 days and that there is higher adsorption to soils with higher humus content. These findings are consistent with previous reports.

8.5.3 Exisiting data on residue depletion on Australian wool and fate during scouring

The following summary is derived from a previous supplementary environmental assessment of triflumuron.

8.5.3.1 Fate in Fleece

Triflumuron will mainly remain at the site of treatment following application of the product along the backline of sheep and lambs, with the highest residues at the tip of the staple where it is applied. The data indicate that high concentrations persist at the backline, and that residues are likely to remain mainly at the tip of the growing fleece with only minor amounts to be found at skin level when sheep are shorn. While some degradation is expected in fleece, limited distribution around the animal will occur.

Half-life estimates based on point sampling data are of limited value because of high sampling errors, and cannot be used to predict average wool residues likely to be found in a fleece at shearing. Bale sampling conducted on 1 tonne of wool that had been treated with *Zapp* off-shears for the pilot scale scouring study indicated residues of 31.9 mg/kg on average, while sampling across the 1996-97 clip indicated an average of 25 mg/kg in wool that had been treated. The average for the whole clip, determined from 600 samples, was 3.5 mg/kg.

Solvent extraction of three half-fleeces with 12 months wool growth also found residues of 25 mg/kg, but caution needs to be exercised in extrapolating to whole fleece. Detergent extraction of whole fleeces returned similar results, with residues of 31 mg/kg in 8 months lambs wool, declining to 17 mg/kg in 11 months lamb's wool. A half-life of 6-7 months was estimated.

There were limitations in the available wool residues data. However, the weight of evidence indicated that residues in the order of 25-30 mg/kg are likely to prevail in fleece at shearing following use 12 months previously, increasing to about 100 mg/kg in early shorn lambs carrying 6 months wool growth. Given that a dose of 500 mg triflumuron per sheep would leave residues of 100 mg/kg through a 5 kg fleece if no dissipation occurred, the estimated half-life on the sheep was about 6-7 months.

8.5.3.2 Fate in Scouring

Triflumuron residues in greasy wool will largely be removed at scouring, with some remaining on the scoured wool and significant amounts recovered with wool grease. Pilot scale scouring trials indicate that about 25% of total residues is likely to be discharged with aqueous effluent, unless additional on-site treatment occurs, in which case discharges will be much less than 1% of the original level on greasy wool.

For discharge to sewer, further removal is likely to occur during sewage treatment, mainly through hydrophobic partitioning to sludge. No specific data are available, but

it was assumed some 80% of incoming triflumuron residues may be expected to be removed during sewage treatment.

Remaining residues will be discharged to ocean outfall where rapid dilution and a more gradual degradation is expected to reduce concentrations below measurable levels.

Triflumuron appeared unlikely to persist in marine environments following ocean discharge, as studies with model freshwater systems, in flooded pasture, and seawater indicate that levels dissipated with half-lives in the order of a month. Detection of metabolites in water samples confirmed that degradation occurs in freshwater systems, but test limitations meant that no such confirmation was available for marine waters. However, similar breakdown pathways in fresh and marine waters were assumed.

8.5.3.3 New data on residue depletion on Australian wool and fate during scouring

Additional wool residue data and wool scouring data for triflumuron were provided for this review. These include the published data of wool residue studies by Campbell et al (1998 and 1999) and Morcombe et al. (1999), a New Zealand wool scouring study (Robinson and Joyce 1999) and the laboratory wool scouring (Grundy et al 1998). These studies are described below.

8.5.3.4 Modelling pesticide residues on greasy wool: experimental studies

Campbell et al. (1998) conducted band sampling trials and measured the rate of breakdown of triflumuron and other chemicals at Werribee and other locations in Australia. In these studies Merino wethers or dry ewes, 3-6 years old with mean live weights of 45-55 kg were treated with a range of louse and blowfly control chemicals. In this trial a group of 10 animals were treated off-shears with *Zapp* at the label dose rate applied as a single strip from the poll to the tail. Five sheep in each group were sampled on at least 4 occasions between treatment and shearing. Sheep were shorn 12 months after their previous shearing. Band samples were shorn around the girth of the animal. The samples included all the fleece wool from the circumference of the girth but excluded the belly wool. Samples were stored at 4°C until analysed.

On the basis of the trial performed in Werribee, the authors developed a residue decay model and derived the data presented in Table 8.1.

Table 8.1: Degradation data for triflumuron based on the Campbell Model

Chemical applied per sheep (mg)	750
Modelled chemical per sheep (mg)	799
Half-life, initial (days)	95
Half-life, final (days)	122
Half-life, average (days)	119
Half-life, range (days)	91-171
Final concentration, average (mg/kg)	22
Final concentration, range (mg/kg)	9.1-34

The results indicate that triflumuron applied off-shears had an initial half-life of 95 days, increasing to 122 days over 12 months and averaging 119 days over the year's

study. It should be noted that even when applied off-shears triflumuron has a relatively slow rate of breakdown during the course of the year.

8.5.3.5 Pesticide treatments for louse and fly control to meet future market requirements

In this trial (Campbell et al 1999) merino wethers, 1.5-6 years old and mean body weights ranging from 40-55 kg, were treated with a range of louse and blowfly products. A group of 20 animals was treated with *Zapp* off-shears at the label dose rate as a single strip from the poll to the tail using the manufacturer's applicators. Ten sheep in each group were sampled on 3-6 occasions between treatment and the following shearing. Sheep were shorn 12 months after their previous shearing. Band samples were shorn from around the girth of the animal. This included all the fleece wool from the circumference of the girth but excluded the belly wool. The triflumuron concentrations were measured to determine the effects of climatic conditions upon fleece residues. The results are shown in Table 8.2.

Table 8.2: Triflumuron degradation data at four sites based on the Campbell model

Sites	Half-life (days)	Final concentration (mg/kg)	Breakdown rate relative to Werribee
Werribee, Victoria	141	26	1
Esperance Western Australia	77	4.2	1.81
Longreach Queensland	80	4.1	1.76
Cressy Tasmania	167	34	0.84

The results indicate that in common with other actives, triflumuron degrades faster in warmer climates. Thus it is not surprisng that Tasmania has the highest residue concentration of 34 mg/kg and the lowest relative breakdown rate of 0.84 at shearing. Note that band sampling probably overestimates residue levels as other methods such as bale sampling would include dilution by other non-treated parts of the fleece.

8.5.3.6 Modelling pesticide residues on greasy wool: surveys of the insect growth regulators triflumuron and diflubenzuron

Morcombe et al. (1999) surveyed wool producers known to have used an IGR and measured the wool residues in core samples after shearing. On the basis of the experimental breakdown rate in the Campbell model, the amount of the chemical taken up by wool can be estimated at application.

The data indicated that when used off-shears within 24 h of shearing, triflumuron was normally applied at a higher rate than that recommended and left on average residues of 30 mg/kg greasy wool at shearing 12 months later.

The model can be used to estimate the expected residue level and the likely range of results from most IGR treatments.

8.5.3.7 The fate of Zapp (triflumuron) during aqueous wool scouring

Robinson and Joyce (1999) treated two hundred hogget lambs with *Zapp* at the initial dose rate of 290 mg/kg wool (based on >30 kg live weight carrying 1.7 kg wool). The treated sheep was shorn 3.5 months later and 200 kg of wool was transported to Wool

Research Organisation of New Zealand Inc. (WRONZ) and stored prior to scouring. Analysis of greasy wool prior to scouring indicated a residue level of 47 mg/kg, suggesting that the half-life of triflumuron is of the order of 39 days in long wool.

The shorn wool was scoured in the WRONZ pilot plant wool scour. Samples of greasy and scoured wool, open waste (dust), flowdown, rinse water and final bowl liquors and recovered grease were analysed for triflumuron. Flow rates, volume and masses of all matrixes were recorded and used to determine an overall mass balance for triflumuron. The results of the scouring process are shown in Table 8.3.

Table 8.3: Mass balance for triflumuron in WRONZ scouring study

Samples	**Mass/Volume**	**Mass of TFM (mg)**	**% of greasy mass**
Greasy wool	153 kg	**7007 ± 2319**	100 ± 33
Opener waste	1.8 kg	139	2.0
Heavy flowdown	290 L	502	7.1
Bowl flowdown	1870 L	0	0
Bowl 5 flowdown	2647 L	60	0.8
Bowl 1	760 L	1663	23.4
Bowl 2	760 L	769	10.8
Bowl 3	760 L	103	1.5
Bowl 4	760 L	0	0
Bowl 5	760 L	69	1.0
Bowl 6	760 L	0	0.0
Grease	3.5 kg	298	4.3
Scoured wool	122 kg	**76**	1.1
Recovered mass	-	3680	52.5

The scour study indicates that there were a number of deficiencies such as the mass of recovered sludge not being recorded and that the scour had not reached equilibrium at the end of the scouring period. The results indicate that only 52.5% of input triflumuron was recovered. The authors claimed that the variance of residues in some samples might have contributed to this. This study also found that all but 1% of triflumuron was removed from the wool. This may be attributed to triflumuron being applied to sheep with long wool and present in the wool for less time. Thus it would have less time to dissolve in wool grease and into the interior lipids. A calculated mass of 298 mg of triflumuron was recovered in 3.5 kg of extracted grease indicating triflumuron concentration of 85 mg/kg grease. The results of the proportion of triflumuron in the different scour fractions is summarised in Table 8.4 below.

Table 8.4: Final bowl and flowdown concentration of triflumuron and the proportion of triflumuron in different fractions of the liquors

Source	Final concentration of triflumuron (mg/kg)	Grease content (%)	Triflumuron concentration (mg/kg) in recovered grease	Sludge content (%)	Triflumuron (%) in sludge	Triflumuron concentration (mg/L) in aqueous phase
Bowl 1	2.19	2.0	64.1	4.6	19.19	0.03
Bowl 2	1.01	0.8	73.86	2.2	18.50	0.01
Bowl 3	0.14	0.1	81.9	0.31	18.20	0.002
Heavy flowdown	2.70	1.5	105.3	3.9	27.90	0.03

The results indicate that triflumuron is present largely in recovered grease (105.3 mg/kg triflumuron) as compared to other fractions. The registrant claimed that this technique probably extracts triflumuron in the flowdown as a particulate solid; the actual triflumuron value is probably lower. Triflumuron residues in rinse water were very low. The results contrast with those below, and are of limited value as early shorn wool from treated long wool sheep (breed unknown) was used.

8.5.3.8 Aqueous scouring of wool treated with triflumuron: Laboratory study

Because of the poor solubility in wool wax and water, previous studies indicated amounts of triflumuron passing to aqueous effluent in pilot scale scouring trials (Russell et al., 1997) were relatively low at around 20-25%.

In a commercial scour, when scoured with other wool containing little or no triflumuron, triflumuron from treated wool would be expected to dissolve into wool wax. If concentrations are limited by the solubility in wax, scour times may permit triflumuron to begin dissolving into wool wax from other fleeces, and discharges with aqueous effluent after primary wax recovery may be prolonged. Triflumuron concentrations in recovered wool wax were lower in one wool trial where less time was available for triflumuron to dissolve into wool wax. There was doubt as to the assumption that particulate triflumuron in the scour liquors may dissolve into wool grease derived from the untreated wool.

This assumption was tested in the study below (Grundy et al. 1998) that involved the laboratory scale scouring of wool from sheep treated off-shears with *Zapp*. Wool with high and low concentrations of triflumuron were scoured to determine whether triflumuron associates with the dirt fraction or wool wax fraction in strong flow liquors.

Core samples of triflumuron contaminated wool were taken from wool treated with *Zapp* off-shears. The wool cores originally contained 31.9 mg/kg triflumuron. Six core samples of raw wool were taken from each bale and blended thoroughly, and further analysed to give a mean concentration of 25.5 mg/kg as the high concentration for the wool scouring study. A sub-sample of this wool was blended with pesticide-free wool to yield a mean concentration of 4.2 mg/kg as the low concentration for the study.

Treated wool at concentrations of 25.5 and 4.2 mg/kg were scoured individually in 4 L of water in a beaker (70ºC) to produce strong flow scour liquors containing approximately 1% wool wax. A sample of each strong flow liquor was centrifuged while still hot to isolate a wool wax and a dirt fraction. Triflumuron in each fraction

was analysed to determine whether triflumuron behaves as a particulate material and associates with dirt in either liquor, or dissolves in wool wax derived from triflumuron-free wool. The triflumuron in each fraction was extracted and analysed using HPLC. The results are shown in Tables 8.5 and 8.6 where the upper part of the table describes the overall mass balance in the liquor before centrifugation. The lower part of the tables represents the analysis of separate components after centrifugation.

Table 8.5: Analysis of wool and scouring products from hand scouring of wool with 25.5 mg/kg triflumuron.

Sample	**Mass**	**% of wax**	**Mass of wool wax (g)**	**Calculated concentration of triflumuron in wax (mg/kg)**	**Mass of triflumuron (mg)**
Greasy wool	367 g	13	**47.8**	**196**	**9.38**
Scoured wool	291 g	3.16	**9.2**	407	**3.74**
Liquor (post-scouring)	3.4 L	1.28	43.4	108	4.68
Total recovered			**52.6**		**8.42**
Centrifugation of scour liquor: analysis of liquor components					
Centrate	1.5 L	1.01	15.11	74	1.12
Dirt recovered	2.47 g (63.5% water)	8.3	0.21	486	0.10
Wax recovered	2.83 g	100	2.83	**84**	0.24

The data for the recovery of both wool wax and triflumuron before and after scouring prior to centrifugation indicate reasonable agreement. The wool retained much higher wax and triflumuron content. Approximately 20% of the original mass of wool wax and 40% of the mass of triflumuron remained on the scoured wool. It appears that triflumuron is removed less easily from the wool than the wool wax.

The lower half of the table showed the isolation of a wax-rich cream and a particulate 'dirt' fraction after centrifugation. The wool wax in this cream had a concentration less than half the concentration calculated in the wax on the incoming wool. It is noted that the 2.47 g of wet dirt recovered from the centrifuged liquors was correspondingly high in triflumuron concentration in the wax.

Table 8.6: Analysis of wool and scouring products from scouring of wool blend with 4.2 mg/kg triflumuron.

Sample	**Mass**	**% of wax**	**Mass of wool wax (g)**	**Calculated concentration of triflumuron in wax (mg/kg)**	**Mass of triflumuron (mg)**
Greasy wool	400 g	12	48.1	35	1.68
Scoured wool	326 g	4.0	13.0	74	0.97
Liquor (post-scouring)	3.2 L	1.5	**47.6**	14	0.66
Total recovered			**60.6**		**1.63**
Centrifugation of scour liquor: analysis of liquor components					
Centrate	1.5 L	0.99	14.8	10	0.15
Dirt recovered	2.41 g (57.2% water)	5.53	0.13	123	0.016
Wax recovered	2.83 g	100	0.51	11	0.01

The data indicate that the wax content determined in the scour liquor appears to be high resulting in high wax recovery (60.6 g) as compared to the incoming greasy wool wax of 48.1 g. These results are inconsistent with the centrifugation study where 1% of the wax content was recovered. Again, the wool retained much higher wax and triflumuron than would be expected from a normal scouring. Approximately 27 % of the original wool wax and 58% of the original mass of triflumuron remained on the scoured wool. Similarly, triflumuron is removed less easily from the wool than the wool wax. The wax that was in the dirt is therefore calculated to contain 123 mg/kg of triflumuron.

The concentration of triflumuron in the recovered wool wax was only 11 mg/kg indicating that triflumuron does not re-dissolve in the wool wax that of the other clean wool. This study showed that there was no tendency for triflumuron released from treated wool to dissolve in the wool grease derived from the untreated wool, and appears to indicate that the solubility kinetics of triflumuron in emulsified wool wax are slow.

8.5.3.9 Summary and conclusions from new studies

The additional studies on the degradation of triflumuron on wool fleece are consistent with the previous study where the half-life of triflumuron on the sheep appeared to be about 6-7 months. The Campbell et al. (1998 and 1999) studies indicate that when applied off-shears, triflumuron has a relatively slow rate of breakdown during the course of the year with half-lives ranging from 2.5-5.5 months depending on the climatic conditions. The data also indicate that the average residues ranged from 4.1-34 mg/kg following shearing 12 months later, which is consistent with the study by Morcombe et al (1999) where an average residues concentration of 30 mg/kg greasy wool was found on treated wool fleece at 12 months after treatment.

A wool scouring trial conducted in New Zealand was shown to be deficient where only 52.2% of the input triflumuron was recovered after scouring. In contrast to below, the trial indicated that triflumuron is present largely in recovered grease and very low triflumuron was found in the aqueous phase.

On the basis of a laboratory scouring study, the registrant concludes that less triflumuron will be discharged from wool scours consistent with the pilot scale studies where only 20 and 25% of triflumuron was discharged in strong flow liquors when wool with high concentrations of triflumuron were scoured (Russell et al. 1997). Note that in the studies below DEH has assumed 75% is removed during scouring.

The laboratory data indicate that if the strong flow liquors are centrifuged, it is expected that low triflumuron levels would be found in liquor and wax fractions and a high triflumuron content in the dirt fraction. It also appears that triflumuron is removed less easily from the wool than the wool wax. This study also showed that there was no tendency for triflumuron released from treated wool to dissolve in the wool grease of untreated wool.

8.6 ENVIRONMENTAL EFFECTS

8.6.1 Summary of previous studies

In previous assessments, the ecotoxicological profile of triflumuron was found to be typical of the benzoylphenylurea insect growth regulators, with little or no toxicity to most species but very high toxicity to terrestrial and aquatic arthropods, particularly their juvenile forms. The marine organism mysid shrimp is most sensitive to acute effects, with a 96 h LC50 of 3.9 µg/L. For freshwater species, a no observed effect concentration of 0.018 µg/L has been reported in semi-static 21 day reproductive testing in *Daphnia magna* exposed to a wettable powder formulation, while a higher result of 8.1 µg/L was obtained in flow-through life cycle testing of the active constituent. The former result is considered more reliable as there were flaws identified in the latter study.

8.6.2 Assessment of new toxicity studies

The registrant has provided additional studies on the ecotoxicological effects of triflumuron, which are summarised below.

8.6.2.1 The effect of an insect chitin synthesis inhibitor on honey bees

Triflumuron was shown to disrupt brood production in both caged and free-flying colonies of honey bees (Herbert et al. 1986). Brood rearing was temporarily terminated for a period of 2-3 weeks depending on the level of triflumuron. Normal brood production resumed after the treatment was terminated. This study is of limited relevance to this review.

8.6.2.2 Bee toxicity test for registration purposes - tent test

This two page report (Pinsdorf, 1988) is of limited relevance to this review. The results indicate that triflumuron is non-toxic to bees.

8.6.2.3 SIR 8514 technical acute toxicity trial in carp

This trial (Takada and Akima, 1987) was conducted at dosage concentrations of 10, 5, 2.5, 1.0, 0.5 and 0.1 mg/L to determine the TLm values at 48 and 96 h as an "index of triflumuron on carps" in accordance with the Japanese Ministry for Agriculture, Fisheries and Food manual of application for pesticide registration of agricultural chemical inspection station. TLm values obtained at 48 and 96 h were 0.63 and 0.37 mg/L, respectively, and no abnormalities were observed in carp. Again this study is of limited relevance to this review.

8.6.2.4 Acute toxicity of triflumuron (technical) to earthworms

In this study (Heimbach, 1986), triflumuron was tested for acute toxicity to earthworms in accordance with the OECD Test Guideline No. 207. The test animals were exposed to different concentrations of triflumuron in an artificial soils consisting of sand, clay mineral and peat. After 14 days, the number of surviving animals and their weight alteration during the 14 day period was determined.

The results indicate that the LC50 for the test species, *Eisenia foetida* is >1000 mg ai/kg dry weight substrate. The NOEC is 1000 mg ai/kg dry weight substrate. No

mortalities were observed at the highest concentration of 1000 mg ai/kg dry weight substrate tested.

8.6.2.5 Influence of Alsystin SC 480 on the reproduction rate of water fleas

In this study (Heimbach, 1990) Alsystin SC 480 (a triflumuron suspension concentrate formulation) was tested for inhibition of reproduction of water fleas according to OECD Test Guideline No. 202. In this 21 days semi-static test 4 X 5 female water fleas (*Daphnia magna*) at each concentration were transferred three times a week to freshly prepared test medium and fed with green algae and fishfood extract. Each time the number of dead adult daphnia and new born water fleas were recorded for a test period.

In this test an untreated control, a blank formulation control and nominal concentrations of 0.083, 0.26, 0.83, 2.6, 4.6, 8.3 and 14.5 μg/L were tested. During the test, the active constituent content in the test medium was between 93-170% of nominal concentrations except for concentration at 0.83 μg/L. Because of the difficulties of analysis of the active constituent and the fluctuating analytical results, nominal concentrations were used instead. The mortality of 4% in the control is distinctly lower than 20% considered to be the natural mortality. In the control the mean number of 130 offspring/adult was high. At all concentrations higher than 0.26 μg/L, the mortality of parent daphnia was 100%. Compared to the control, there was a statistically significant reduction of reproduction at the test concentration of 0.26 μg/L.

The NOEC and LOEC of 0.083 and 0.26 μg formulation/L (nominal concentrations), respectively, were determined from the effects of Alsystin SC 480 on the reproduction and mortality of *Daphnia magna* during the 21 day test period. Based on the active constituent content, the NOEC and LOEC for reproduction rate were 0.032 and 0.10 μg/L, respectively.

8.6.3 End points used in the hazard assessment

Based on the ecotoxicological data available, the most sensitive marine organism to acute toxic effects of triflumuron is the mysid shrimp with a 96 h LC50 of 3.9 μg/L. After application of an assessment factor of 10, a PNEC of 0.39 μg/L will be used for for estimating the hazard under Australian scouring conditions. For freshwater species, a 21 day NOEC of 0.018 μg/L has been reported for *Daphnia magna* in semi-static reproductive testing on the active ingredient, which has now been confirmed by the above study (Heimbach, 1990). In the absence of UK EQS and MAC values, the above values will be used in the hazard assessment of potential trade effects from use of triflumuron.

8.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN WOOL SCOURING

The risk that triflumuron would impact adversely in aquatic environments when scouring effluent is disposed of to land is low because of the low mobility of triflumuron in soils to which effluent would be applied. The main concerns arise in relation to discharge to sewer. Knowledge of sewage volumes, scouring rates and wool residues can be used to estimate concentrations leaving the outfall, which can then be compared with toxicity data to determine environmental hazard.

8.7.1 Residue Levels in Wool Clip

Based on the Australian Wool Innovations (AWI) survey data (Scott Williams AWI , personal communication), the mean residues of triflumuron in Australian fleece wool ranged from 3.5 to 8.8 mg/kg greasy wool from 1996-7 to 2000-2001. However, in 2001-2002 the mean residue concentration in the clip was found to be 11.5 mg/kg. Of the wool sales lots sampled 34.9% tested positive for triflumuron, with the average triflumuron residues in the positive samples being 32.8 mg/kg, and with 190 mg/kg being the highest residue in the survey. Residues above 50 mg/kg constituted 7% of sales lots and 44% of the residue load, with 13% (43% of residue load) of sales lots having residues in the range 25-49.5 mg/kg. In total 27% of residues were >10 mg/kg, and these constituted 98% of the total residues load.

The figures for wool survey results for 2002-2003 are closely similar to those for 2001-2002, with an average of 11.1 mg/kg and a mean when treated of 31.5 mg/kg. While the average for 2003-2004 dropped to 9.7 mg/kg, with the mean when treated down to 27.3 mg/kg, but with a highest residue of 220 mg/kg (Russell, 2004), in all 3 years close to 35% (range 34.8-35.2%) of wool sale lots had residues above the Limit of Resolution (LoR)

Due to this, the highest figure of 11.5 mg/kg will be used as the input concentration for the hazard calculation of triflumuron in the scouring process. The figure of 32.8 mg/kg, representing the highest mean residue for sales lots testing positive for triflumuron over the past 3 seasons will also be used for comparison as representing a potential "hot spot".

8.7.2 Australian Model

The Australian model (Savage 1998) has been used by DEH to predict the worst case levels of triflumuron present in sewage effluent entering the Barwon waters from the Black Rock treatment plant. The results of the calculation performed by DEH take into consideration the following parameters as shown in Table 8.7.

Table 8.7: Determination of Q values by DEH under Australian conditions

Parameters	**Mean residues in clip**	**Average residue when detected**
Concentration of triflumuron in wool at harvest (mg/kg)	11.5	32.8
Mass of wool scoured in one day (tonnes)	50	50
Mass of triflumuron entering scouring plant on wool (g)	575	1640
Percentage remaining on scoured wool (%)	4	4
Percentage removed (including that on wool fibre and recovered wool wax) during scouring	75	75
Percentage removed during sewage treatment (%)	80	80
Mass of triflumuron discharged (g)	27.6	78.7
Flow rate of sewage treatment plant (ML/day)	50	50
Predicted concentration in sewage outflow (ng/L)	552	1574
Dilution in plume[#]	0.02	0.02
Predicted Environmental Concentration (PEC) (ng/L)	**11.04**	**31.5**
Predicted No Effect Concentration (PNEC) (ng/L)	390	390
Quotient (PEC/PNEC)	**0.028**	**0.08**

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).

The Q values from using both the mean residues in the 2001-2002 wool clip and the mean residues when detected are considerably less than 1. Even in the case of the highest residues values detected in the 2003-2004 AWI survey (220 mg/kg), the Q (= 0.54) is still acceptable. Therefore, there is unlikely to be an environmental hazard as a result of triflumuron treatment of sheep at current use levels under Australian conditions.

8.7.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall, ie the PNEC of 390 ng/L to the mysid shrimp. The result is shown in Table 8.8.

Table 8.8: Calculated concentration of triflumuron (ng/L) in raw greasy wool based on the target concentration of 390 ng/L at the Black rock ocean outfall for triflumuron

Parameters	**DEH's estimates**
Target concentration (ng/L)	390
Load entering the ocean which takes into account the plume dilution factor of 50 (ENV) (g)	50 ML X 390 ng/L X 50 = 975
Load entering sewage treatment plant (STP) (g)	100/20 X 975 = 4875
Load entering wax recovery (WAX) (g)	100/25 X 4875 = 19,500
Load entering scour (SCR) (g)	100/96 X 19,500 = 20,312
Concentration of residues on wool (mg/kg)	20,312/50 = **406.3**

On the basis of the 2001-2002 AWI wool residue monitoring data of 11.5 mg/kg for triflumuron, there is unlikely to be an environmental hazard from the current use of triflumuron according to its label instructions. This is even the case when the highest residue of 220 mg/kg found in the survey is used. Therefore it may be concluded that treatment of sheep according to the approved label instructions and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

8.8 TRADE

8.8.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentrations (MAC) are in place for the textile industry to meet environmental standards. However, the EqualS™ database[20], the former website[21] (http://www.basicweb.fsnet.co.uk/index.htm), or Annex G of of the Scottish Environmental Protection Agency web site (available at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf, accessed on 6

[20] The EqualS™ database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[21] Available from 2001 but removed in mid 2003.

March 2006) reveal there are no EQS AA and MAC values for triflumuron. In the absence of the UK values for triflumuron, DEH has assumed AA and MAC values of 18 and 390 ng/L, respectively (see above). The predicted environmental concentrations in the river on the basis of the proposed values are shown in Table 8.9.

Table 8.9: Predicted concentration of triflumuron (ng/L) in river based on the EU/UK model

DEH's EU/UK models estimate		
Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of triflumuron in wool at harvest (mg/kg)	11.5	11.5
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of triflumuron entering scouring plant on wool (g)	317	317
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)*	90	90
Percentage removed during sewage treatment (%)	80	80
Mass of triflumuron discharged (g)	6.1	6.1
Flow rate of river (ML/d)	149	71
Predicted Environmental Concentration in river (ng/L)	**40.9**	**85.9**
DEH's estimated UK/EU requirement (ng/L)	18	390

* The 90% removal rate is derived from Shaw for overseas wool scouring (Savage 1998).

DEH's predicted environmental concentration of 40.9 ng/L is greater than the estimated AA of 18 ng/L. In the case of the MAC, the calculation indicates that the predicted environmental concentration is below the MAC value of 390 ng/L, which remains the same even when the mean residues when detected value of 32.8 mg/kg is used. However, even when considering that the AA value is a mean annual average, which can be exceeded for at least some of the time, the predicted river concentration is so much higher it may be concluded that the use of triflumuron according to label instructions has the potential to give rise to adverse trade effects. This remains the case if the lower mean residue levels of 9.7 mg/kg found in the 2003-2004 survey is used.

8.8.2 Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the outfall as shown in Table 8.10.

Table 8.10: Calculated concentration of triflumuron (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 18 (AA) and 390 (MAC) ng/L for triflumuron

DEH calculations based on UK/EU possible EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)*	18	390
Load entering the river (ENV) (g)	149 ML X 18 ng/L = 2.68	71 ML X 390 ng/L = 27.7
Load entering sewage treatment plant (STP) (g)	100/20 X 2.68 = 13.4	100/20 X 27.7 = 138.5
Load entering on-site treatment plant (OST) (g)	100/10 X 13.4 = 134	100/10 X 138.5 = 1385
Load entering scour (SCR) (g)	100/96 X 134 = 140	100/96 X 1385 = 1,442.7
Concentration of residues on wool (mg/kg)	140/27.6 = **5.06**	14,427/27.6 = **52.3**

* DEH's estimated AA and MAC of 18 and 390 ng/L, respectively, for the UK/EU requirements. These values have no legal standing.

On the basis of the above model the 2001-2002 wool residue data of 11.5 mg/kg for triflumuron have exceeded the target concentration of 5.06 mg/kg for the AA, though it is well below the MAC maximum target value of 52.3 mg/kg. Therefore, the current use of triflumuron according to its label instructions has the potential to unduly prejudice Australia's export trade, noting that the assumed AA has no legal standing.

8.9 WOOL WITHHOLDING PERIODS (WWPs)

WWPs of 101 (UK EQS AA), 45 (UK MA) and 11 (Australia) days have been proposed for triflumuron based on the scour lot maxima of 7.9, 70 and 70 mg/kg, respectively and using the 2000-2001 AWI mean wool residue data of 8.2 mg/kg (Horton and Campbell 2001).

However, based on the above calculations, a WWP of >12 months is required to meet the possible EQS for the UK. The APVMA would need to consider the use of Horton and Campbell's model to determine if it is possible to amend the use of triflumuron in arriving at the appropriate WWPs for the registered products.

8.10 CONCLUSIONS

Triflumuron is a synthetic insect growth regulator with very high toxicity to aquatic and terrestrial arthropods. It has very low water solubility and will partition to soil or sediment following release to the environment. Triflumuron is slightly to moderately persistent in soils and aquatic systems. The main environmental concern is that residues of triflumuron on harvested wool may impact on aquatic biota when scouring effluents are discharged.

The calculations indicate that there is unlikely to be an environmental hazard under the registered use of triflumuron under Australian conditions. The DEH is therefore able to conclude that the use of selected sheep ectoparasiticide products containing triflumuron in accordance with approved label instructions and the current WWP would not be likely to have an effect that is harmful to animals, plants, or things or to the Australian environment under Australian scouring conditions.

However, the DEH comparative analysis of likely scour residues and their likely impact on future exports of Australian raw wool shows that a potential trade prejudice could arise from use of triflumuron according to label instructions when the possible target concentration of 18 ng/L for the UK EQS AA is taken into account. The use of Horton and Campbell's model in arriving at the appropriate WWP for the registered products may provide additional information.

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CHAPTER 9 - DIFLUBENZURON

9.1 INTRODUCTION

Four veterinary products containing diflubenzuron for use as lousicides on sheep were included in the Sheep Ectoparasiticide Review in accordance with the APVMA Gazette of 7 September 1999.

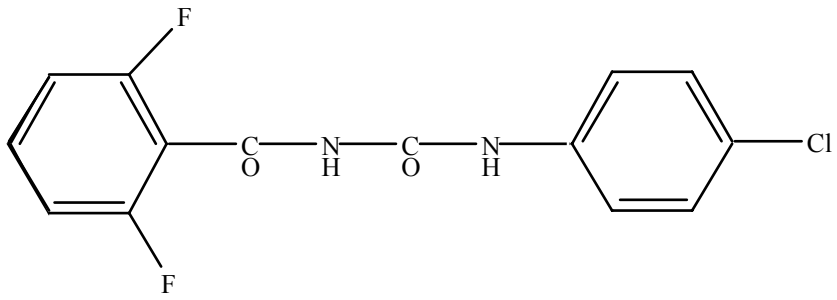
Diflubenzuron belongs to the benzoylphenylurea family of insect growth regulators and acts by inhibition of chitin synthesis, which interferes with the formation of insect cuticle. It is most effective at the time of insect moulting or hatching of eggs. It is currently registered for a number of purposes both as an agricultural and veterinary chemical.

This report is based on the additional data submitted for the Sheep Ectoparasiticide Review by affected registrants. It will incorporate mainly the wool scouring effects of diflubenzuron as a result of veterinary use on sheep and update the previously available assessment reports. A Wool withholding Period (WWP) of 6 months has been set for diflubenzuron products.

9.2 CHEMICAL IDENTITY

Name:	1-(4-Chlorophenyl)-(2,6-difluorobenzoyl)urea (IUPAC)
	N[[(4-chlorophenyl)amino]carbony]-2,6-difluorobenzamide (CAS)
Common name:	Diflubenzuron
Other names:	PH-40, TH6040, DU 112307
CAS number:	35367-3-5
Molecular formula:	$C_{14}H_9ClF_2N_2O_2$
Molecular weight:	310.7

Structural formula:



Purity of active: >95% (by weight)

Impurities: The original application identified numerous impurities consisting of what appear to be process intermediates and by-products and levels all below 3%

9.3 PHYSICO-CHEMICAL PROPERTIES

9.3.1 Previously available data

The following have been taken from previous assessments conducted by DEH.

Appearance: White, crystalline solid

Melting point: 230-232˚ C

Relative density: 1.56 at 20˚ C

Vapour pressure: <1.3 X 10^{-5} Pa at 50˚ C. Mabury and Crosby (1996) calculated a value of 6.8 x 10^{-5} Pa using water solubility and Henry's law constant.

Water solubility: 0.1 mg/L at 20-25˚ C. Mabury and Crosby (1996) reported values of 88.8 ± 4.0 µg/L in Milli-Q water and 92.6 ± 3.5 µg/L in filtered field water. These values were obtained using a generator column, which they regarded as the most reliable method. Mabury and Crosby also note that their solubility values were lower than those reported by the manufacturer and some previous researchers.

Henry's law constant: 2.34 ± 0.02 x 10^{-1} Pa.m^3.mole (Mabury and Crosby, 1996)

N-octanol/water partition coefficient: Log K_{ow} = 3.89

Dissociation Constant: Not applicable

9.3.2 New Data

Some additional data were provided for this review, which are summarised briefly below. The results are consistent with those above.

9.3.2.1 Vapour pressure

The maximum vapour pressure of diflubenzuron at 25^{o}C was determined to be 1.2 X 10^{-7} Pa using the gas saturation method, with random errors estimated at 30% (Harteveld, 1988).

9.3.2.2 Water solubility

Two reports were submitted describing the determination of the water solubility of diflubenzuron using the column method. Balder *et al* (1989) obtained a solubility of 80 µg/L in bidistilled water, and van Kempen *et al* (1995) found that solubility varied slightly with pH (100 µg/L at pH 4, 80 µg/L at pH 7 and 320 µg/L at pH 10) consistent with the weak acidity of the urea functionality.

9.3.2.3 Partition coefficient

The log P values for diflubenzuron (3.89) and its two metabolites, 4-chlorophenylurea (1.14) and 2,6-difluorobenzoic acid (-0.02), were determined using the HPLC method (Thus, 1984).

9.4 ENVIRONMENTAL EXPOSURE

9.4.1 Volume

The amount used on Australian sheep suggests that diflubenzuron is used to treat around 10% of the flock.

9.4.2 Application and use pattern

The dipping and jetting products are non-stripping and are applied at a rate of 1.5 L per 1000 L water for body lice and 2.0 L per 1000 L water for blowfly control, on or before the onset of a fly wave.

The solution up take depends on the length of wool. For short wool treatment, the estimated average taken up is 2.5 L (roughly 1 g diflubenzuron) per animal. The estimated average off-take for long wool is in the order of 2.5-3 L as use is mainly as a lousicide for sheep with up to 6 months wool. Roughly half the applied dose may drain from the sheep.

Backline treatment is used to treat lice (*Bovicola ovis*) off-shears. The rate of application per sheep varies from 240 mg for small animals (10-20 kg) to 600 mg for large animals (> 75 kg) with the applied dose based on the weight of the heaviest animal in a group. The average sheep (31-55 kg) receives 400 mg diflubenzuron. All sheep in a group are treated. The product is applied along the midline of the animal, from the poll to the base of the tail.

As off-shears treatments, the pour-on products are applied at 0.3 g/sheep for small animals (15-20 kg) increasing to 0.63 g/sheep for larger animals (56-75 kg). Larger animals receive an additional 0.13 g for every 10 kg over 75 kg body weight. The average sheep (31-55 kg) receives 500 mg diflubenzuron.

Product can also be used in long wool for blowfly control. Two bands (0.85 g/sheep) are applied for body strike, and three bands (1.3 g/sheep) for body and crutch strike.

Diflubenzuron products must not be used within 6 months of the next shearing.

9.5 ENVIRONMENTAL CHEMISTRY AND FATE

9.5.1 Summary of previous environmental fate studies

As discussed in more detail in previous environmental assessment reports, diflubenzuron is resistant to abiotic degradation (hydrolysis, photolysis on glass, leaf or soil surfaces) under normal environmental conditions, but is rapidly degraded by microbes with typical half-lives of a few days in soil and a few days or weeks in aquatic environments. Diflubenzuron has very low mobility in the environment, being of low volatility and sorbing strongly to soils.

9.5.2 Summary of new environmental fate studies

New data submitted for the review included further environmental chemistry and fate data, which are summarised below. These do not significantly alter the foregoing brief summary.

9.5.2.1 Hydrolysis

The hydrolysis of diflubenzuron (184 µg/L, uniformly radiolabelled in both rings) in aqueous buffers (pH 5, 7 and 9) containing 1% acetonitrile was studied at 25^{o}C in the dark for 4 weeks (Boelhouwers *et al*, 1988a). Some sorption (around 10%) occurred to the walls of the hydrolysis flasks in neutral and acidic buffers, where diflubenzuron was hydrolytically stable. The half-life in the alkaline buffer was estimated as 32.5 days. The two main hydrolysis products were 4-chlorophenylurea and 2,6-difluorobenzoic acid. Only one of two minor products could be identified, as 2,6-difluorobenzamide.

9.5.2.2 Photolysis

The extrapolated half-life of radiolabelled diflubenzuron in the pH 7 buffer as used for the hydrolysis study was 40 days under continuous irradiation for 15 days from a 450 W xenon arc lamp. The major degradation product was 4-chlorophenylurea, accompanied by the minor products 2,6-difluorobenzoic acid, 2,6-difluorobenzamide and 2,6-difluorobenzene (Boelhouwers *et al*, 1988b).

9.5.2.3 Biodegradation

Biodegradability was determined in an adapted modified Sturm test, using radiolabelled diflubenzuron to allow detection of evolved carbon dioxide at the low concentration used (11 µg/L). Degradation was rapid (half-life about 2.5 days) with

the formation of 4-chlorophenylurea and 2,6-difluorobenzoic acid, the latter degrading further to carbon dioxide (van der Laan-Straathof and Thus, 1993).

9.5.2.4 Aquatic metabolism

Radiolabelled diflubenzuron (0.94 mg/kg) was added as suspension to two model ditch systems using hydrosoils (sandy loam pH 5.6, 18.3% organic matter and silt loam pH 7.3, 6.6% organic matter) and water from two Dutch ponds (Thus and van der Laan-Straathof, 1994). Analysis by HPLC and measurement of radioactivity over the ensuing 45 days at 20^{o}C indicated a rapid loss from the water phase (initial half-life 1-2 days) with the formation of 4-chlorophenylurea, 2,6-difluorobenzoic acid and carbon dioxide as the main metabolites. Initial half-lives for the total system were 25 days for sandy loam and 10 days for silt loam.

A second study used two aquatic systems equilibrated for 7 weeks after sampling from the Rhine river and a Swiss pond, with natural water filtered through a 0.2 mm seive and the uppermost 3 cm of sediment through a 2 mm mesh (Völkel, 1999). The river sediment was a loamy sand (pH 7.05, 0.83% organic carbon) and the pond sediment a loam (pH 6.77, 5.58% organic carbon). Radiolabelled diflubenzuron was added at a target concentration of 104 µg/L and the systems were incubated under aeration for up to 104 days. Radioactivity was lost rapidly from the water, with concurrent increases in extractable radioactivity in the sediment. Evolution of carbon dioxide reached 33-38% of applied. The first half-life of diflubenzuron was 5.4 days in the river system and 3.7 days in the pond system. Corresponding results for the metabolites were 1.6 and 4.4 days for 2,6-difluorobenzoic acid and 26.9 and 52.5 days for 4-chlorophenylurea.

9.5.2.5 Bioaccumulation

Bluegill sunfish were exposed under flow-through conditions for 28 days to 9.3 µg/L radiolabelled diflubenzuron, followed by 14 days of depuration in clean water. The bioconcentration factor was 320, with 2 days required to reach 90% of steady state, and a half-life for depuration of 0.6 days (Burgess, 1989). The bulk of the residues in fish (around 80%) was diflubenzuron (Boelhouwers *et al*, 1992).

9.5.3 Summary of previous data for depletion of residues on wool

Diflubenzuron appears to undergo slow photolysis in aqueous solution, but this is of marginal relevance to its fate on sheep and during wool processing. According to a recent international review (WHO, 1996) it appears that after direct spraying diflubenzuron is persistent on foliage. Residues remain almost completely at the site of application on the surface. Similar persistent behaviour may be expected on the surface of wool fibres, although mobility may be slightly higher due to slow dissolution in wool grease. Diflubenzuron is stable to sunlight as a solid.

Diflubenzuron has low solubility in water and apolar solvents such as wool grease. These properties are expected to limit the distribution of the insecticide on the sheep, particularly for the particulate formulations. Simulated scouring studies using recently treated fleece samples found no residues in the grease fraction or on the scoured wool as the insecticide particles had not had time to partition significantly to the grease fraction.

The slow rate for dispersion of diflubenzuron around the sheep may be expected to slow the degradation of the insecticide in fleece, particularly for the particulate formulations. Persistence may also be expected to increase with increased particle size, as particle interiors are protected from degradation. Larger particles have been shown to be more persistent in soils (WHO, 1996).

Apart from particle size, the other key formulation variable that may influence dissipation rates of diflubenzuron in fleece is the solvent or carrier used. Solvent based formulations may be expected to allow better and faster spreading into the fleece compared with water based formulations. Better spreading could be expected to favour faster dissipation, although better fleece penetration in long wool may retard dissipation by protecting the chemical against photodegradation or physical dislodgement.

The key questions to be addressed in assessing environmental exposure to diflubenzuron used on sheep are the persistence in fleece and the behaviour during scouring and subsequent sewage treatment. Data addressing these aspects are discussed in more detail below.

9.5.3.1 Persistence of residues in fleece

Declining pesticide residue concentrations in wool reflect a combination of dilution and dissipation. The latter may involve degradation of diflubenzuron or physical removal. Residue dissipation on the sheep is best understood if the data are presented as loads rather than concentrations, as dilution need not be considered. Residue concentrations as determined by band sampling are available from previous studies and have been reported in previous DEH assessment reports for diflubenzuron. These data are presented below as loads, based on the assumption that wool growth adds 0.1 kg/week to the fleece.

Wool harvested from treated sheep is likely to contain around 50 mg/kg diflubenzuron, but with considerable variation above and below this figure. In general, short wool treatments are likely to leave lower residues, and long wool treatments higher residues. Studies from which these conclusions are drawn are outlined below.

Note that the residue data outlined below cover use of dipping/jetting formulations in long wool, and backline formulations in short and long wool. Very few data are available for dipping/jetting formulations in short wool. One trial (Anderson *et al*, undated) has been reported, involving the shower dipping of sheep at 336 mg/L diflubenzuron 5 weeks after shearing. A spot sample taken from the back of a single sheep 85 days after treatment contained 450 mg/kg diflubenzuron in the top third of the staple, and 120 mg/kg in the bottom third. At 163 days after treatment, 130 mg/kg was found in the top third of the staple, taken from an equivalent sampling site on the same sheep, 60 mg/kg in the middle third, and none in the bottom. Significant dissipation appears to have occurred, but the data are too limited to allow any firm conclusions.

9.5.3.2 Previous band sampling data

Early data from Campbell (1995) were obtained by band sampling following jetting. Note that these data have not been fully reported. One group of five sheep carrying 30 weeks wool was treated with three parallel strips along the back from poll to tail and retained an average 144 mg/kg at shearing. The average dose was 3.2 L (1.2 g diflubenuron, DFB) with 1.7 L (0.64 g DFB) retained on the sheep. Although this product is nonstripping, some retention of the particulate formulation may be expected as a result of filtration when the dipping fluid drains through the fleece. The average results in Table 9.1 were obtained. Note that these data were included in the review by Savage (1998) with the observation that 0.7 g diflubenzuron was applied to each sheep (see Table 9 in that report).

Table 9.1: Band sampling data for sheep treated with 30 weeks wool

Sampling time (weeks)	4	9	17	26
Residue concentration (mg/kg)	302	210	124	144
Diflubenzuron residue (g/sheep)	1.03	0.82	0.58	0.81

The second group carried 34 weeks wool at treatment, which consisted of two strips along the back plus the crutch. The take up was 2.2 L (1.1 g DFB) with 1.3 L (0.65 g DFB) retained. The average residue at shearing was 90 mg/kg. Average residue loads at the various sampling times are in Table 9.2 below.

Table 9.2: Band sampling data for sheep treated with 34 weeks wool

Sampling time (weeks)	4	9	15	22
Residue concentration (mg/kg)	158	142	100	90
Diflubenzuron residue (g/sheep)	0.60	0.61	0.49	0.50

Summary data are also available from similar studies with sheep hand jetted in 7, 8 or 9 months wool (Campbell *et al*, 1998). Respective average residues at shearing, which occurred 13 months after the previous shearing, were 138, 99 and 185 mg/kg. Estimated average half-lives ranged from 238 to 284 days, with an apparent slowing in dissipation rates with time. In this report the data are presented graphically in terms of total residue per sheep, but the scale is clearly incorrect as it shows residues to be in the order of 100 mg.

Data are also available for a backline formulation in which the diflubenzuron (20 g/L) is present in solution. An early study (Little, 1998) included residue determinations in 9 and 11 months wool, although it was unclear whether these were obtained from the same animals. The estimated average residue loads were 0.22 g/sheep at 9 months and 0.06 g/sheep at 11 months. The registrant was requested to clarify details of the study, such as initial dose, season of treatment and results for other sampling times as specified in the study protocol. No further details were provided.

9.5.3.3 Band sampling data submitted for this review

Average residues from band samples taken from a group of six sheep treated off-shears with 0.4 g diflubenzuron (Pollock, 1999) are in Table 9.3 below. The average residue at shearing was 60.6 mg/kg.

Table 9.3: Average residues from Pollock (1999)

Sampling time (weeks)	26	39	52
Residue concentration (mg/kg)	183.5	69.2	60.6
Diflubenzuron residue (g/sheep)	0.48	0.27	0.32

Results from a similar trial using a group of ten sheep (Pollock, 2000) are in Table 9.4 below. The average residue at shearing was 73 mg/kg.

Table 9.4: Average residues from Pollock (2000)

Sampling time (weeks)	16	33	41
Residue concentration (mg/kg)	303	142	73
Diflubenzuron residue (g/sheep)	0.48	0.47	0.30

A backline treatment product containing 25 g/L diflubenzuron in suspension was also tested. Band samples taken from ten sheep treated off-shears at 0.5 g/head (Shepherd, 1998) contained the following mean residues (Table 9.5). The average residue at the end of the trial (268 days after treatment) was 110 mg/kg. Core sampling at 179 days after treatment returned residues of 95 mg/kg, 56% of the corresponding band sample result of 168 mg/kg.

Table 9.5: Average residues over time from Shepherd (1998)

Sampling time (weeks)	4	9	13	17	21	26	38
Residue concentration (mg/kg)	1000	712	532	340	268	168	110
Diflubenzuron residue (g/sheep)	0.40	0.64	0.69	0.58	0.56	0.44	0.42

Note that residues determined by band sampling, as in the above studies, tend to overstate the true residue. Core sampling is regarded as more reliable, and generally gives residues that are around half those determined from band samples. However, even if the above residue determinations exceed the true residue, as seems likely given that many determinations exceed the nominal treatment rate, this should not alter the kinetics. Sampling intervals in the above studies extend up to around 8 months, but the maximum reduction in residue load is only 33%, in the final 6 months of the trial by Pollock (1999).

It appears that half-lives of a year or more may be expected with this active, with indications that persistence is more protracted for some types of formulations.

9.5.3.4 Core sampling data

Core sampling of two bales of wool obtained from efficacy trials in which sheep were shorn 6 months after off-shears treatment with a product containing 500 mg diflubenzuron returned residues of 90 and 100 (mean 95) mg/kg (France, 1998). The recorded residues equate to a load of around 250 mg in a 2.5 kg fleece.

Core sampling of single bales from two efficacy trials in NSW returned residues of 37 and 62 mg/kg. Sheep were shorn 6 months after treatment with a 25 g/L spray on formulation for fly control in 6 months wool. Band samples taken from five of the sheep involved in one of these trials contained an average 78 mg/kg. A blended sample from the four bales harvested at this site contained 49 mg/kg (Russell, 1998). The measured residues equate to a load of around 250 mg in a 5 kg fleece, considerably below the 1.3 g applied, suggesting some degradation on the wool.

Core samples have also been taken from bales of wool prior to pilot scale scouring studies. Residues of 45 mg/kg were determined in wool harvested 12 months after treatment off-shears with an aqueous 25 g/L pour-on formulation (Russell and Shepherd, 1999a). Residue dissipation is again apparent, from an applied dose of 500 mg to an estimated residue of about 200 mg at shearing. Treatment in 6 months wool with a 25 g/L aqueous spray-on formulation left 62 mg/kg diflubenzuron at shearing, 6 months after treatment (Russell and Shepherd, 1999b). The applied dose of 1.3 g was reduced to an estimated 0.3 g over a 6 month period, again indicating dissipation.

A newly submitted study (Shepherd, 2000a) determines cumulative residues after treatment off-shears at 500 mg/head for body lice, followed after 22 weeks by backline/crutch treatment at 1275 mg/head for blowfly control. Core sampling of the two bales of wool obtained from the trial indicated residues of 115 and 175 mg/kg (mean 145 mg/kg) or an average residual load of 725 mg assuming fleece weight of 5 kg at shearing.

A study with lambs treated at marking (1.5-7.5 weeks old) with 250 mg diflubenzuron found 150 and 160 (mean 155) mg/kg in blended core samples from wool shorn 108 days after treatment. It appears that only a few lambs were treated as the final fleece sample provided for sampling and analysis weighed only 8 kg (Shepherd, 2000b).

A study with lambs at foot treated when the mother was shorn (2-6 weeks old) with 200 mg diflubenzuron found 2.5 and 1.9 (mean 2.2) mg/kg in blended core samples from wool shorn 132 days after treatment. Some 452 lambs were treated. A single bale of wool was submitted for analysis (Shepherd, 2000c).

The first of the two lamb trials described above was carried out in NSW with treatment occurring in October 1999. The second took place in Victoria, with treatment in August 1999. The main difference between the two trials appears to have been the breed of sheep. Merino wether lambs were used in the first trial, and first cross merino lambs in the second. Persistence of residues is thought to be higher in the denser and greasier merino fleece.

9.5.3.5 Summary of fleece residue data

Available fleece residue data are tabulated below, together with estimated half-lives. Note that half-lives calculated on the basis of total residue load generally appear to be well in excess of 6 months, and likely to extend beyond a year in many cases. Relatively short half-lives (around 3 months) are apparent when one product is used for fly control, but these data were obtained from a single field trial, at Manildra, NSW. Significant dissipation is also apparent when the product is used for fly control in long wool after an off-shears treatment, but half-lives are more difficult to estimate because of the dual treatment. As indicated in Table 9.6 below, a 6 month half-life for short and long wool treatments would fit these data, but so would a longer half-life (» 6 months) in short wool and a shorter half-life (~ 3 months) in long wool. The latter option is more consistent with the data obtained from single treatments.

Table 9.6: Summary of fleece residue data

Treatment	Sampling	Residue at shearing	Half-life	Reference
7 months wool	Band	144 mg/kg	» 6 months	Campbell, 1995
8 months wool	Band	90 mg/kg	» 6 months	Campbell, 1995
Pour-on backliner	Band	61 mg/kg	» 6 months	Pollock, 1999
Pour-on backliner	Band	73 mg/kg	» 6 months	Pollock, 2000
Off-shears	Band	110 mg/kg (9 months wool)	» 6 months	Shepherd, 1998
Off-shears	Core	95 mg/kg (6 months wool)	~ 6 months	France, 1998
Long wool	Core	49 mg/kg	~ 3 months	Russell, 1998
Off-shears	Core	45 mg/kg	> 6 months	Russell & Shepherd, 1999a
Long wool	Core	62 mg/kg	~ 3 months	Russell & Shepherd, 1999b
Off-shears and long wool	Core	145 mg/kg	~ 6 months	Shepherd, 2000a

Interpretations can only be tentative with such limited data. The apparent lengthy persistence (half-life at least 6 months) of diflubenzuron residues following use of one off-shears product appears to conflict with their more rapid breakdown (half-life about 3 months) following use in long wool. The main difference between off-shears and long wool treatments is that the diflubenzuron particles would mainly remain associated with the tip of the wool fibre when applied to long wool. Photolysis is an obvious route for degradation at the tip of the wool fibre, particularly with backline formulations, but diflubenzuron is expected to be photostable on the surface of the wool fibre, particularly as particles. Physical dislodgement of particles may provide an explanation for the apparent faster breakdown in long wool, but the mechanism for this phenomenon, if it is real, must remain speculative. Core samples from bales of greasy wool indicate that residues are about a quarter of those that would be expected if no losses had occurred, but there are no data to show the kinetics of this residue decline. A heavy storm soon after treatment could conceivably have led to the bulk of these losses. If a half-life of 3 months is to be assigned to the product for long wool use, kinetic data would be needed to clarify the observed residue losses.

Residue concentrations on the sheep decline through a combination of dissipation and dilution in wool growth. The latter factor is particularly relevant to short wool (up to 42 days after shearing) as subsequent wool growth can be expected to reduce residue concentrations by an order of magnitude. Dilution effects are much less of a factor in long wool.

The resistance of diflubenzuron to dissipation in fleece means that dilution in wool growth is the main factor that will reduce residue concentrations through the season, with the possible exception of the backline product where residues appear to be lost through physical dislodgement, particularly after long wool treatment.

9.5.3.6 Behaviour of residues during sewage treatment

Recent work by Russell *et al* (2001) has led to some changes in the assumptions regarding the degree of removal of various chemicals during sewage treatment. This work involved measuring pesticide residues at entry to and exit from the Black Rock

sewage treatment plant that services the Geelong catchment. This treatment plant operates in a "semi-continuous" mode by cyclically directing incoming sewage into separate tanks that operate on a four hourly cycle, with 10% of the supernatant drawn down after each cycle. Average sewage retention time is 36-48 hours.

Average residues in greasy wool for one study were 7.7 mg/kg diflubenzuron. The removal efficiency in this study was 96%, although the authors caution that the true value may be as low as 93% as special batches of high residue wool were scoured to ensure detection at discharge, and some of these residues may not have cleared the system.

A second study used only commercial wool, containing an average 0.88 mg/kg diflubenzuron. The estimated removal rate for diflubenzuron was 85%, perhaps a little low as residues from previous highly contaminated batches appeared to still be clearing the system in early samples.

Removal efficiency may be expected to increase at higher concentrations. The study using only commercial wool is likely to better reflect the actual scouring conditions in Australia.

Based on this study, removal of diflubenzuron during sewage treatment will be assumed to occur with 85% efficiency, rather than the 80% assumed in the review by Savage (1998). This factor is applied to both local and overseas scouring below.

An earlier, unpublished report of this work (Grundy *et al*, 2000) includes the observation that the design engineer for the Black Rock sewage treatment plant estimated a 50 fold dilution of the sewage discharge plume at the surface of the sea immediately above the outfall diffuser system. Effluent discharged from deepwater outfalls undergoes rapid initial dilution before reaching either a level of neutral buoyancy or the ocean surface. After ejection from the outfall diffusers, the sewage effluent plumes rise rapidly through the water column due to their buoyancy relative to the surrounding ocean waters. As they rise, they are diluted by entrainment of the ambient ocean water resulting in a gradual increase in plume density. Again this factor is applied to local scouring below.

9.6 ENVIRONMENTAL EFFECTS

9.6.1 Summary of previously submitted data

As discussed in more detail in previous environmental assessment reports, diflubenzuron has low toxicity to vertebrates (birds, mammals and fish) but is very highly toxic to some invertebrates because of its chitin inhibiting properties. Aquatic arthropods are of particular concern because of their sensitivity and the likelihood that they will be exposed to residues discharged to aquatic environments after treatment of sewage containing scouring effluent.

9.6.2 Assessment of recently submitted data

A registrant submitted further environmental toxicology data for the review. These data are summarised below.

9.6.2.1 Acute toxicity to fish

The following results (mean measured concentrations) in Table 9.7 were obtained in testing with fish, using a single test concentration.

Table 9.7: Summary of new results for fish toxicity

Species	Result	Reference
Rainbow trout	96 hour LC50 > 200 µg/L	Berends and van der Laan-Straathof (1994a)
Zebra fish	96 hour LC50 > 200 µg/L	Berends and van der Laan-Straathof (1994b)
Sheepshead minnow	96 hour LC50 > 130 µg/L	Nicholson, 1987
		Graves and Swigert, 1993
Rainbow trout	96 hour LC50 > 133 mg/L	Berends and van der Laan-Straathof (1994c)
Zebra fish	96 hour LC50 > 81 mg/L	Berends and van der Laan-Straathof (1994d)

Technical diflubenzuron was dispensed into the test media as acetone solution and proved stable to hydrolysis with no significant losses apparent from analysis in the static studies with trout and zebra fish (first two entries in Table 9.7).

The static and flow-through studies with the saltwater species sheepshead minnow were conducted at respective nominal concentrations of 100 and 0.5 mg/L technical diflubenzuron, added in acetone solution. Test reports state that all fish appeared normal throughout the tests, but this is contradicted in the former case by observations in attached tables that a single mortality occurred among the exposed fish, with all survivors remaining lethargic through the first 72 hours of exposure.

Dimilin WG80 (a wettable granules formulation of diflubenzuron) was added directly to the test media, and maintained in suspension by stirring daily. The results are expressed as mean measured concentrations of the product (last two entries in Table 9.7). All fish appeared normal throughout the tests, but could only be seen when near the walls of the test vessels because of the turbidity of the test suspensions.

The results indicate that diflubenzuron is not toxic to fish up to the limit of its water solubility.

9.6.2.2 Semi-chronic toxicity to fish

Rainbow trout were also tested for 21 days in a static renewal study with technical diflubenzuron. Concentrations of 200 µg/L could be maintained between renewals, as in the acute study. A single fish died in one of the acetone controls and in one of the test solutions (Berends *et al*, 1994), suggestive of low chronic toxicity to fish.

9.6.2.3 Acute toxicity to invertebrates

The additional results are summarised in Table 9.8.

Table 9.8: Summary of new results for toxicity to aquatic invertebrates

Species	Result	Reference
Daphnia magna	48 hour EC50 = 7.1 µg/L	Kuijpers, 1988
	48 hour EC50 = 1.6 µg/L	Groeneveld *et al*, 1995a
Mysidopsis bahia	96 hour LC50 = 2.1 µg/L	Nimmo *et al*, 1980

The first daphnid test was conducted under static conditions, with diflubenzuron added as a stock solution in triethylene glycol. Consistent measured concentrations were obtained at initiation and termination.

The second daphnid test was also conducted under static conditions, but with acetone as solvent. Concentrations were again confirmed by analysis. Identical LC50 results were obtained with technical material and the Dimilin WG80 formulation, but the NOECs differed (100 and 380 ng/L, respectively).

The mysid result was obtained under flow-through conditions, with nominal concentrations confirmed by analysis as in the daphnid tests.

An embryo/larval toxicity test with Quahog clams found no effects at the solubility limit and a fivefold excess (mean measured concentrations of 79 and 320 µg/L). Earlier observations of reduced larval production at a nominal 100 mg/L are thought to reflect a physical effect of the fine white precipitate thrown from solution at this concentration, which is well above the solubility limit (Surprenant, 1989).

The above results confirm that diflubenzuron is highly toxic to aquatic invertebrates.

9.6.2.4 Chronic toxicity to invertebrates

No effects were noted on survival, growth or reproduction of *Daphnia magna* exposed for 21 days to a mean measured concentration of 40 ng/L diflubenzuron. Survival dropped to about 50% at 93 ng/L, with no reproduction and reduced body length in survivors (Surprenant, 1988).

The 21 day LC50 in chronic testing with mysid shrimp was 1.24 µg/L, compared with the acute result of 2.06 µg/L. Reproduction was decreased at an estimated concentration of 75 ng/L (the lowest tested) with suggestions that reproduction was also affected in progeny (Nimmo *et al*, 1980).

Parent survival and reproduction were the most sensitive responses in 28 day life cycle testing with mysid shrimp. The NOEC for mortality was 45 ng/L (mean measured concentration) with deaths occurring throughout the exposure period at higher concentrations. Statistically significant reductions in reproductive success were seen at 86, 140 and 210 ng/L (Breteler, 1987a).

Supplemental studies with mysid shrimp found a statistically significant reduction in reproductive success after 21 days at 93 ng/L, but no mortality. Mortality was observed in second generation mysids during chronic exposures at 123 ng/L, but survival and reproduction returned to normal on return to clean water. Acute (24 hour) exposures at 298 ng/L had no subsequent effects on survival, growth or reproduction (Breteler, 1987b).

Again these results indicate very high chronic toxicity to aquatic invertebrates.

9.6.2.5 Acute toxicity to algae and aquatic plants

Additional results are summarised in Table 9.9.

Table 9.9: Summary of new results for toxicity to algae and aquatic plants

Species	Result	Reference
Selenastrum capricornutum	72 hour NOEC = 200 µg/L	Berends and Thus, 1992
	120 hour NOEC = 300 µg/L	Thompson and Swigert, 1993a
	72 hour NOEC = 100 mg/L	Groeneveld *et al*, 1994
Anabaena flos-aquae	120 hour NOEC = 330 µg/L	Thompson and Swigert, 1993b
Navicula pelliculosa	120 hour NOEC = 380 µg/L	Thompson and Swigert, 1993c
Skeletonema costatum	120 hour NOEC = 270 µg/L	Thompson and Swigert, 1993d
Lemna gibba G3	14 day NOEC = 190 µg/L	Thompson and Swigert, 1993e

The first test with the green alga *Selenastrum capricornutum* used a single exposure concentration of 200 µg/L, confirmed by analysis to remain stable throughout the exposure period. The second test used a nominal concentration of 500 µg/L, which assayed at about 400 µg/L at initiation and 200 µg/L at termination. The third test used the Dimilin WG80 formulation, concentrations of which remained stable and close to nominal throughout the exposure period.

Similar declines in diflubenzuron concentration were observed in the blue-green alga and diatom bioassays, conducted at a nominal 500 µg/L. Initial measured concentrations for *Anabaena flos-aquae* were about 400 µg/L, declining to about 200 µg/L at termination with the exception of one of three replicates which assayed at 330 µg/L. For the freshwater diatom *Navicula pelliculosa*, initial concentrations were slightly above nominal, but declined to 200-300 µg/L after 120 hours. Initial concentrations in the marine diatom bioassay were only about 300 µg/L, also declining to about 200 µg/L after 5 days.

Testing with duckweed also used a nominal concentration of 500 µg/L, which declined from an initial measured concentration of about 300 µg/L to below 100 µg/L after 14 days.

The above results indicate lower toxicity to algae and aquatic plants, but the actual level likely to cause toxic effects is unclear as studies on the active constituent were all limit tests conducted at relatively low concentrations.

9.6.2.6 Metabolite toxicity

Zebra fish suffered complete mortality after 24 hours at a mean measured 98.2 mg/L 4-chlorophenylurea but survived through 96 hours at 50 mg/L. The LC50 was

estimated at 70 mg/L, the geometric mean of these two concentrations (Groeneveld and Berends, 1993).

Daphnia magna responded less abruptly to this toxicant, with mortality occurring between 52 and 242 mg/L. The 48 hour EC50 was 104 mg/L (Groeneveld and Thus, 1993). Cleavage of the urea linkage is attended by a dramatic decline in toxicity.

The EC50s based on biomass and growth in the green alga *Selenastrum capricornutum* were 30 and 95 mg/L 4-chlorophenylurea, respectively (Keetelaar-Jansen *et al*, 1994).

The other main metabolite, 2,6-difluorobenzoic acid, had no effect on zebra fish exposed for 96 hours to a nominal 100 mg/L, confirmed by analysis at initiation and termination of exposure (Groeneveld *et al*, 1993a).

Daphnia magna were also insensitive to this metabolite, although complete mortality occurred within 24 hours at 180 mg/L. The estimated EC50 was 73 mg/L, but would have been 104 mg/L but for the single mortality that occurred at 60 mg/L (Groeneveld *et al*, 1993b).

The EC50s based on biomass and growth in the green alga *Selenastrum capricornutum* were 68 and 71 mg/L 2,6-difluorobenzoic acid, respectively. Neutralisation with sodium hydroxide moderated the toxicity, such that growth rate inhibition was much less than 50% at the highest exposure concentration of 100 mg/L (Groeneveld *et al*, 1995b).

The data indicate that diflubenzuron metabolites are much less toxic that parent.

9.6.3 Data from other sources

The database of the Environmental Fate and Effects Division of the US EPA's Office of Pesticide Programs[22] contains results from acute tests with a variety of aquatic arthropods. The most sensitive organism with respect to acute toxicity of diflubenzuron in this database is the pre-moult stage of the grass shrimp (*Palaemonetes pugio*) with a 96 h LC50 of 0.64 µg/L. It should be noted, however, that this was considered a supplementary test[23], for unclear reasons. According to this

[22] The database is maintained by the Ecological Fate and Effects Division of the Office of Pesticide Programs database, US EPA. Contact: Brian Montague, U. S. Environmental Protection Agency (7507C), Ariel Rios Building, 1200 Pennsylvania Ave., N.W., Washington, D.C.,20460. Phone:703-305-6438 FAX:703-305-6309 EMAIL Address: Montague.Brian@epa.gov.
The toxicity data is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable).

[23] Studies in this category are scientifically sound; however, they were performed under conditions that deviated substantially from recommended protocols. Results do not meet guideline requirements; however, the information may be useful in a risk assessment. Some of the conditions that may place a study in a supplemental category include:

- Unacceptable or non-native test species
- Test material not properly identified
- Dosage levels tested were less than 5000 ppm (or 100 ppm for aquatics), but not high enough to produce an effect on the tested organisms or a precise LC50/EC50(exceptions sometimes made for highly insoluble chemicals).

database, fiddler crabs are also highly sensitive (96 h LC50 = 1.0 µg/L). Very high acute toxicity is also evident in *Daphnia magna* (48 h LC50 = 1.0 µg/L) and mysid shrimp (96 h LC50 = 2.1 µg/L).

The review by Fischer and Hall (1992) also contains the 0.64 µg/L value as the LC50 (time of test not stated, but likely 96 h – see below) for male and non-ovigerous female grass shrimps[24]. This is referenced to an unpublished EG&G Bionomics (1975) report, which is the same year as indicated in the US EPA database, and these results are therefore probably derived from the same source. Note that the document outlining the proposed Environmental Quality Standards (EQSs) for diflubenzuron in the UK (Hedgecott *et al*, 1997) does not list this result but contains an even more sensitive value of an EC50 (time not stated) of 0.063 µg/L for limb regeneration of the same grass shrimp species (*P pugio*), as cited by Fischer and Hall (1992), referencing a paper by Touart and Rao (1987). The latter is part of a book.

Table 5.2 of Hedgecott *et al* (1997) also contains results of 100% mortality at 0.5 µg/L to the early life-stage of the stone crab (*Menippe mercenaria*), as well as to the blue crab (*Callinectes sapidus*). These are both saltwater species and again are cited in Fischer and Hall (1992) based on a paper by Costlow (1979), again in a book. It appears these should be considered as chronic results. Note, however, a similar citing in Table 5.1 of the UK document of an 48 h LC50 of 0.15 µg/L to the freshwater clam shrimp (*Eulimnadia sp*). This is based on a paper by Miura and Takahashi (1974), which does not seem to have been included in Fischer and Hall (1992).

Note DEH has not seen any of the original references supporting the results in this Section except for Miura and Takahashi (1974).

9.6.4 Summary of available toxicity data

Diflubenzuron has low toxicity to vertebrates (birds, mammals and fish) but is very highly toxic to some invertebrates because of its chitin inhibiting properties. Aquatic arthropods are of particular concern because of their sensitivity and the likelihood that they will be exposed to residues discharged to aquatic environments after treatment of sewage containing scouring effluent. A number of results in the order of 1.0 µg/L have been reviewed by DEH, though the literature and other sources make it clear that there are even more toxic results available. The most sensitive freshwater acute result appears to be the 48 h LC50 of 0.15 µg/L to the freshwater clam shrimp (*Eulimnadia sp*). For saltwater it is the 96 h LC50 of 0.64 µg/L for the male and non-ovigerous female grass shrimp (*P pugio*). The most sensitive freshwater chronic result is the 21 d reproduction of EC50 of 0.062 µg/L to *D magna*, while the saltwater chronic result is the EC50 (time not stated) of 0.063 µg/L for limb regeneration of the grass shrimp species (*P pugio*).

- Deviations from recommended diet preparation measures
- Deviations from recommended water quality characteristics which may have stressed test organisms and affected toxicological response(e.g., low D.O. in aquatic studies)
- Tested organisms were older or younger than required age.

[24] Erroneously quoted as 640 µg/L but the preceding test description (organisms exposed continuously to the technical grade diflubenzuron with acetone) makes clear the result should be 0.640 µg/L (= 640 ng/L, nominal).

9.6.5 End points used in the hazard assessment

Diflubenzuron is a well studied chemical. As noted above and below, the worst case Australian release will be through a marine outfall. As the most sensitive saltwater result is the grass shrimp 96 h LC50 of 0.64 µg/L (see 9.6.3 above), this will be used for the hazard assessment for use under Australian conditions. Following the application of an assessment factor of 10 (considering the extent of data available), the PNEC is 64 ng/L, though this could be considered as not sufficiently protective enough considering 48 h LC50 of 0.15 µg/L to the freshwater clam shrimp (*Eulimnadia sp*) and that it is equal to the both the fresh and seawater chronic EC50s.

In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentrations (MAC) are in place for the textile industry to meet environmental standards. According to the EqualS™ database[25] and the former website (http://www.basicweb.fsnet.co.uk/index.htm)[26] the proposed AA and MAC EQSs for diflubenzuron in fresh water are 1 and 15 ng/L. Saltwater criteria of 5 and 100 ng/L have also been proposed. All appear to be listed as final in Annex G of of the Scottish Environmental Protection Agency web site (accessed on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf). The freshwater values are used in the hazard assessment below.

Hedgecott *et al* (1997) make clear the derivation of these values. For freshwater the lowest reliable acute and chronic effects concentrations were considered to be the 48 h LC50 of 0.15 µg/L (nominal based on technical diflubenzuron) to the freshwater clam shrimp (*Eulimnadia sp,*) and the 21 day reproduction of EC50 of 0.062 µg/L to *Daphnia magna* (again technical diflubenzuron but analytically-confirmed). To protect against short-term exposure a safety factor of 10 was applied to the clam shrimp result, ie a MAC of 15 ng/L. However, for chronic exposure a safety factor of 50, on the basis that there appear to be organisms that are more sensitive than daphnids, was applied, leading to an AA EQS of 1 ng/L.

For saltwater a safety factor of 10 was applied to the nominal 96 h LC50 of 1.11 µg/L to *P pugio* (MAC = 100 ng/L, not clear why the more sensitive result of 0.64 µg/L was overlooked), while for long-term exposure a safety factor of approximately 10 was applied to the the EC50 (time not stated) of 0.063 µg/L for limb regeneration of *P pugio,* leading to an AA of 5 ng/L. Hedgecott *et al* (1997) considered this result as an ecologically significant effect as the lack of limb regeneration could significantly reduce shrimp viability.

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[25] The EqualS™ database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

[26] This contained more recent information than in EqualS and was on-line from about 2000, but was removed towards the end of 2002.

9.7 ENVIRONMENTAL HAZARD FROM AUSTRALIAN SCOURING

The risk that diflubenzuron would impact adversely in aquatic environments when scouring effluent is disposed of to land is low because of the low mobility of diflubenzuron in soils to which effluent would be applied. The main concerns arise in relation to discharge to sewer. Knowledge of sewage volumes, scouring rates and wool residues can be used to estimate concentrations leaving the outfall, which can then be compared with toxicity data to determine environmental hazard.

9.7.1 Residue levels in wool clip

Based on the Australian Wool Innovations (AWI) survey data (Scott Williams, personal communication, March 2003), the mean residues of diflubenzuron in Australian fleece wool increased from 1.2 mg/kg in 1996-7 to 3.6 mg/kg in 1997-8, before decreasing slightly to 3.5 mg/kg in 1998-9 and further to 2.9 mg/kg in 1999-2000, but increasing significantly to 5.5 mg/kg in 2000-2001. However, in 2001-2002 the mean residue concentration in the clip had dropped to 4.3 mg/kg.

There was a notable sharp rise in the wool residue survey results for 2002-2003, with a mean residue on all wool of 7.2 mg/kg, with 23.4% of samples testing positive for diflubenzuron and the average diflubenzuron residues in positive samples being 30.3 mg/kg, and with 360 mg/kg being the highest residue in the survey. Residues above 50 mg/kg constituted 4.1% of sales lots and 55% of the residue load, with 4% (23% of residue load) of sales lots having residues in the range 25-49.5 mg/kg. In total 15% of residues were >10 mg/kg, and these constituted 95% of the residues load (Russell, 2004). However, the mean residue on all wool dropped to 5.9 mg/kg in 2003-2004, with the mean residue when treated being 27.3 mg/kg, but with 27.3% of samples being positive (up from 19.4% in 2001-2002).

In the context of the latest survey results and an apparent general upward trend for use and residue levels of diflubenzuron, the figure of 7.2 mg/kg will be used as the input concentration for the hazard calculation of diflubenzuron in the scouring process. The figure of 30.3 mg/kg, representing the mean residue for sales lots testing postive for diflubenzuron, will also be used for comparison as representing a potential “hot spot”.

9.7.2 Australian Model

The Australian model (Savage 1998) has been used by DEH to predict the worst case level of diflubenzuron present in sewage effluent entering the Barwon waters from the Black Rock treatment plant. The results of the calculation performed by DEH take into consideration the following parameters as shown in Table 9.10.

Table 9.10: Determination of Q values by DEH under Australian conditions

Parameters	**Mean residues in 2002-2003 clip**	**Average residue when detected**
Concentration of diflubenzuron in wool at harvest (mg/kg)	7.2	30.3
Mass of wool scoured in one day (tonnes)	50	50
Mass of diflubenzuron entering scouring plant on wool (g)	360	1515
Percentage remaining on scoured wool (%)	4	4
Percentage removed (including that on wool fibre and recovered wool wax) during scouring	30	30
Percentage removed during sewage treatment (%)	85	85
Mass of diflubenzuron discharged (g)	36.288	152.7
Flow rate of sewage treatment plant (ML/day)	50	50
Predicted concentration in sewage outflow (ng/L)	725.76	3054.2
Dilution in plume[#]	0.02	0.02
Predicted Environmental Concentration (PEC) (ng/L)	**14.52**	**61.11**
Predicted No Effect Concentration (PNEC) (ng/L)	64	64
Quotient (PEC/PNEC)	**0.23**	**0.95**

A plume dilution factor of 0.02 was derived from the Grundy et al. (2000) study.

The Q values from using both the mean residues in the clip and the mean residues when detected are less than 1. However, the safety margin for the latter is very narrow. This represents a "hot spot", ie wool coming from an area of grazing country where most farmers use diflubenzuron and the wool grown is such that little if any mixing occurs prior to processing. This is quite possible as at least 25% of sheep appear to have been treated with diflubenzuron last season. Therefore, the possibility that diflubenzuron could be an environmental hazard as a result of treatment on sheep at current use levels under Australian conditions cannot be ruled out, given the general trend.

9.7.3 Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall, ie the PNEC of 64 ng/L to the grass shrimp. The result is shown in Table 9.11.

Table 9.11: Calculated concentration of diflubenzuron (ng/L) in raw greasy wool based on the target concentration of 64 ng/L at the Black rock ocean outfall for diflubenzuron

Parameters	**DEH's estimates**
Target concentration (ng/L)	64
Load entering the ocean which takes into account the plume dilution factor of 50 (ENV) (g)	50 ML X 64 ng/L X 50 = 160
Load entering sewage treatment plant (STP) (g)	100/15 X 160 = 1066.6
Load entering wax recovery (WAX) (g)	100/70 X 1066 = 1523.81
Load entering scour (SCR) (g)	100/96 X 1524 = 1587.3
Concentration of residues on wool (mg/kg)	1587.3/50 = **31.75**

On the basis of the 2002-2003 AWI wool residue monitoring data of 7.2 mg/kg for diflubenzuron, there is unlikely to be an environmental hazard from use of diflubenzuron according to the currently approved label instructions. This is also the case for the mean residues when detected of 30.3 mg/kg found in the 2002-2003 survey (though the safety margin is very narrow).

As noted above 8% of 2002-2003 sales lots had residues >25 mg/kg, and diflubenzuron was used on close to 25% of Australian sheep. For a processing lot to contain above 31.75 mg/kg it would have to result from a small pocket of grazing country where most farmers use diflubenzuron and wool is subsequently managed in such a way that little if any mixing occurs prior to processing. The likelihood of this occurring is unknown but the above calculations indicate that diflubenzuron residues in Australian wool may present a problem for local processors. It is therefore difficult to conclude that use of diflubenzuron according to the approved label instructions, including a 6 month wool withholding period, and scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

9.8 TRADE

9.8.1 UK/EU EQS Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, Environmental Quality Standards (EQS) for Annual Average (AA) and Maximum Allowable Concentrations (MAC) are in place for the textile industry to meet environmental standards. According to the EqualS™ database[27] and the former website (http://www.basicweb.fsnet.co.uk/index.htm) the proposed AA and MAC EQSs for diflubenzuron in fresh water are 1 and 15 ng/L. Saltwater criteria of 5 and 100 ng/L have also been proposed. All are listed as final in Annex G of of the Scottish Environmental Protection Agency web site (accessed on 6 March 2006 at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf). The predicted environmental concentrations in the river on the basis of the proposed values are shown in Table 9.12.

[27] The EqualS™ database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

Table 9.12: Predicted concentration of diflubenzuron (ng/L) in river based on the use of the EU/UK model

DEH's EU/UK models estimate		
Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of diflubenzuron in wool at harvest (mg/kg)	7.2	7.2
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of diflubenzuron entering scouring plant on wool (g)	198.72	198.72
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)*	85	85
Percentage removed during sewage treatment (%)	80	80
Mass of diflubenzuron discharged (g)	5.72	5.72
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	**38.4**	**80.6**
DEH's proposed UK/EU requirement (ng/L)	1	15

* The 90% removal rate is derived from Shaw for overseas wool scouring (Savage 1998).

The predicted environmental concentration of 38.4 ng/L from the 2002-2003 mean wool residue data is much greater than the proposed AA of 1 ng/L and the 80.6 ng/L also exceeds the proposed MAC value of 15 ng/L by over 5 times. This is still the case if the much lower 2001-2002 mean residue on Australian fleece wool of 4.3 mg/kg is used. Therefore, as both the EQS values are exceeded, the use of diflubenzuron according to label instructions has a high potential to adversely affect trade at current use levels.

9.8.2 Conceptual Model for EU/UK requirements

On the basis of the conceptual model described on page 6, the maximum mean concentration in raw wool can be estimated from the target concentration at the outfall as shown in Table 9.13.

Table 9.13: Calculated concentration of diflubenzuron (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 1 (AA) and 15 (MA) ng/L for diflubenzuron

Estimate based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**EQS (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)	1	15
Load entering the river (ENV) (g)	149 ML X 1 ng/L = 0.149	71 ML X 15 ng/L = 1.065
Load entering sewage treatment plant (STP) (g)	100/15 X 0.149 = 0.993	100/15 X 1.065 = 7.1
Load entering on-site treatment plant (OST) (g)	100/20 X 0.993 = 4.97	100/20 X 7.1 = 35.5
Load entering scour (SCR) (g)	100/96 X 4.97 = 5.17	100/96 X 35.5 = 37.0
Concentration of residues on wool (mg/kg)	5.17/27.6 = **0.19**	37.0/27.6 = **1.34**

The above model presented indicates that the 2002-2003 AWI wool residue data mean result of 7.2 mg/kg for diflubenzuron (and even the 2001-2002 result of 4.3 mg/kg) greatly exceeds the target concentration of 0.19 mg/kg for the AA as well as the MAC maximum value of 1.34 mg/kg. Therefore, there is a high potential for trade issues under the current use pattern according to label instructions for diflubenzuron.

In conclusion the mean diflubenzuron residue in the Australian wool clip already exceeds the above limits, even with a 6 month wool harvest interval. Given the resistance of diflubenzuron to dissipation in fleece, it would appear that wool withholding periods (WWP) would need to be in excess of one year in order to comply

with the above requirements. This is clearly impractical. The only realistic option would appear to be labelling of wool that has received diflubenzuron treatment, and the exclusion of such wool from the export market. It would appear likely that overseas buyers of Australian wool will increasingly require assurances of low residue status (essentially a declaration that diflubenzuron has not been used) as they are required to comply with strict discharge limits based on EQSs in receiving waters.

9.9 WOOL WITHHOLDING PERIODS (WWP)

Considerable blending of wool occurs before scouring. Residues in treated sheep that are higher than the mean acceptable residue can therefore be tolerated, provided that high residue wool is mixed with low residue wool before processing. As noted in earlier chapters, this concept has been modelled, using national wool residue survey data. High residue wool sale lots can be excluded until the average residue conforms to requirements. Future situations can be modelled by increasing the proportion of high residue lots for products that are increasing their market penetration. If residue concentrations in each wool sale lot are first converted to estimated time periods since treatment, the wool harvest interval needed to meet residue requirements can be estimated in the same way.

Conversion of residue concentrations in a wool sale lot to wool withholding periods is not a simple process, as residue concentrations could correspond to a range of time periods since treatment, reflecting differences between sheep, climatic variation, mode of application and other factors. In practice, the conversion entailed generation of a further ten new wool sale lots with the same average residue according to the log normal distribution expected for the treatment under question. Times since treatment are then estimated for each wool sale lot using model dissipation curves that have been fitted to results from experimental application of diflubenzuron. The model allows for different breakdown rates due to the method of application and length of wool and for changes in the rate of breakdown between application and shearing.

The wool residue breakdown model provided the suggested WWPs in Table 9.14 for diflubenzuron products (Horton and Campbell, 2001). These are based on maximum mean concentrations (processing lot maximum limits) of 1.3 (AA EQS), 4.2 (MA EQS) and 7.4 (Australia) mg/kg, as compared with figures proposed in this report of 0.19, 1.34 and 31.75 mg/kg, respectively.

Table 9.14: Calculated WWPs for diflubenzuron treatments by Horton and Campbell (2001)

Treatment	**Wool harvesting interval (days)**		
	AA EQS	**MAC EQS**	**Australia**
Backlash off-shears	244	263	112
Magnum off-shears	297	303	175
Long wool backliner	>365	>365	290
Lice dipping (low dose)	314	313	181
Lice dipping (standard)	>365	>365	331
Flystrike dipping	>365	>365	343
Jetting for lice	330	326	0
Jetting for flystrike	352	356	32

The wool blending model is not user friendly. If this model is to be used to determine wool harvest intervals for the residue limits proposed in this report, this would best be done under contract to the model creators. However, it would appear likely that WWPs to meet UK requirements would extend beyond a year for all treatments if current cut offs are applied. The WWPs (>365 days) suggested for long wool backliners indicate that the data used to generate Table 9.14 do not support a shorter half-life for this method of treatment.

It is not clear how the authors were able to do the calculations for the eight different treatments and it would appear from the level of detail in the above table that considerably more wool residue data exist for diflubenzuron than have been submitted for this review or otherwise made available to DEH. Certainly DEH does not have kinetic data (residues at various time points through the season for all treatments).

It appears that at least some of the additional data comes from the paper by Morcombe et al. (1999), who surveyed wool producers known to have used an IGR and measured the wool residues in core samples after shearing. Seventeen lots were tested following jetting and 14 following dipping and the average residue was 40 mg/kg on wool when sheep were shorn with 12 months wool. There was evidence that much less than the recommended rate appeared to be applied, and without access to the individual data, these results are of limited value for DEH's use.

9.10 CONCLUSIONS

Diflubenzuron degrades rapidly in the environment but is highly persistent in fleece, where dissipation half-lives are generally above 6 months and likely to extend to a year or more. Formulation characteristics affect persistence, with particulate formulations appearing to degrade more slowly, except when applied as pour-on formulations in long wool, where breakdown appears to be faster. More rapid dissipation (half-life around 3 months) is indicated in this situation, apparently as a result of physical dislodgement, but data to support this conclusion are few and in some cases conflicting. Similarly, climate is likely to be influential, with more rapid degradation expected in warmer climates, but no data on variation of breakdown rates with geography have been submitted. Use of diflubenzuron for lice and blowfly control appears likely to leave residues in the order of 50 mg/kg at shearing based on core sampling, but considerable variation above and below this figure may be expected depending on the time and mode of treatment.

Environmental exposure to diflubenzuron residues in sewage effluent discharged to the environment has been estimated using models. The Australian model, based on a target PNEC of 64 ng/L after initial dilution of the plume, indicates that average residues up to around 32 mg/kg greasy wool could be tolerated. Recent residue surveys indicate mean residues in the order of 4.3-7.2 mg/kg, and it does not appear likely that scouring in Australia will give rise to environmental problems in relation to diflubenzuron residues in discharged effluent as long as average clip residues do not approach 32 mg/kg. However, as the mean residue when treated is approaching this level, there is a concern that some scour lots could contain potentially environmentally harmful levels of diflubenzuron.

Available data are insufficient to enable DEH to support the current 6 month wool withholding period. On the basis of this assessment the DEH is unable to conclude that the use of selected sheep ectoparasiticide products containing diflubenzuron in accordance with approved labels under Australian scouring conditions and the current WWP would not be likely to have an effect that is harmful to animals, plants or things or to the Australian environment under Australian scouring conditions.

The overseas situation is also problematic. Mean residues of diflubenzuron in the Australian clip are already in excess of target concentrations based on expected environmental quality standards, and use appears likely to increase, possibly with substitution of dipping products by backliners. Diflubenzuron residues in treated fleece will considerably exceed target concentrations and potential adverse effects on trade are likely unless wool withholding periods are increased to an impractically long interval (well in excess of a year). In order to remain confident that Australian wool will continue to be accepted in overseas markets, it appears that mechanisms are needed to identify wool that has been treated with diflubenzuron and isolate it from wool intended for export. Overseas customers can be expected to increasingly require such assurances, in order that they can meet their discharge limits when these are formally introduced. The DEH conclusion is that there is a potential trade risk associated with the future exports of Australian raw wool containing residues of diflubenzuron.

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CHAPTER 10 - CYPERMETHRIN AND ALPHA-CYPERMETHRIN

10.1 INTRODUCTION

The APVMA Gazette notice of 7 September 1999 announcing the special review noted that products containing synthetic pyrethroids would be among those that the review would focus on in the first instance. The Gazette notice included twelve cypermethrin/alpha-cypermethrin products for review. Of these only two (Vanquish and Duracide) contain alpha-cypermethrin.

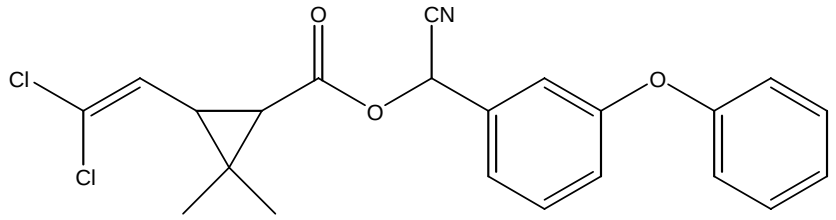
Barricade 'S' Cattle Dip and Spray (Product No 45211, Fort Dodge Australia Pty Ltd) and *Cooper's Blockade 'S' Cattle Dip and Spray* (Product No 46815, Schering-Plough Animal Health Ltd) remain on the market. However, instructions for use on sheep have been removed from the label for the former, and only treatment of sheep for ticks and buffalo fly (a very minor use) remains on the label for the latter. Note also that several new products have been registered since the review was announced.

Cypermethrin and alpha-cypermethrin are currently registered for a number of purposes both as agricultural and veterinary chemicals. The main use of synthetic pyrethroids by the Australian wool industry is for control of the sheep louse *Bovicola ovis*, with one long wool product also claiming blowfly strike prevention.

Cypermethrin and alpha-cypermethrin belong to the pyrethroid group of insecticides, synthetic derivatives of pyrethrin with improved physical and chemical properties compared with the natural compound. Alpha-cypermethrin is a purified form of cypermethrin. As the two forms can be difficult to distinguish analytically, and one is just a purified form of the other, they are considered together in this report.

10.2 CHEMICAL IDENTITY AND PROPERTIES

Cypermethrin contains three chiral centres (two on the cyclopropane ring and one at the alpha-cyano carbon) and can therefore exist as eight stereoisomers (four enantiomeric pairs) which are commonly grouped into four *cis* and four *trans* isomers with reference to the cyclopropane ring. The *cis* isomers carry more insecticidal activity. Cypermethrin is a racemic mixture of all eight stereoisomers, with the *cis*:*trans* ratio varying from 50:50 to 40:60. Alpha-cypermethrin is a racemic mixture of the two more insecticidally active *cis* isomers, present to about 25% in cypermethrin.



The physical and chemical properties of these two pyrethroids are described in published monographs (WHO, 1989, 1992). Cypermethrin and alpha-cypermethrin have low water solubility (< 10 µg/L), low vapour pressure (< 1 µPa) and high octanol/water partition coefficient (logP > 5).

The strong hydrophobicity of the synthetic pyrethroids makes it difficult to obtain accurate measurements of water solubility, because of the formation of colloids and micelles in the aqueous phase, and analytical uncertainties associated with the low concentrations involved. Soil partition coefficients are also difficult to determine because sorption to colloids or dissolved organic carbon in the aqueous phase suppresses the results obtained, particularly at the high solids ratios (typically 1:25) that are normally used. Reported water solubilities and partition coefficients therefore need to be treated with caution.

10.3 ENVIRONMENTAL EXPOSURE

10.3.1 Volume

Analysis of wool industry survey data, as described later in this report, indicates that cypermethrin and alpha-cypermethrin are used on about 15% of the Australian flock.

10.3.2 Application and use pattern

The pour-on products are applied as a single backline strip from the head to the base of the tail, at 2 mL (50 mg cypermethrin) per 10 kg body weight. Most sheep receive around 250 mg cypermethrin. *Kleenclip* is applied at the same rate but is first diluted with four parts of water before application as a double strip along both sides of the backline.

The off-shears spray-on product (*Duracide*) is applied as a 12 cm spray band evenly distributed about the backline from poll to rump, at 10 mL for 21-50 kg sheep and 15 mL for 51-70 kg sheep (200-300 mg alpha-cypermethrin). The long-wool product

(*Vanquish*) is applied in the same way, at application rates that depend on the length of the wool (5 mL for sheep with less than 2 months wool growth, 10 mL for 2-6 months, and 20 mL at 6-10 months growth, or 250-1000 mg alpha-cypermethrin for lice control). If fly strike prevention is intended, the application rate is 20 mL (1 g alpha-cypermethrin) at 2-10 months wool.

10.4 ENVIRONMENTAL CHEMISTRY AND FATE

10.4.1 Summary of environmental fate

As no data were provided by registrants, the summary below has been taken from the available literature.

The low water solubility and low vapour pressure of synthetic pyrethroids restrict their mobility in the environment. Residues contacting soil sorb strongly to organic matter and remain essentially immobile until they degrade, mainly through aerobic microbial processes. Cypermethrin has typical half-lives of 2-4 weeks in fertile soils, and about 2 weeks in natural waters (WHO, 1989). Residues entering water sorb rapidly to dissolved organic matter, suspended solids and sediments. The evidence suggests residues are effectively immobile on sheep, with little translocation through the fleece from the site of application.

Recently conducted adsorption studies in three sediments containing 1, 3 or 13% organic carbon highlight the strong tendency of cypermethrin to partition from the water column to sediment (Maund *et al*, 2002). Radiolabelled cypermethrin (nominal concentrations of 15, 45, 135 or 405 μg/L, considerably above the stated solubility of 4 μg/L) was added in acetone solution to the aqueous phase (0.01 M $CaCl_2$) and shaken with the sediment (1:25 ratio) at approximately 1300 revolutions per hour. More than 98% of the added cypermethrin had partitioned to the sediment phase within 2 hours, with at least 99% in the sediment at equilibrium, which was reached in less than 24 hours. Mean sediment partition coefficients were 2360, 15700 and 23600, respectively (238000, 502000 and 177000 normalised to organic carbon). These are likely an underestimate, as it was difficult to quantify the very low concentrations remaining in the aqueous phase, which was mostly cypermethrin (typically at least 60%) but small amounts of more polar compounds were sometimes present. In calculating the partition coefficients, it was assumed that all radio-activity in the aqueous phase was unchanged cypermethrin.

10.4.2 Fate of residues in fleece

Studies with deltamethrin, described in the deltamethrin chapter of this report, show that movement away from the site of application along the backline is limited in extent and duration. The studies conclude that treatment should occur within 24 hours of shearing, and preferably within 6 hours, as this maximises the distribution around the skin in freshly secreted wool grease and is a factor in minimising the residues remaining at shearing.

Dissipation from fleece may occur through volatilisation, photooxidation or microbial activity. Losses are expected to occur more rapidly in hot and sunny climates. Savage

(1998) reports typical half-lives of 14-15 weeks for synthetic pyrethroids on sheep, although shorter half-lives are reported for topical formulations such as those currently registered.

Alpha-cypermethrin also undergoes isomerisation on the sheep, which complicates residue analyses. Cypermethrin and alpha-cypermethrin can be difficult to distinguish in residue analyses.

The main influence on residue levels in shorn wool is the timing of treatment. Wool from sheep treated with an off-shears pour-on pyrethroid typically contains residues of around 1 mg/kg, while wool from sheep treated with a long wool backline pyrethroid typically contains 20-100 mg/kg greasy wool (Joshua, 1999).

Savage (1998) includes more detail on the above estimates. It cites a number of sources in concluding that off-shears treatment with pyrethroids is likely to leave residues of around 2 mg/kg in shorn wool.

For long wool treatments, Savage (1998) reports on two sets of trials, known as the Avcare task force and the Victorian studies.

The Avcare data show that use of backline products (a cypermethrin/diazinon combination was used) at 3 months before shearing leaves residues of 81 mg/kg in shorn wool. The estimated half-life was about a year. This study used patch sampling to determine residues. The high residues along the backline with this method of application lead to high variability using this sampling technique; for example, cypermethrin residues recorded 6 weeks after treatment were double those at 1 week after treatment.

The Victorian studies used the same cypermethrin/diazinon combination, which applied 1.5 g cypermethrin per sheep, and *Vanquish*, which applied 1 g alpha-cypermethrin per sheep. Both were applied to sheep with 9 months wool growth. Residues were determined from band samples, which are less prone to variability than patch samples but tend to overestimate residues, although half-life determinations are reasonably reliable. In the first year, residues at 3 months after treatment were 216 and 117 mg/kg, respectively, with half-lives of about a month over this period (note that half-lives are likely to increase with the passage of time). Residues remained at the site of application with little translocation around the sheep. Sheep were treated with 6 months wool growth in the second year. Cypermethrin residues were still high (134 mg/kg) at 6 months after treatment (half-life 78 days) but alpha-cypermethrin residues were lower (23 mg/kg, half-life 45 days).

Savage (1998) also reports results for sheep treated with backline formulations at 8 weeks after shearing. Estimated residue levels at 10 months after treatment were 1.4 mg/kg cypermethrin and 9.3 mg/kg alpha-cypermethrin for sheep treated at Werribee (Vic). The effects of climate on degradation are illustrated by the much lower residues (0.3 and 0.8 mg/kg, respectively) for sheep treated at Charleville (Qld). Note that these residues were based on analysis of 'worst case' backline patch samples.

10.4.3 Recent residue depletion studies

Further residue depletion trials had recently been conducted in Queensland, Victoria, Tasmania and Western Australia at the time Savage (1998) was published. The studies included a wide range of off-shears and short wool treatments, with wool sampled at least three times between treatment and shearing. Residue data were not available for the Savage (1998) document, but were to be incorporated into residue depletion models (Campbell *et al*, 1998) as they became available.

The residue depletion kinetics of cypermethrin, alpha-cypermethrin and cyhalothrin on sheep have been modelled by Campbell *et al* (1998). A number of variables influence the final residue at shearing (for example, amount applied, method of treatment, wool length and climate) and cannot be optimised independently of each other. The residue depletion model used a genetic algorithm method that allows simultaneous variation of all these variables until a set is found that best fits the data. It was not possible to show distinct differences between these three synthetic pyrethroids. Initial breakdown following long wool backline application proceeded at a moderate rate (half-life 39 days) but degradation slowed (half-life 85 days) after 6 months. The average half-life was 48 days over the first three months, increasing to 58 days over six months.

The residue depletion model has been used to estimate half-lives of various ectoparasiticides including alpha-cypermethrin and cypermethrin following off-shears treatments. Band samples were taken on 3-6 occasions between treatment and shearing. Estimated half-lives for alpha-cypermethrin were 45 days at Esperance and 64 days at Werribee. These increased slightly (52 and 73 days) for cypermethrin. The model estimated that residues remaining at shearing would be 0.5 mg/kg or less (Campbell *et al*, 1999).

Survey data (Plant *et al*, 1999) also did not reveal any significant difference between cypermethrin, alpha-cypermethrin, deltamethrin and cyhalothrin. When cypermethrin and alpha-cypermethrin were used off-shears, mean residues (± standard error) were 2.53 (± 0.39) and 2.50 (± 0.33) mg/kg at shearing. Given application rates of 250 mg, a final residue of 12.5 mg (assuming fleece weight of 5 kg) indicates the passage of a little over 4 half-lives, or an average half-life through the season in the order of 80 days.

10.4.4 Behaviour of residues during sewage treatment

Recent work by Russell *et al* (2001) has led to some changes in the assumptions regarding the degree of removal of various chemicals during sewage treatment. This work involved measuring pesticide residues at entry to and exit from the Black Rock sewage treatment plant that services the Geelong catchment. This treatment plant operates in a "semi-continuous" mode by cyclically directing incoming sewage into separate tanks that operate on a four hourly cycle, with 10% of the supernatant drawn down after each cycle. Average sewage retention time is 36-48 hours.

Average residues in greasy wool for one study were 0.23 mg/kg cypermethrin. The removal efficiency in this study was at least 95% as residues were undetectable (<10 ng/L cypermethrin) at discharge.

A second study used only commercial wool, containing an average 0.43 mg/kg cypermethrin. Again, cypermethrin could not be detected at discharge, meaning that the removal rate must be at least 97% for this strongly hydrophobic substance.

An earlier, unpublished report of this work (Grundy *et al*, 2000) includes the observation that the design engineer for the Black Rock sewage treatment plant estimated a 50 fold dilution of the sewage discharge plume at the surface of the sea immediately above the outfall diffuser system. Effluent discharged from deepwater outfalls undergoes rapid initial dilution before reaching either a level of neutral buoyancy or the ocean surface. After ejection from the outfall diffusers, the sewage effluent plumes rise rapidly through the water column due to their buoyancy relative to the surrounding ocean waters. As they rise, they are diluted by entrainment of the ambient ocean water resulting in a gradual increase in plume density.

The above assumptions are used in the hazard calculations below.

10.5 ENVIRONMENTAL EFFECTS

10.5.1 Summary of environmental effects

Again as no data were provided by registrants, the summary below has been taken from the available literature.

Synthetic pyrethroids are highly potent insecticides. They are characterised by low toxicity to terrestrial vertebrates (typical LD50s for birds and mammals are above 1000 mg/kg) but very high toxicity to fish and particularly to aquatic arthropods. Effects on aquatic arthropods are the primary concern with sheep ectoparasiticides as residues are discharged to aquatic environments after wool scouring and effluent treatment.

The review by WHO (1989) reports that Crustacea, particularly marine decapod Crustacea, are highly susceptible to cypermethrin, with mortality occurring at levels below 0.05 µg/litre, but that the rapid dissipation of cypermethrin from the water column provides an opportunity for affected populations to rapidly re-establish. The most sensitive test result available (from the US EPA Ecological Effects Branch Pesticide EcoToxicity Database[28], which contains presently known ecotoxicity endpoints for registered pesticides used in the US) is a 96 hour LC50 of 4.7 ng/L for the marine species *Mysidopsis bahia*.

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[28] The database is maintained by the Ecological Fate and Effects Division of the Office of Pesticide Programs database, US EPA. Contact: Brian Montague, U. S. Environmental Protection Agency (7507C), Ariel Rios Building, 1200 Pennsylvania Ave., N.W., Washington, D.C.,20460. Phone:703-305-6438 FAX:703-305-6309 EMAIL Address: Montague.Brian@epa.gov.

The toxicity data is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable).

The acute toxicities of cypermethrin and alpha-cypermethrin to *Daphnia magna* and *Gammarus pulex* are similar (WHO, 1992). The most sensitive organism with respect to alpha-cypermethrin is the scud, *Gammarus pulex*, with a 24 hour LC50 of 50 ng/L.

A recent distributional analysis of the large volume of acute aquatic toxicity data available for cypermethrin (58 data points) found 10^{th} centile values of 10 ng/L for all organisms, 6.4 ng/L for arthropods and 380 ng/L for vertebrates. The acute aquatic toxicity of cypermethrin appears typical of the synthetic pyrethroids used on sheep, as 10^{th} centile values for lambda-cyhalothrin (9 data points) and deltamethrin (21 data points) were 10 and 9 ng/L, respectively. The 5^{th} centile value for cypermethrin was 4 ng/L (Solomon *et al*, 2001).

The laboratory toxicity data for cypermethrin have been compared with the results from four mesocosm studies (Giddings *et al*, 2001). These studies integrate physical, chemical and ecological processes that are not represented in simpler laboratory tests, such as the rapid dissipation of pyrethroids from the water column. Information obtained from field studies about spatial variability of exposure and recovery of affected populations was also considered.

Mesocosms were treated with cypermethrin at nominal concentrations of 62-10000 ng/L, with peak concentrations of 30-1000 ng/L measured. Multiple treatments were made, mostly by spray application, except for a single spray treatment (100 g/ha) at the highest exposure level. The measured concentrations were about 50-90% of nominal, except at the highest application rate where they dropped to around 10%.

The mesocosm studies revealed a trend in sensitivity to cypermethrin, with amphipods, isopods, midges, mayflies, copepods and cladocerans most sensitive and fish, snails, oligochaetes and rotifers least sensitive. Similar trends were evident with another pyrethroid (esfenvalerate). With few exceptions, affected populations recovered to normal before the end of the year of exposure, mostly within weeks. This was presumed to reflect a number of factors, such as internal refuges (areas of low exposure), resistant life stages, rapid generation times and repopulation from areas outside the mesocosms. Indirect effects on fish due to reductions in invertebrate prey were recognised as possible outcomes, but did not occur.

The most sensitive organisms appeared to be amphipods, which declined in mesocosms exposed to 30 or 100 ng/L cypermethrin and did not recover. These organisms rely mainly on migration for population recovery as they have no resistant life stages, nor aerial dispersive life stages. Adult Coleoptera and Hemiptera, which experience higher exposure as surface dwellers, were also obviously affected at 30 ng/L, but these organisms are mobile and typically recover quickly. No other organisms were adversely affected at this lowest concentration, but populations of mayfly, snails and oligochaetes increased.

The lack of recovery for amphipod populations was regarded as an artefact of the enclosed systems studied, as even modest immigration rates in open systems allow rapid population recovery for these organisms. The effects noted at 30 ng/L were

regarded as nonsignificant from the ecosystem perspective as they were taxonomically limited and, except for the amphipods, transitory.

The lowest concentration of cypermethrin that caused ecologically significant effects in the mesocosms was 100 ng/L. Population reductions at this concentration were also seen in cladocerans, copepods, midges and isopods, with no recovery in the last group of organisms.

The authors note that the lowest adverse effect concentration of 100 ng/L in the mesocosms exceeds the 10^{th} centile of laboratory toxicity (10 ng/L) by an order of magnitude, implying that risk assessment based on the 10^{th} centile would be protective of aquatic ecosystems.

10.5.2 End points to be used for hazard assessment

Environmental quality standards (EQSs) have been established for cypermethrin in the UK (see below). The tentative annual average (AA) EQS of 0.2 ng/L approximates the chronic no effect concentration and the maximum acceptable concentration (MAC) EQS of 2 ng/L the acute no effect concentration.

EQSs are defined as "the concentration of a substance which should not be exceeded in the receiving water in order to protect the use of the water". EQSs for protection of aquatic life are derived to protect all aquatic species. The approach followed in the UK is to collate and critically assess available data for a substance, and to apply appropriate extrapolation factors to the lowest reliable and relevant adverse effects concentration (Zabel and Cole, 1999). Use of extrapolation factors tends to be a conservative approach to establishing standards for water quality.

For Australian conditions, the target concentration at the sewage outfall is the product of the plume dilution factor (50) and the acute no effect concentration. The MAC EQS of 2 ng/L, protective of more than 95% of aquatic species, will be used for this parameter. Use of this conservative endpoint allows confidence that meeting the target concentration will be protective of aquatic life.

10.6 ENVIRONMENTAL HAZARD OF AUSTRALIAN WOOL SCOURING

10.6.1 Wool monitoring data

National surveys conducted by Australian Wool Innovations (AWI, Scott Williams AWI, personal communication, March 2003) show declining synthetic pyrethroid residues in recent years. Residues fell from around 6 mg/kg between 1992 and 1996 to 3-4 mg/kg in 1997-1998 and further to 1.3-2.0 mg/kg in 1999-2001.

For 2001-2002 cypermethrin mean residues on Australian fleece wool were 0.8 mg/kg, with 11.9% of samples showing residues. The mean residues when wool had been treated with cypermethrin were 6.6 mg/kg, with the highest residue in sales lots tested being 80 mg/kg (for alpha-cypermethrin – see below). For total synthetic pyrethroids, the mean residues and highest residues were also 0.8 and 80 mg/kg, respectively.

Synthetic pyrethroid residues are almost exclusively cypermethrin and alpha-cypermethrin. These two active ingredients are not distinguished by the analytical procedure used in the AWI survey. More than 80% of the total residue load in the 2000-2001 season (to 30 April 2001) came from just 1% of the clip, reflecting long wool treatment with the only long wool product remaining on the market (Brightling, 2001). This indicates that mean residues in the remaining 99% of the clip were about 0.3 mg/kg (average for the clip was 1.5 mg/kg). Assuming an average residue of 2 mg/kg in wool shorn from sheep treated off-shears, it is estimated that 15% of the Australian flock is treated off-shears with synthetic pyrethroids (mainly cypermethrin and alpha-cypermethrin).

Despite not being distinguished by the analytical procedure used in the AWI survey, some specific data on cypermethrin and alpha-cypermethrin residues are available for the 2000-2001 and 2001-2002 seasons (Russell, 2002). A total of 77 from 600 samples contained residues above 0.5 mg/kg in the 2001-2002 survey. For cypermethrin (32 detections) the range was 0.54-9 mg/kg, with a mean of 2.1 mg/kg and median of 1.3 mg/kg. The range for alpha-cypermethrin (45 detections) was 0.65-80 mg/kg, with a mean of 14.7 mg/kg and median of 8 mg/kg. The five highest samples contained 40, 40, 42, 50 and 80 mg/kg alpha-cypermethrin, compared with 58, 65, 65, 120 and 200 mg/kg for the 2000-2001 season. While these data show an apparent decline in the last season, such trends are difficult to determine because of the small number of very high residue samples, which may be picked up more often in some years than in others.

The results reported for 2002-2003 are consistent with previous years, reflecting a general slow decline in the presence of synthetic pyrethrins in wool. However, in 2003-2004 the mean residues of cypermethrin on Australian fleece wool had risen to 1.1 mg/kg, with 9.4% of samples showing residues. The mean residues when wool had been treated with cypermethrin were 11.1 mg/kg, with the highest residue in the survey 120 mg/kg (Ian Russell, 2004).

For the purposes of this assessment, a mean cypermethrin residue of 1.5 mg/kg in wool will be assumed. The mean residues in 2001-2002 when wool had been treated with cypermethrin of 6.6 mg/kg will also be used to represent a “hot spot”.

10.6.2 Wool Scouring under Australian Conditions

The main environmental issue is the potential effect of cypermethrin and alpha-cypermethrin in wool scouring effluent. The model (Savage, 1998) based on scouring at Geelong, where primary treated effluent from scouring of wool is discharged daily through the Geelong sewerage system to the Black Rock ocean outfall, is used in DEH’s calculations, which are shown in Table 10.1.

Table 10.1: Determination of Q value for cypermethrin and alpha-cypermethrin by DEH

Parameters	**DEH estimate**
Concentration in wool at harvest (mg/kg)	1.5
Mass of wool scoured in one day (tonnes)	50
Mass of cypermethrin entering scouring plant on wool (g)	75
Percentage remaining on scoured wool (%)	4
Percentage removed with grease during scouring	30
Percentage removed during sewage treatment (%)	95
Mass of cypermethrin discharged (g)	2.52
Flow rate of sewage treatment plant (ML/day)	50
Concentration in effluent (ng/L)	50.4
Dilution in plume#	0.02
Predicted Environmental Concentration (EEC) (ng/L)	**1.01**
Predicted No Effect Concentration(PNEC, ng/L)*	2
Quotient (PEC/PNEC)	**0.5**

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).
*DEH has used an acute PNEC of 2 ng/L derived from the overseas MAC value.

DEH's calculations yield a Q value of <1 indicating that there is unlikely to be an environmental hazard. While the safety margin is small, the mean residue value for 2001-2002 and 2002-2003 was 0.8 and 0.7 mg/kg respectively, about half of that assumed above, though it is not clear whether this trend is continuing as the 2003-2004 value was 1.1 mg/kg. However, there is a potential hazard if the mean residues when treated value of 6.6 mg/kg, representing a potential "hot spot", is used as the Q = 2.2. Note that this value was 11.1 mg/kg in the 2003-2004 survey, and the Q = 3.7.

10.6.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall, ie. the PNEC of 2 ng/L is used in this model. The result is shown in Table 10.2.

Table 10.2: Calculated concentration of cypermethrin (ng/L) in raw greasy wool based on the target concentration of 2 ng/L at the outfall for cypermethrin

Parameters	**DEH's estimates**
Target concentration (ng/L)*	2
Load entering the ocean (ENV) (g)	50 ML X 50 X 2 ng/L = 5
Load entering sewage treatment plant (STP) (g)	100/5 X 5 = 100
Load entering wax recovery (WAX) (g)	100/70 X 100 = 142.9
Load entering scour (SCR) (g)	100/96 X 143 = 148.9
Concentration of residues on wool (mg/kg)	149/50 = 2.98

Australian wool industry survey data indicate that current average synthetic pyrethroid residues in the clip are below half the maximum mean tolerable concentration as determined by the revised Black Rock model. Note that the estimated residue limit of about 3 mg/kg in raw wool is a lower bound as it assumes 95% removal during sewage treatment. Recent measurements at Black Rock indicate that this is the minimum level of removal to be expected, and that removal efficiencies in excess of 97% are likely to be achieved in practice.

However, there is a potential hazard if the mean residues when treated values of 6.6 and 11.1 mg/kg, representing potential "hot spots", are used. Since about 15% of sheep are treated with cypermethrin and alpha-cypermethrin, this level of residue is only likely to occur if a processing lot resulted from a small pocket of grazing country where most farmers use the remaining long wool product and the wool grown is such that little if any mixing occurs prior to processing. Therefore there would be no hazard if this product was removed from the market (see further below).

10.7 TRADE

10.7.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, environmental quality standards (EQS) for Annual Average (AA) and Maximum Acceptable Concentration (MAC) are in place for the textile industry to meet environmental standards. While the EqualS^{TM} database[29] says that drafts were still under discussion, the former website: http://www.basicweb.fsnet.co.uk/index.htm indicated values for AA of 0.1 ng/L and MAC of 2 ng/L, respectively. The former has been modified to a tentative value of 0.2 ng/L in Annex G of of the Scottish Environmental Protection Agency web site (available at http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_g.pdf).

The predicted environmental concentration in rivers on the basis of EU/UK requirements are shown in Table 10.3.

Table 10.3: Predicted concentration of cypermethrin (ng/L) in river based on the EU/UK model by DEH

DEH EU/UK models estimate		
Parameters	**AA (chronic)**	**MAC (acute)**
Concentration of cypermethrin in wool at harvest (mg/kg)	1.5	1.5
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of cypermethrin entering scouring plant on wool (g)	41.4	41.4
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	95	95
Mass of cypermethrin discharged (g)	0.4	0.4
Flow rate of river (ML/d)	149	71
Predicted Environmental concentration in river (ng/L)	**2.7**	**5.6**
UK/EU expected requirement (ng/L)	0.2	2

[29] The EqualS^{TM} database CD may be purchased from:
National Centre for Environmental Toxicology WRc-NSF Ltd
Henley Road, Medmenham, Marlow, Bucks SL7 2HD
Telephone: 01491 636500 Fax 01491 636501
Email: cet@wrcplc.co.uk
Contact Officer: Dr Guy Franklin, EQualS Product Co-ordinator

DEH's calculations indicate the predicted environmental concentrations for both AA and MAC are higher than the UK/EU requirements indicating a significant potential for adverse trade effects, particularly for AA.

10.7.2 Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the outfall as shown in Table 10.4.

Table 10.4: Calculated concentration of cypermethrin (ng/L) in raw greasy wool based on the proposed EU/UK model with the target concentrations of 0.1 (AA) and 2 (MAC) ng/L for cypermethrin

DEH estimates based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)	0.2	2
Load entering the river (ENV) (g)	149 ML X 0.2 ng/L = 0.0298	71 ML X 2 ng/L = 0.142
Load entering sewage treatment plant (STP) (g)	100/5 X 0.0298 = 0.596	100/5 X 0.142 = 2.84
Load entering on-site treatment plant (OST) (g)	100/20 X 0.298 = 2.98	100/20 X 2.84 = 14.2
Load entering scour (SCR) (g)	100/96 X 2.98 = 3.10	100/96 X 14.2 = 14.8
Concentration of residues on wool (mg/kg)	3.10/27.6 = 0.112	14.8/27.6 = 0.54

Based on the above model, it is clear that the mean synthetic pyrethroid residue in the Australian wool clip in recent years of between 0.7-1.5 mg/kg exceeds the above limits. Given that off-shears treatments leave residues in the order of 2 mg/kg at shearing, and assuming 15% of the flock is treated, from the estimated residue level (2 X 0.15 = 0.3 mg/kg) it would appear that wool withholding periods need to be extended beyond a year in order to comply with the above requirements. This is clearly impractical, and potential adverse effects on Australia's trade would remain even if the remaining long wool product were to be removed from the market.

10.8 WOOL WITHHOLDING PERIOD (WWP)

Considerable blending of wool occurs before scouring. Residues in treated sheep that are higher than the mean acceptable residue can therefore be tolerated, provided that high residue wool is mixed with low residue wool before processing. This concept has been modelled, using national wool residue survey data. High residue wool sale lots can be excluded until the average residue conforms to requirements. Future situations can be modelled by increasing the proportion of high residue lots for products that are increasing their market penetration. If residue concentrations in each wool sales lot are first converted to estimated time periods since treatment, the wool harvest interval needed to meet residue requirements can be estimated in the same way.

Conversion of residue concentrations in a wool sale lot to wool harvesting intervals is not a simple process, as residue concentrations could correspond to a range of time periods since treatment, reflecting differences between sheep, climatic variation, mode of application and other factors. In practice, the conversion entails generation of a further ten new wool sale lots with the same average residue according to the log

normal distribution expected for the treatment under question. Times since treatment are then estimated for each wool sales lot using model dissipation curves that had been fitted to results from experimental application. The model allows for different breakdown rates due to the method of application and length of wool and for changes in the rate of breakdown between application and shearing.

Use of the model provides the following suggested wool withholding periods (see Table 10.5) for synthetic pyrethroid products (Horton and Campbell, 2001). These correspond to maximum mean concentrations (processing lot maximum limits) of 0.1 (AA EQS), 0.84 (MA EQS) and 1.5 (Australia) mg/kg, as compared with figures proposed in this report of 0.1, 0.54 and 3.0 mg/kg, respectively. Note that the former estimates were based on a MA EQS of 3.1 ng/L, and a discharge concentration of 50 ng/L for Australia. Use of the targets in this report (2 and 100 ng/L, respectively) would extend the wool harvest intervals estimated for the MA EQS and relax those estimated for Australia.

Table 10.5: Calculated WWPs for cypermethrin treatments by Horton and Campbell (2001)

Treatment	**AA EQS**	**MAC EQS**	**Australia**
Alpha-cypermethrin off-shears	238 days	151 days	88 days
Cypermethrin off-shears	265 days	172 days	100 days
Long wool backliner	> 365 days	357 days	207 days

10.9 CONCLUSIONS

The synthetic pyrethroids cypermethrin and alpha-cypermethrin degrade rapidly in the environment but are more persistent in fleece, where dissipation half-lives through the season are likely to be in the order of 80 days after a brief period of more rapid dissipation. Treatment off-shears is likely to leave residues in the order of 2 mg/kg at the next shearing. Long wool treatments leave much higher residues, likely to extend well over 100 mg/kg where treatments are made late in the season.

Environmental exposure to synthetic pyrethroid residues in sewage effluent discharged to the environment has been estimated using models. The Australian model, based on a discharge concentration of 100 ng/L (2 ng/L after initial dilution of the plume), indicates that average residues up to around 3 mg/kg greasy wool could be tolerated. Recent residue surveys indicate mean residues below 1.5 mg/kg with some evidence for a declining trend. On the basis of this assessment the DEH it is unable to find that the use of selected sheep ectoparasiticide products containing alpha-cypermethrin or cypermethrin in accordance with approved labels under Australian scouring conditions and the current WWP would not be likely to have an effect that is harmful to animals, plants or things or to the Australian environment under Australian scouring conditions.

However, the high residues recorded after long wool use indicate that a wool withholding period in excess of that currently stipulated (2 months) may be warranted. The survey data for 2000-2001 indicate that 80% of the total synthetic pyrethroid residue load comes from just 1% of the clip, reflecting long wool treatment with *Vanquish*. The five highest samples contained more than 100 mg/kg on average. As the mean residue was 1.5 mg/kg, this indicates that an increase in long wool treatments to 2% of the flock, would be likely to increase the average residue to 2.7 mg/kg, while

an increase to 3% of the flock would be likely to increase average residues to 3.9 mg/kg, in excess of the Australian target of 3 mg/kg.

The Victorian studies found residues of 117 mg/kg in shorn wool when sheep were treated with *Vanquish* in 9 months wool, but only 23 mg/kg when treatment occurred in 6 months wool. These residues are likely an overestimate as they are based on band samples. *Vanquish* can currently be applied to sheep in up to 10 months wool. The high residues (up to 200 mg/kg) present in 1% of the 2000-2001 clip indicate that long wool synthetic pyrethroid treatments tend to be applied late in the season, leaving limited time for dissipation before shearing occurs.

This use pattern leaves little margin for safety. Based on the survey results for 2000-2001, a doubling of long wool use would be expected to increase mean residues to around the threshold of 3 mg/kg for locally scoured wool. If residues from long wool treatment were restricted to 50 mg/kg, use could increase fivefold before this threshold was reached. Such restriction would likely require that 3-6 months elapse between treatment and shearing. Data in this report are insufficient to define this interval more accurately. If the one long wool product remaining on the market is to be retained, the residue depletion model (Campbell *et al*, 1998) should be used to determine acceptable wool harvest intervals. This is especially important for colder climates where breakdown proceeds more slowly. The DEH concludes, therefore, that it is not satisfied that the use of selected sheep ectoparasiticides containing alpha-cypermethrin or cypermethrin on long wool (more than 6 weeks off shears) would not be likely to have an effect that is harmful to animals, plants or things or to the Australian environment.

The overseas situation is more problematic. Mean residues of synthetic pyrethroids in the Australian clip are already in excess of target concentrations (0.056 mg/kg for the AA EQS and 0.54 mg/kg for the MAC EQS) based on expected environmental quality standards, and even off-shears use is likely to breach those requirements. If 15% of the flock is treated (the best currently available estimate) and off-shears treatments leave residues of around 2 mg/kg in shorn fleece, an average residue of 0.3 mg/kg may be estimated for the Australian clip. It thus appears likely that residues of cypermethrin and alpha-cypermethrin will present problems for Australian wool in sensitive export markets, even if considered in isolation. The model results suggest that synthetic pyrethroids should only be used off-shears if wool is intended for export to sensitive markets, and that use should ideally be declared.

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CHAPTER 11 - DELTAMETHRIN

11.1 INTRODUCTION

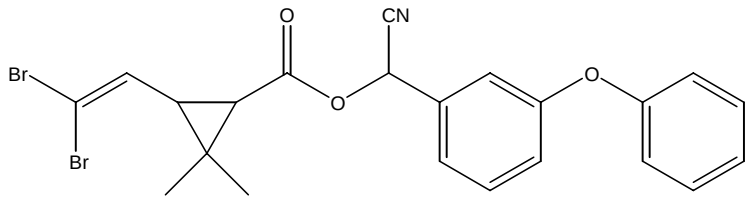
Three products containing deltamethrin were included in the APVMA Gazette notice of 7 September 1999 that announced the special review of sheep ectoparasiticides. However, only one is still registered and subject to the present review.

Deltamethrin is currently registered for a number of purposes both as an agricultural and veterinary chemical. The main use of synthetic pyrethroids by the Australian wool industry is for control of the sheep louse *Bovicola ovis*.

Deltamethrin belongs to the pyrethroid group of insecticides, synthetic derivatives of pyrethrin with improved physical and chemical properties compared with the natural compound.

11.2 CHEMICAL IDENTITY AND PROPERTIES

Deltamethrin contains three chiral centres (two on the cyclopropane ring and one at the alpha cyano carbon) and can therefore exist as eight stereoisomers (four enantiomeric pairs). In practice, deltamethrin exists as a single stereoisomer.



The physical and chemical properties of deltamethrin are described in a published monograph (WHO, 1990). Deltamethrin has low water solubility (< 2 μg/L), low vapour pressure (< 2 μPa) and high octanol/water partition coefficient (logP = 5.43).

The strong hydrophobicity of the synthetic pyrethroids makes it difficult to obtain accurate measurements of water solubility, because of the formation of colloids and micelles in the aqueous phase, and analytical uncertainties associated with the low concentrations involved. Soil partition coefficients are also difficult to determine because sorption to colloids or dissolved organic carbon in the aqueous phase suppresses the results obtained, particularly at the high solids ratios (typically 1:25) that are normally used. Reported water solubilities and partition coefficients therefore need to be treated with caution.

11.3 ENVIRONMENTAL EXPOSURE

11.3.1 Volume

Analysis of wool industry survey data, as described later in this report, indicates that deltamethrin is used on about 3% of the Australian flock.

11.3.2 Application and use pattern

The product is applied within 24 hours of shearing as a single backline strip from poll to tail, at 2 mL (20 mg deltamethrin) per 10 kg body weight. Most sheep receive around 100 mg deltamethrin.

The label indicates (as a restraint) that the product must only be used within 24 hours of shearing.

11.4 ENVIRONMENTAL CHEMISTRY AND FATE

11.4.1 Summary of environmental fate

As no data were provided by registrants, the summary below has been taken from the available literature.

The low water solubility and low vapour pressure of synthetic pyrethroids restrict their mobility in the environment. Residues contacting soil sorb strongly to organic matter and remain essentially immobile until they degrade, mainly through aerobic microbial processes. Deltamethrin degrades readily in aerobic soils, with half-lives generally in the 11-72 day range (WHO, 1990). Residues entering water sorb rapidly to dissolved organic matter, suspended solids and sediments. Available evidence indicates residues are effectively immobile on sheep, with little translocation through the fleece from the site of application.

11.4.2 Fate of residues in fleece

A number of studies have been conducted to determine the dispersion of deltamethrin through fleece following backline treatment (Hennessey, 1999). Dispersion occurs predominantly by diffusion along concentration gradients in wool grease, and tends to be slow and variable. Less than 10% of the dose left the backline in the 24 hours following application, and movement was almost complete within 14 days with only low concentrations found on the flank.

Deltamethrin remained at the tip of the staple as the wool grew, with little at the skin surface where lice prefer to feed on freshly secreted wool grease. Even though deltamethrin residues remained high at the tip of the staple, insecticidal activity declined as oxidation of the wool grease reduced the bioavailability of the associated pyrethroid.

Label instructions specify backline treatment should occur within 24 hours of shearing, and preferably within 6 hours, to take advantage of the increased grease that is produced in response to shearing. Conditions at this time, with most lice removed and

a hostile and exposed environment for those remaining, are most conducive to eradication. Much of the pesticide applied off-shears is degraded by ultra-violet radiation and/or removed by physical weathering through the growing season.

Savage (1998) cites a number of sources in concluding that off-shears treatment with pyrethroids is likely to leave residues of around 2 mg/kg in shorn wool.

Results for sheep treated with backline formulations at 8 weeks after shearing estimated residue levels at 10 months after treatment were 0.4 and 0.3 mg/kg deltamethrin for sheep treated at Werribee(Vic) and Charleville (Qld). Note that these residues were based on analysis of 'worst case' backline patch samples.

Further residue depletion trials had recently been conducted in Queensland, Victoria, Tasmania and Western Australia at the time Savage (1998) was published. The studies included a wide range of off-shears and short wool treatments, with wool sampled at least three times between treatment and shearing. Residue data were not available for the Savage (1998) publication, but were to be incorporated into residue depletion models being developed by Campbell and Horton as they became available.

A brief description of the residue depletion model is contained in the cypermethrin chapter of this report. The model has been used to estimate half-lives of various ectoparasiticides including deltamethrin following off-shears treatments. Band samples were taken on 3-6 occasions between treatment and shearing. Estimated average half-lives were 47 days at Esperance, 30 days at Longreach, 67 days at Werribee and 84 days at Cressy. The model estimated that residues remaining at shearing would be 0.4, 0.01, 0.5 and 1.0 mg/kg, respectively (Campbell *et al*, 1999).

Survey data (Plant *et al*, 1999) did not reveal any significant difference between cypermethrin, alpha-cypermethrin, deltamethrin and cyhalothrin. When deltamethrin was used as an off-shears backline treatment, the mean residue (± standard error) from 70 sales lots was 1.89 (± 0.92) mg/kg at shearing. Given application rates of 100 mg, a final residue of 9.5 mg (assuming fleece weight of 5 kg) indicates the passage of between 3 and 4 half-lives, or an average half-life through the season in the order of 100 days.

11.4.3 Behaviour of residues during sewage treatment

Two studies at the Black Rock sewage treatment plant have shown minimum removal efficiencies of 95 and 97% for cypermethrin. An estimated 50 fold dilution of the sewage discharge plume is reported for the ocean outfall from this treatment plant. These studies are described in the cypermethrin chapter of this report, and are used in the hazard calculations below.

No specific studies have been conducted with deltamethrin, but similarly high removal may be expected. Recent studies have shown that deltamethrin sorbs more strongly than cypermethrin to mineral surfaces, consistent with its greater hydrophobicity (Oudou and Hansen, 2002).

11.5 ENVIRONMENTAL EFFECTS

11.5.1 Summary of environmental effects

As no data were provided by registrants, the summary below has been taken from the available literature.

Synthetic pyrethroids are highly potent insecticides. They are characterised by low toxicity to terrestrial vertebrates (typical LD50s for birds and mammals are above 1000 mg/kg) but very high toxicity to fish and particularly to aquatic arthropods. Effects on aquatic arthropods are the primary concern with sheep ectoparasiticides, as residues are discharged to aquatic environments after wool scouring and effluent treatment.

The review by WHO (1990) reports that Northern lobsters are highly susceptible to deltamethrin, with an LC50 of 1.2 ng/L. Large numbers of invertebrates have reportedly been killed where deltamethrin is used for mosquito and blackfly control, but populations recovered by the following season through recolonisation and immigration. The most sensitive test result listed on the US EPA Ecological Effects Branch's Pesticide EcoToxicity Database[30], which contains presently known ecotoxicity endpoints for registered pesticides used in the US, is a 96 hour LC50 of 1.7 ng/L for the marine species *Mysidopsis bahia*.

A recent distributional analysis of the large volume of acute aquatic toxicity data available for deltamethrin (21 data points) found a 10^{th} centile values of 9 ng/L. The acute aquatic toxicity of deltamethrin appears typical of the synthetic pyrethroids used on sheep, as 10^{th} centile values for lambda-cyhalothrin (9 data points) and cypermethrin (58 data points) were 10 ng/L. The 5^{th} centile value for deltamethrin was 3 ng/L (Solomon *et al*, 2001).

11.5.2 End points to be used for hazard assessment

As noted in Chapter 10, environmental quality standards (EQSs) have been established for cypermethrin in the UK. The annual average (AA) EQS of 0.1 ng/L approximates the chronic no effect concentration and the maximum acceptable concentration (MA) EQS of 2 ng/L the acute no effect concentration.

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[30] The database is maintained by the Ecological Fate and Effects Division of the Office of Pesticide Programs database, US EPA. Contact: Brian Montague, U. S. Environmental Protection Agency (7507C), Ariel Rios Building, 1200 Pennsylvania Ave., N.W., Washington, D.C.,20460. Phone:703-305-6438 FAX:703-305-6309 EMAIL Address: Montague.Brian@epa.gov.

The toxicity data is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable).

EQSs are defined as "the concentration of a substance which should not be exceeded in the receiving water in order to protect the use of the water". EQSs for protection of aquatic life are derived to protect all aquatic species. The approach followed in the UK is to collate and critically assess available data for a substance, and to apply appropriate extrapolation factors to the lowest reliable and relevant adverse effects concentration (Zabel and Cole, 1999). Use of extrapolation factors tends to be a conservative approach to establishing standards for water quality.

No EQS has been established for deltamethrin, but the similarity in toxicity with cypermethrin suggests a similar EQS would be derived.

For Australian conditions, the target concentration at the sewage outfall is the product of the plume dilution factor (50) and the acute no effect concentration. The cypermethrin MA EQS of 2 ng/L, protective of more than 95% of aquatic species, will be used for this parameter. Use of this conservative endpoint allows confidence that meeting the target concentration will be protective of aquatic life.

11.6 ENVIRONMENTAL HAZARD OF AUSTRALIAN WOOL SCOURING

11.6.1 Wool monitoring data

National surveys conducted by Australian Wool Innovations (AWI) show declining synthetic pyrethroid residues in recent years. Residues fell from around 6 mg/kg between 1992 and 1996 to 3-4 mg/kg in 1997-1998 and further to 1.4-2.4 mg/kg in 1999-2001 (Brightling, 2001).

Savage (1998) reports a mean deltamethrin residue of 0.06 mg/kg for the 1997-1998 season. This corresponds to 1.2 mg/kg for sheep treated with deltamethrin, based on the assumption that 5% of the flock is treated. For 2001-2002 the mean deltamethrin residues on Australian fleece wool was very low at <0.1 mg/kg, with 2.7% of samples having detectable residues, the mean residue when found being 1.0 mg/kg and the highest residues in sales lots being 6.0 mg/kg (Scott Williams AWI, personal communication, March 2003). Levels in the 2002-2003 and 2003-2004 surveys were below this (Russell, 2004).

For the purposes of this assessment a mean residue level of 0.1 mg/kg for deltamethrin in wool will be assumed. The mean residues in 2001-2002 when wool had been treated with deltamethrin of 1.0 mg/kg will also be used to represent a "hot spot".

11.6.2 Wool Scouring under Australian Conditions

The main environmental issue is the potential effect of deltamethrin in wool scouring effluent. The model (Savage, 1998) based on scouring at Geelong, where primary treated effluent from scouring of wool is discharged daily through the Geelong sewerage system to the Black Rock ocean outfall, has been used in DEH's calculations shown in Table 11.1.

Table 11.1: Determination of Q value for deltamethrin by DEH

Parameters	**DEH estimate**
Concentration in wool at harvest (mg/kg)	0.1
Mass of wool scoured in one day (tonnes)	50
Mass of deltamethrin entering scouring plant on wool (g)	5.0
Percentage remaining on scoured wool (%)	4
Percentage removed with grease during scouring	30
Percentage removed during sewage treatment (%)	95
Mass of deltamethrin discharged (g)	0.168
Flow rate of sewage treatment plant (ML/day)	50
Concentration in effluent (ng/L)	3.36
Dilution in plume#	0.02
Predicted Environmental Concentration (PEC) (ng/L)	**0.0672**
Predicted No Effect Concentration (PNEC) (ng/L)*	2
Quotient (PEC/PNEC)	**0.034**

A plume dilution factor of 0.02 was derived from the diflubenzuron study (Grundy et al. 2000).
*DEH has used an acute PNEC of 2 ng/L derived from the overseas MAC value for cypermethrin.

DEH's calculations yield a Q value of <<1 indicating that there is unlikely to be an environmental hazard. This is also the case if the mean residues when treated value of 1.0 mg/kg, representing a potential "hot spot", is used as the Q = 0.34. While there is a potential hazard when the highest residue in the 2001-2002 survey (6.0 mg/kg) is used (Q = 2.04), the possiblity of this occurring under present use levels is remote.

11.6.3 DEH's Conceptual Model under Australian Conditions

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the ocean outfall, ie the PNEC of 2 ng/L is used in this model. The result is shown in Table 11.2.

Table 11.2: Calculated concentration of deltamethrin (ng/L) in raw greasy wool based on the target concentration of 2 ng/L at the outfall for cypermethrin

Parameters	**DEH's estimates**
Target concentration (ng/L)*	2
Load entering the ocean (ENV) (g)	50 ML X 50 X 2 ng/L = 5
Load entering sewage treatment plant (STP) (g)	100/5 X 5 = 100
Load entering wax recovery (WAX) (g)	100/70 X 100 = 143
Load entering scour (SCR) (g)	100/96 X 143 = 149
Concentration of residues on wool (mg/kg)	149/50 = 2.98

Australian wool industry survey data indicate that current average deltamethrin residues in the clip are well below the maximum mean tolerable concentration as determined by the revised Black Rock model. This is also the case if the mean residues when treated value of 1.0 mg/kg, representing a potential "hot spot", is used. Note that the estimated residue limit of about 3 mg/kg in raw wool is a lower bound as it assumes 95% removal during sewage treatment. Recent measurements at Black Rock indicate that this is the minimum level of removal to be expected, and that removal efficiencies in excess of 97% are likely to be achieved in practice.

It may therefore be concluded that use of deltamethrin according to label instructions at current levels, scouring of wool under Australian conditions would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

11.7 TRADE

11.7.1 UK/EU EQS/MAC Requirements

Pesticide residues in greasy wool can have implications for trade. There is increasing pressure from international sources to reduce both the biological oxygen demand and pesticide residue levels in scours. In the UK, environmental quality standards (EQS) for Annual Average (AA) and Maximum Acceptable Concentration (MAC) are in place for the textile industry to meet environmental standards. As noted in Chapter 10 the AA and MAC values for cypermethrin are established as 0.2 (tentative) and 2 ng/L, respectively, and will be used in the absence of values for deltamethrin.

The predicted environmental concentration in rivers on the basis of EU/UK requirements are shown in Table 11.3.

Table 11.3: Predicted concentration of deltamethrin (ng/L) in river based on the EU/UK model

DEH's EU/UK models estimate		
Parameters	**AA (chronic)**	**MA (acute)**
Concentration of deltamethrin in wool at harvest (mg/kg)	0.1	0.1
Mass of wool scoured in one day (tonnes)	27.6	27.6
Mass of deltamethrin entering scouring plant on wool (g)	2.76	2.76
Percentage remaining on wool (%)	4	4
Percentage removal as recovered wool grease and by associated on-site effluent treatment processes (%)	80	80
Percentage removed during sewage treatment (%)	95	95
Mass of deltamethrin discharged (g)	0.0265	0.0265
Flow rate of river (ML/d)	149	71
Predicted Environmental Concentration in river (ng/L)	**0.18**	**0.37**
UK/EU expected requirement (ng/L)	0.2	2

On the basis of the DEH calculations, the predicted environmental concentrations for the AA EQS are similar to the UK/EU requirements indicating a potential environmental hazard. However, the actual residue level was <0.1 mg/kg. The predicted environmental concentrations for the MAC are lower than the UK/EU requirements.

11.7.2 Conceptual Model for EU/UK requirements

On the basis of the conceptual model described in the introduction to this report, the maximum mean concentration in raw wool can be estimated from the target concentration at the outfall as shown in Table 11.4.

Table 11.4: Calculated concentration of deltamethrin (ng/L) in raw greasy wool based on the proposed EU/UK model with the likely target concentrations of 0.1 (EQS) and 2 (MAC) ng/L for deltamethrin

DEH estimates based on UK/EU proposed EQS (AA/MAC) Requirements		
Parameters	**AA (Chronic)**	**MAC (Acute)**
Target concentration (ng/L)	0.2	2
Load entering the river (ENV) (g)	149 ML X 0.2 ng/L = 0.0298	71 ML X 2 ng/L = 0.142
Load entering sewage treatment plant (STP) (g)	100/5 X 0.0298 = 0.596	100/5 X 0.142 = 2.84
Load entering on-site treatment plant (OST) (g)	100/20 X 0.596 = 2.98	100/20 X 2.84 = 14.2
Load entering scour (SCR) (g)	100/96 X 2.98 = 3.10	100/96 X 14.2 = 14.8
Concentration of residues on wool (mg/kg)	3.10/27.6 = 0.112	14.8/27.6 = 0.54

The estimations confirm the potential unacceptable environmental hazard for the AA but an acceptable hazard for the MAC. While the mean levels for deltamethrin were actually <0.1 mg/kg, it is not possible to completely rule out potentially adverse effects on Australia's trade, though the likelihood of this might be expected to be low, noting this is a mean annual average.

11.8 WOOL WITHHOLDING PERIOD (WWP)

Considerable blending of wool occurs before scouring. Residues in treated sheep that are higher than the mean acceptable residue can therefore be tolerated, provided that high residue wool is mixed with low residue wool before processing. A wool blending model has been developed to estimate wool harvesting intervals, or the minimum time between treatment and shearing that should be observed in order that blended wool meets likely market requirements. This model is described in the cypermethrin chapter of this report.

Data for off-shears treatments with deltamethrin have been incorporated in the wool blending model (Horton and Campbell, 2001) and the results are in Table 11.5 below. These correspond to maximum mean concentrations (processing lot maximum limits) of 0.1 (AA EQS), 0.84 (MAC EQS) and 1.5 (Australia) mg/kg, as compared with figures proposed in this report of 0.1, 0.54 and 3.0 mg/kg total synthetic pyrethroids, respectively. Note that the former estimates were based on a MA EQS of 3.1 ng/L, and a discharge concentration of 50 ng/L for Australia. Use of the targets in this report (2 and 100 ng/L, respectively) would extend the wool harvest interval estimated for the MAC EQS and relax that estimated for Australia.

Table 11.5: Calculated WHIs for deltamethrin treatments by Horton and Campbell (2001)

Treatment	**AA EQS**	**MA EQS**	**Australia**
Deltamethrin off-shears	175 days	105 days	60 days

11.9 CONCLUSIONS

The synthetic pyrethroid deltamethrin degrades rapidly in the environment but is more persistent in fleece, where dissipation half-lives through the season are likely to be in the order of 100 days after a brief period of more rapid dissipation. Treatment off-shears appears likely to leave residues in the order of 1 mg/kg at the next shearing, but few specific data are available.

Environmental exposure to synthetic pyrethroid residues in sewage effluent discharged to the environment has been estimated using models. The Australian model, based on a discharge concentration of 100 ng/L (2 ng/L after initial dilution of the plume), indicates that average residues up to around 3 mg/kg greasy wool could be tolerated. Recent residue surveys indicate mean synthetic pyrethroid residues in the order of 1.5 mg/kg with a declining trend. The contribution of deltamethrin is small as only one product is registered, for use off-shears, and would be likely to leave residues in the order of 1 mg/kg if used on the entire Australian flock. Current use is about 3% of the Australian flock. It does not appear likely that scouring in Australia will give rise to environmental problems in relation to deltamethrin residues in discharged effluent, provided that long wool applications do not occur. This should be ensured with the label restraint "Must only be used within 24 hours of shearing."

On the basis of this assessment the DEH concludes that the use of selected sheep ectoparasiticide products containing deltamethrin in accordance with approved label instructions and the current WWP would not be likely to have an effect that is harmful to animals, plants, or things or to the Australian environment under Australian scouring conditions.

The overseas situation is more problematic. The estimated level of around 1 mg/kg in fleece shorn from sheep treated off-shears with deltamethrin exceeds likely market requirements by more than an order of magnitude. These estimates are based on the assumption that any EQS to be introduced for deltamethrin would be the same as that for cypermethrin (AA = 0.1 ng/L). If 5% of the flock is treated, estimated average residues reduce to 0.05 mg/kg, compared with likely market requirements of 0.056 mg/kg.

It appears unlikely that residues of deltamethrin in the Australian clip will present problems for Australian wool in sensitive export markets if considered in isolation, based on the current off-shears use pattern and maximum use on 5% of the flock. However, if deltamethrin is considered collectively with other synthetic pyrethroids rather than in isolation, it would be part of the problems associated with this class of chemicals. The likelihood of trade difficulties depends on the regulatory approach adopted in overseas markets. However, it is the conclusion of the DEH that there is a potential trade risk associated with the use of product containing deltamethrin on future exports of raw wool.

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CHAPTER 12 - LAMBDA-CYHALOTHRIN

One product containing lambda-cyhalothrin was included in the Sheep Ectoparasiticides Review in accordance with the APVMA Gazette of 7 September 1999. However, since that time the registration has been cancelled.

On this basis lambda-cyhalothrin products are no longer subject to an assessment under this review.