The Occurrence of Sheep Dip Pesticides in Environmental Waters

National Centre For Toxic and Persistent Substances June 1997



ENVIRONMENT Agency

#### INTRODUCTION

This report summarises the monitoring data for sheep dip chemicals in surface freshwaters and groundwaters by the Environment Agency in the years 1993-95. The report was produced in response to a request from MAFF (Mike Murray, Environmental Protection - Water Quality and Resources) acting on behalf of the Minister for Agriculture Fisheries and Food.

#### Background to the Database

The data used in this report are taken from the National Pesticide database held by the Environment Agencies National Centre for Toxic and Persistent Substances (TAPS) at Peterborough. These data are the results of the monitoring of controlled waters and discharges for pesticide residues in England and Wales. Data is available from sampling of fresh surface waters, groundwaters, marine waters and also 'trade effluents' by the Agency (and its predecessor, the NRA) in the years 1992 to 1995. Analyses for around 160 pesticides at around 2700 locations are included for each year, giving approximately 250,000 determinations annually. The database contains information about the sample location, date of sampling as well as the concentration of the pesticides present for which analyses were carried out. The data are collated from the eight Environment Agency Regions annually. The data are interpreted and reported on Nationally as part of the work on minimising pesticide contamination of controlled waters.

#### Scope of the Report

The report aims to allow an assessment of pollution of controlled waters by pesticides used in sheep dips. Interpretation of the data is, however complicated by a number of factors, the main ones are listed below.

1) Monitoring is carried out for a whole range of reasons and the same sites are not necessarily sampled for the same determinands each year.

2) Sheep dip chemicals may occur from industrial as well as agricultural sources.

3) Monitoring is likely to be targeted to sites with known pollution problems.

The data is presented graphically wherever possible with some data tables. The data is presented in context by comparison with occurrences of other pesticides not used in sheep dips. The data are generally assessed against both the Environmental Quality Standard (EQS) if available and the drinking water directive for pesticides as a general level for comparison. Maps showing sample sites and sites failing any EQS allow a geographic analysis of the data. Two additional graphics derived from MAFF Agricultural Census data and Central Science Laboratory (PUSG) data are presented to summarise sheep distribution and relative regional sheep dip usage.

#### **Summary Interpretation**

Monitoring for sheep dip chemicals is fairly widespread in surface freshwaters but limited in groundwaters. Sheep dip chemicals occur relatively infrequently in comparison to some other pesticides but cause a large number of EQS failures due to their toxicity to aquatic life. Many EQS failures for sheep dip chemicals are associated with the wool processing industries and textile manufacture but some have been identified as being from agricultural dipping. The Agency monitoring is targeted in these industrial areas and this is likely to overestimate the relative importance of these sources. There is, however, much anecdotal evidence of widespread damage caused by agricultural dipping activities.



#### CONTENTS

### Figure 1. Surface Freshwater Locations where at Least one Sheep Dip Pesticide Sample was taken during 1993.

The map shows sample sites in colour depending on whether any samples greater than the limit of detection (LOD) were found.

### Figure 2. Surface Freshwater Locations where at Least one Sheep Dip Pesticide Sample was taken during 1994.

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### Figure 3. Surface Freshwater Locations where at Least one Sheep Dip Pesticide Sample was taken during 1995.

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#### Table 1. Summary of Samples Analysed for Sheep Dip in the Years 1993-95

The number of samples taken for each determinand is presented as well as a summary of the levels found.

#### Figure 4. Top 50 Pesticides Exceeding 0.1µg/l in Surface Freshwaters 1995.

The chart is ranked on % of samples exceeding  $0.1 \mu g/l$  with the sheep dip chemicals highlighted. The relative importance of these chemicals in terms of general occurrence can be seen. The relative importance in terms of toxicity of the sheep dip chemicals is likely to be greater. Lindane (Gamma-HCH) has many uses including agricultural and timber treatment but it is not used as a sheep dip in the UK. It may, however be used in other countries. A problem of failure of the Environmental Quality Standard (EQS) for lindane was experienced on the R. Aire in Yorkshire when a batch of contaminated wool from Russia was processed by a textile manufacturer. Tetrachlorothioanisole and tetrachloroaniline are breakdown products of the sprout suppressant tecnazene and their occurrence is restricted to a small number of sample sites and samples, they therefore appear disproportionately high when the data is expressed on a % of samples basis.

### Figure 5. Sheep Dip Pesticide Residues in Surface Freshwaters in England and Wales Data for four chemicals used in sheep dip are shown over the years 1993-95.

The bar chart shows % of samples in surface freshwaters greater than  $0.1\mu g/l$ . The data excludes pollution incidents, known polluted sites and data from downstream of known point source discharges. It is difficult to determine trends from these data as the number of samples and sites sampled may vary between years.

### Figure 6. Number of Sites for Pollution Incidents with Results >LOD for sheep Dip Pesticides.

Data is presented for samples taken from known pollution incidents. The number of sites experiencing pollution incidents associated with sheep dip is shown for the years 1992-95.

### Figure 7. Groundwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1993.

The map shows sample sites in colour depending on whether any samples greater than the limit

of detection (LOD) were found. It can be seen that much less groundwater monitoring for these chemicals is carried out than surface water monitoring.

### Figure 8. Groundwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1994.

The map shows sample sites in colour depending on whether any samples greater than the limit of detection (LOD) were found. It can be seen that much less groundwater monitoring for these chemicals is carried out than surface water monitoring.

### Figure 9. Groundwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1995.

The map shows sample sites in colour depending on whether any samples greater than the limit of detection (LOD) were found. It can be seen that much less groundwater monitoring for these chemicals is carried out than surface water monitoring.

### Figure 10. Surface Freshwater Sites Failing Environmental Quality Standards (EQS) for Sheep Dip Pesticides in England and Wales during 1994.

Sites exceeding any EQS (whether statutory or operational, maximum concentration or annual average) are shown on the map. Different symbols are used for different chemicals. The same site may fail the EQS for more than one chemical. EQSs exist for surface freshwater and marinewater but not groundwater.

## Figure 11. Surface Freshwater Sites Failing Environmental Quality Standards (EQS) for Sheep Dip Pesticides in England and Wales during 1995.

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#### Table 2. EQS failure comparison table

This table shows the EQS failures for all pesticides where standards and monitoring data are available. It can be seen that sheep dip chemicals have a disproportionately high number of failures in comparison with their general occurrence (see figure 4). This is partially due to the comparatively high toxicity (and hence low EQS) of these chemicals. It must be remembered that not all pesticides have EQS values and therefore failures will only occur when EQSs exist. 45 of the 160 pesticides monitored by the Environment Agency have an EQS value. Most sheep dip chemicals have EQSs set because of the threat to aquatic life. Of the top ten EQS failures, four are sheep dips, three are mothproofers and lindane (Gamma-HCH) has been partly attributable to imported wool.

#### Table 3. Reasons Given for Sheep Dip Pesticide EQS Failures 1995 (numbers of sites)

Substantiated reasons for EQS failures for 3 sheep dip chemicals are presented. Many are due to industrial sources but others are thought to have originated from dipping of sheep. Much sampling is targeted at sites in lower reaches of catchments that are likely to be affected by discharges so this data does not necessarily give a good overall picture of the relative importance of industrial and agricultural sources of these chemicals.

Figure 12. Sheep Dip Usage 1996

The graphic is derived from 1996 pesticide use data from CSL for each MAFF region and 1995 MAFF agricultural census statistics for each county. Usage rates of four chemicals used in sheep dips are shown. The application rate for each MAFF region from CSL was multiplied by the number of sheep in each county and the total divided by the area of the county to give an estimate of the kg/ha of each chemical used. Some regional differences in chemical use can be seen from this map.

#### Figure 13. Distribution of Sheep in England and Wales

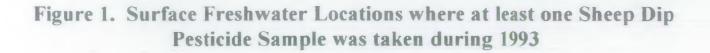
Data for 1995 are shown on a county level from the MAFF agricultural census data. Being able to locate sheep and sheep dip use geographically may assist in the targeting of monitoring and control measures for these chemicals.

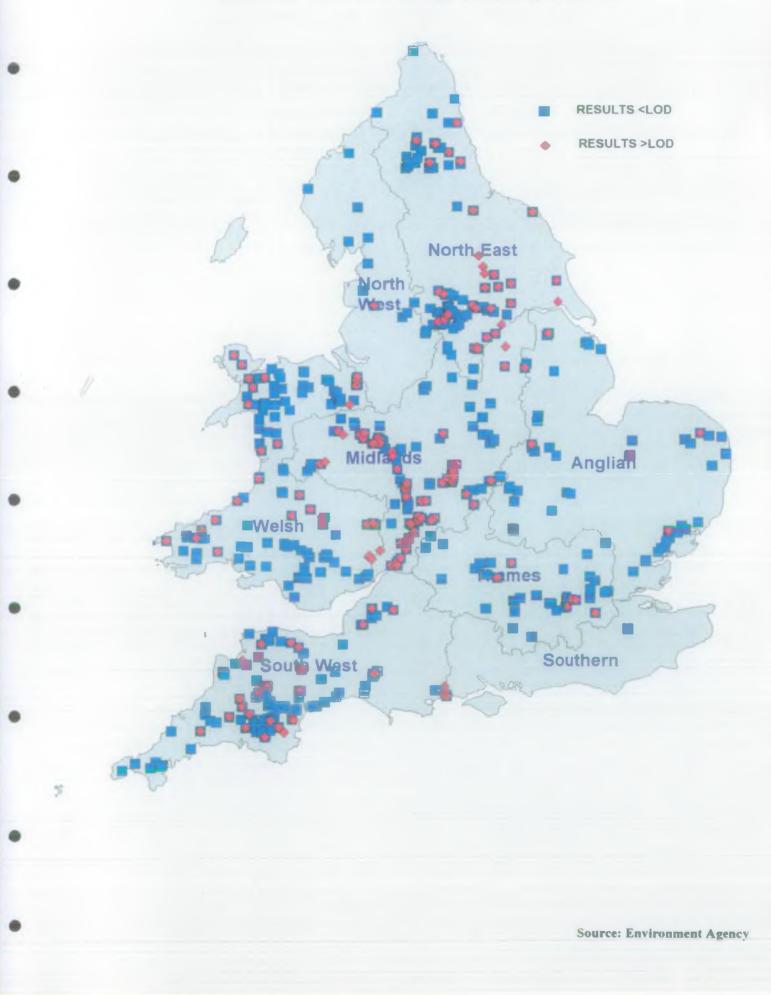
Produced by:

Antony Williamson Sue Hogarth John Binks

June 1997

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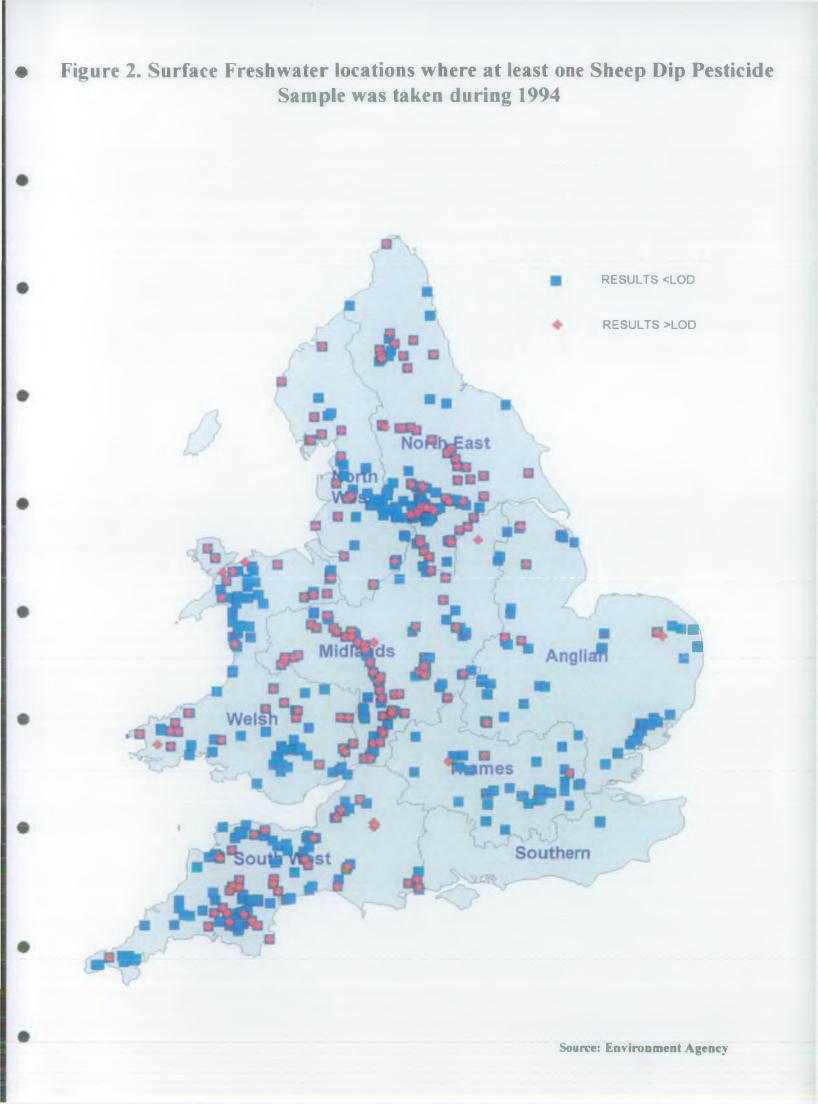
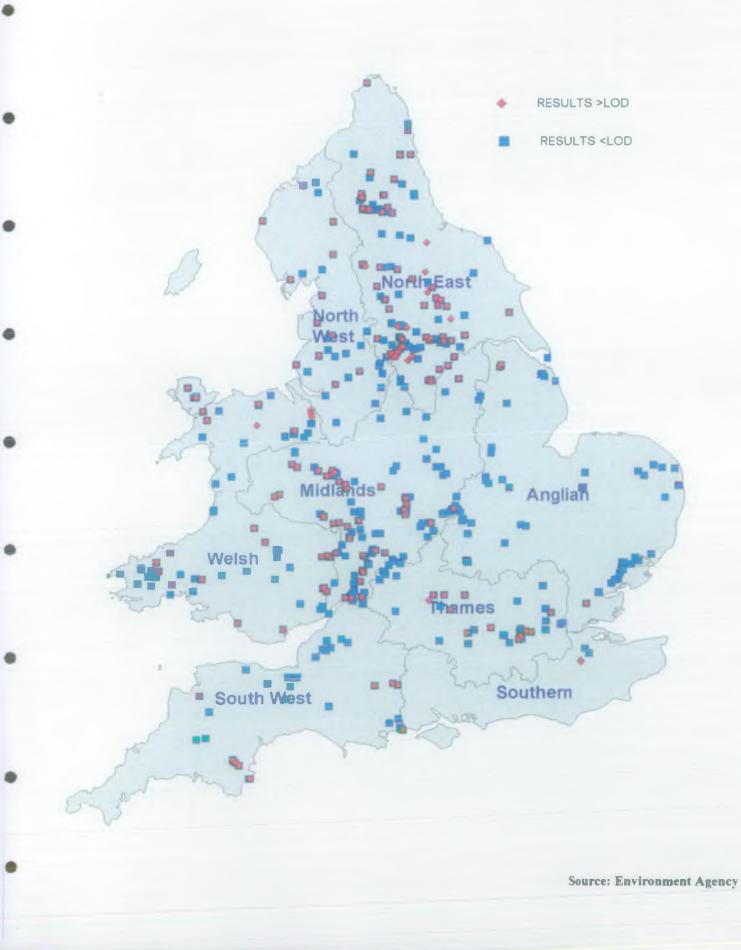


Figure 3. Surface Freshwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1995



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### National Data Summaries for Sheep Dip Pesticides 1993-1995

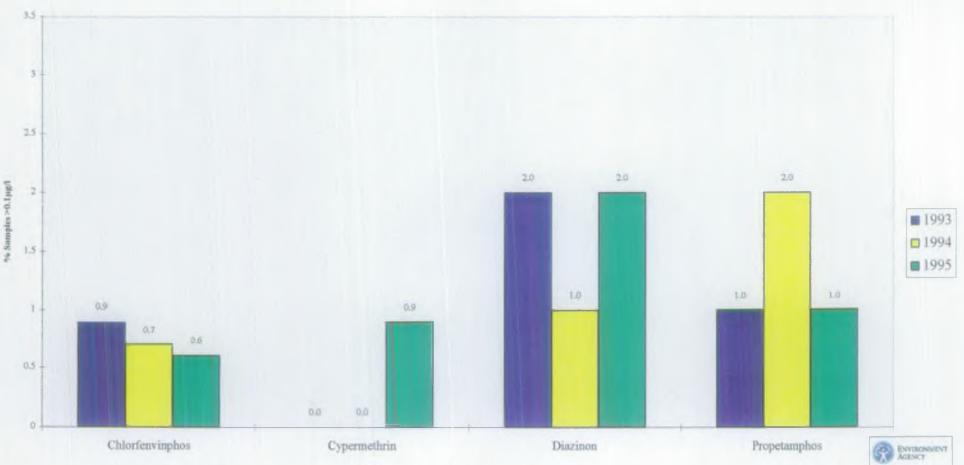
1993				с. С							÷
Type of Sample	Pesticide	No of Samples	No of Samples <lod< th=""><th>No of Samples &gt;LOD</th><th>% of Samples &gt;LOD</th><th>No of Samples &gt;100ng/l</th><th>% of Samples &gt;100ng/l</th><th colspan="2">LOD Range ng/l</th><th>Maximum ng/l</th><th>Average ng/l</th></lod<>	No of Samples >LOD	% of Samples >LOD	No of Samples >100ng/l	% of Samples >100ng/l	LOD Range ng/l		Maximum ng/l	Average ng/l
Fresh Surfacewater	chlorfenvinphos	3468	3364	104	3.00	31	0.89	5.0	150.0	944.0	3.05
Fresh Surfacewater	cypermethrin	481	476	5	1.04	0	0.00	10.0	300.0	90.0	0.52
Fresh Surfacewater	diazinon	3431	3111	320	9.33	63	1.84	4.7	300.0	2500.0	8.20
Fresh Surfacewater	propetamphos	2922	2745	177	6.06	35	1.20	4.5	200.0	1200.0	5.27
Groundwater	chlorfenvinphos	334	334	0	0.00	0	0.00	10.0	50.0	0.0	0.00
Groundwater	diazinon	336	336	. 0	0.00	0	0.00	4.7	100.0	0.0	0.00
Groundwater	propetamphos	239	238	1	0.42	0	0.00	4.7	40.0	40.0	0.17
1994				<u> </u>	<u> </u>		·				
Type of Sample	Pesticide	No of Samples	No of Samples <lod< th=""><th>No of Samples &gt;LOD</th><th>% of Samples &gt;LOD</th><th>No of Samples &gt;100ng/l</th><th>% of Samples &gt;100ng/l</th><th colspan="2">LOD Range ng/l</th><th>Maximum ng/l</th><th>Average ng/l</th></lod<>	No of Samples >LOD	% of Samples >LOD	No of Samples >100ng/l	% of Samples >100ng/l	LOD Range ng/l		Maximum ng/l	Average ng/l
Fresh Surfacewater	chlorfenvinphos	3854	3744	110	2.85	29	0.75	5.0	300.0	1141.0	2.85
Fresh Surfacewater	coumaphos	540	539	1	0.19	0	0.00	10.0	50.0	30.0	0.06
Fresh Surfacewater	cypermethrin	657	655	2	0.30	0	0.00	10.0	100.0	40.0	0.11
Fresh Surfacewater	diazinon	3967	3653	314	7.92	52	1.31	1.0	1000.0	1900.0	6.59
Fresh Surfacewater	propetamphos	3455	3159	296	8.57	55	1.59	4.6	100.0	4180.0	8.76
Groundwater	chlorfenvinphos	258	258	0	0.00	. 0	0.00	5.0	50.0	0.0	0.00
Groundwater	coumaphos	23	23	0	0.00	0	0.00	10.0	10.0	0.0	0.00
Groundwater	diazinon	264	260	4	1.52	0	0.00	5.0	50.0	22.0	0.12
Groundwater	propetamphos	140	136	4	2.86	0	0.00	5.0	20.0	14.0	0.16
1995											
Type of Sample	Pesticide	No of Samples	No of Samples <lod< th=""><th>No of Samples &gt;LOD</th><th>% of Samples &gt;LOD</th><th>No of Samples &gt;100ng/i</th><th>% of Samples &gt;100ng/l</th><th colspan="2">LOD Range ng/i</th><th>Maximum ng/l</th><th>Average ng/l</th></lod<>	No of Samples >LOD	% of Samples >LOD	No of Samples >100ng/i	% of Samples >100ng/l	LOD Range ng/i		Maximum ng/l	Average ng/l
Fresh Surfacewater	chlorfenvinphos	3073	2976	97	3.16	35	1.14	5.0	400.0	30800.0	12.98
Fresh Surfacewater	coumaphos	645	645	0	0.00	0	0.00	5.0	200.0	0.0	0.00
Fresh Surfacewater	cypermethrin	882	847	35	3.97	8	0.91	0.1	500.0	200.0	2.73
Fresh Surfacewater	diazinon	3147	2869	278	8.83	82	2.61	5.0	200.0	1660.0	12.49
Fresh Surfacewater	flumethrin	1	1	0	0.00		0.00		100.0	0.0	0.00
Fresh Surfacewater	propetamphos	2713	2517	196	7.22	58	2.14	4.5	200.0	8220.0	15.44
Groundwater	chlorfenvinphos	447	445	2	0.45	0	0.00	5.0	200.0	70.0	0.16
Groundwater	coumaphos	116	116	0	0.00	0	0.00	10.0	100.0	0.0	0.00
Groundwater	diazinon	446	441	5	1.12	1	0.22	5.0	200.0	216.0	0.83
Groundwater	propetamphos	328	321	7	2.13	1	0.30	4.8	100.0	489.0	1.56

Samples <LOD treated as zero. Greater than results taken at face value. Pollution incidents excluded.

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Figure 5. Sheep Dip Pesticide Residues in Surface Freshwaters in England and Wales



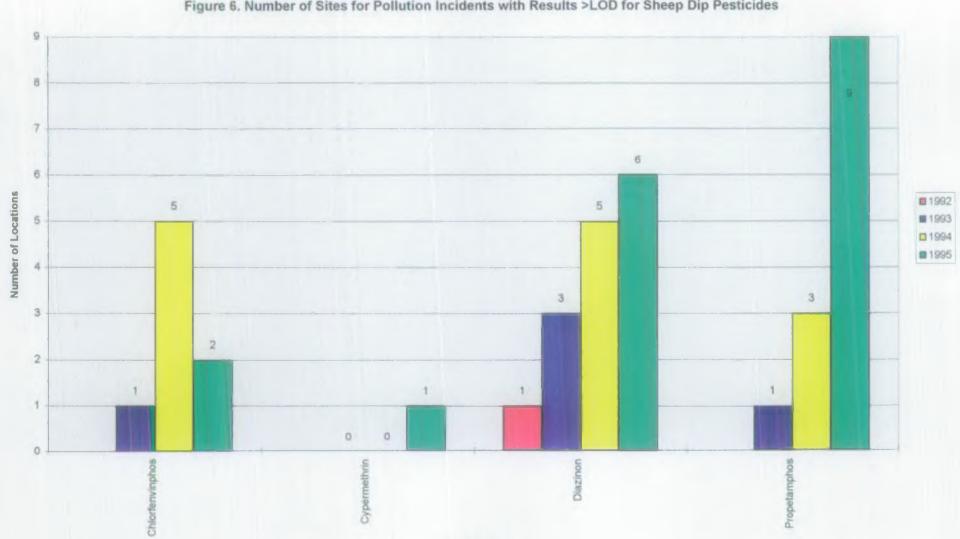
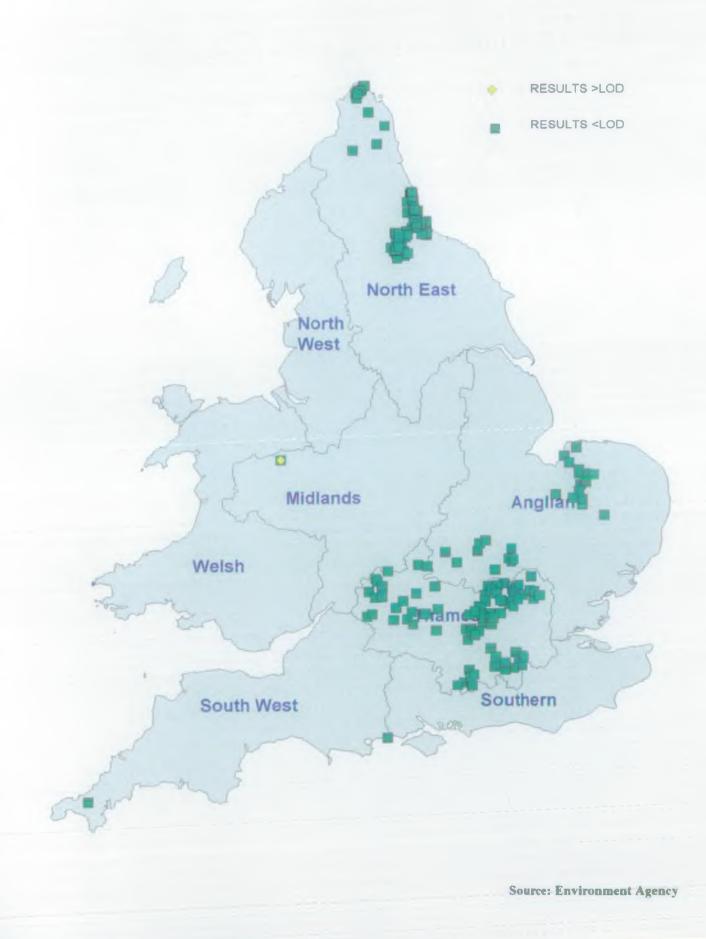


Figure 6. Number of Sites for Pollution Incidents with Results >LOD for Sheep Dip Pesticides

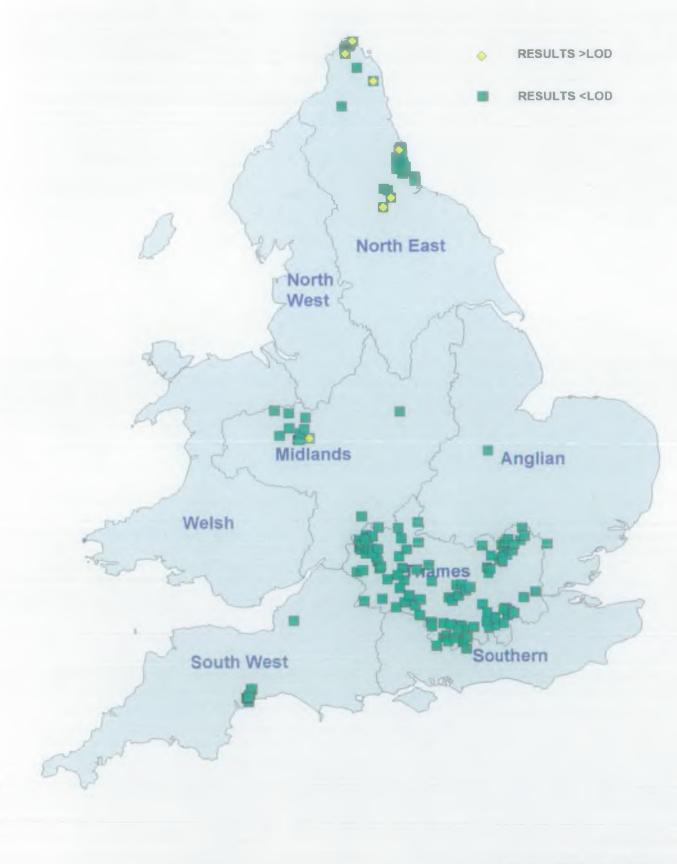
Pesticides

Figure 7. Groundwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1993

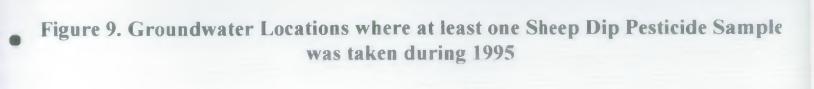


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Figure 8. Groundwater Locations where at least one Sheep Dip Pesticide Sample was taken during 1994



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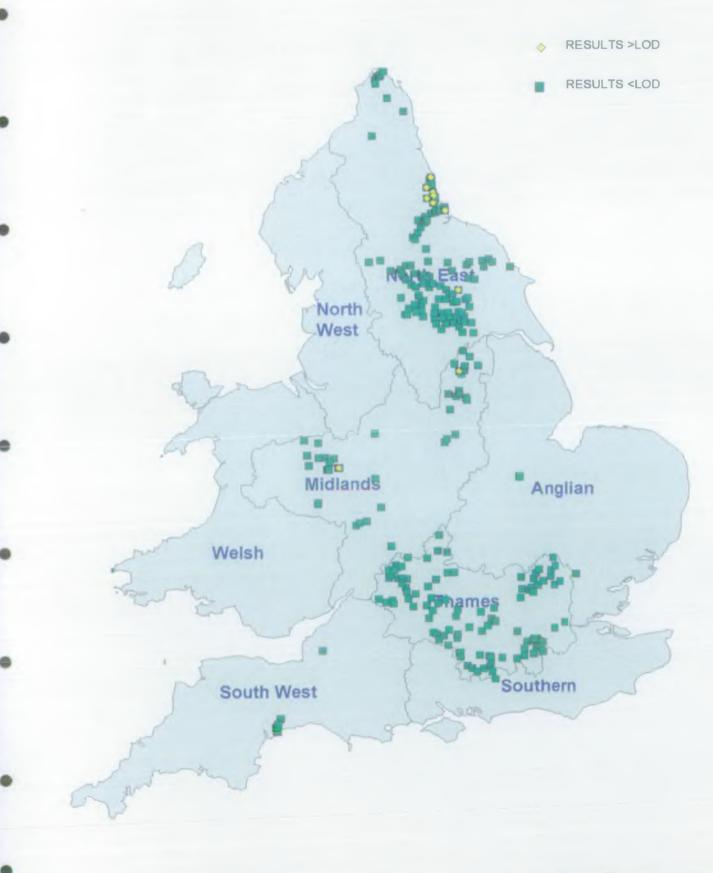


Figure 10. Surface Freshwater Sites Failing Environmental Quality Standards for Sheep Dip Pesticides in England and Wales during 1994

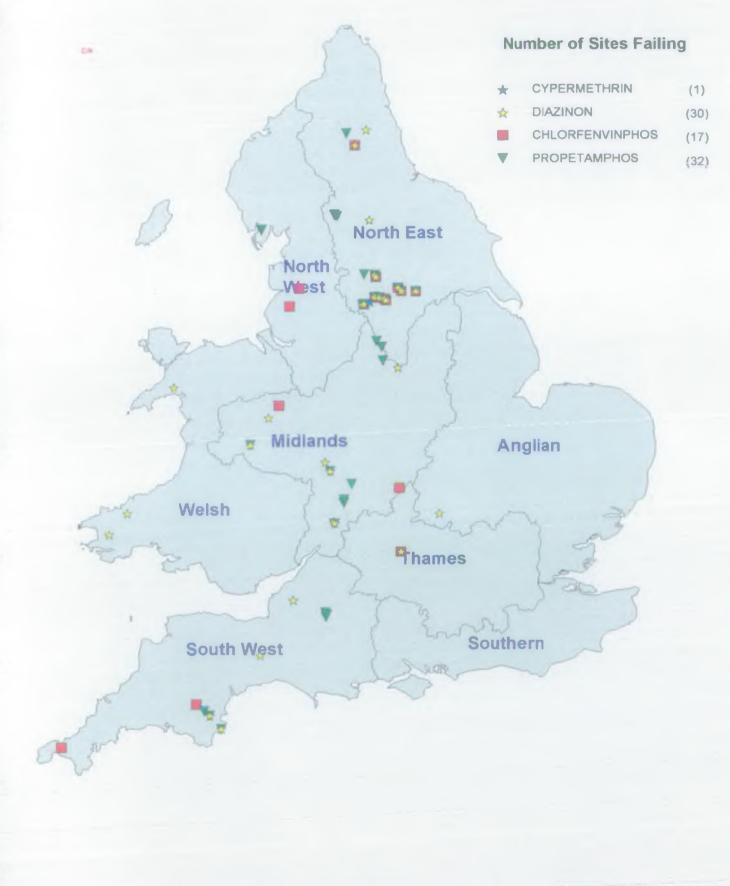


Figure 11. Surface Freshwater Sites Failing Environmental Quality Standards for Sheep Dip Pesticides in England and Wales during 1995



# Table 2. Comparison of EQS Failures for Surface Freshwaters inEngland and Wales1993-1995

	1993 1994		4	1995		
Pesticide	Number of Sites	% of Total Sites	Number of Sites	% of Total Sites	Number of Sites	% of Total Sites
diazinon	• *	1.25		000000000000000000000000000000000000000	35	2.00
permethrin		0.81	21	1.40	28	1.60
cypermethrin	*		1	979-974900	26	1.50
cyfluthrin	*	0.33	15	1.00	24	1.40
propetamphos	•\$		1 31	2.10	15.	0.90
PCSD or eulan	*	0.92	25	1.70	13	0.80
total HCH	*	0.66	18	1.20	14	0.80
total "urons"	*				12	0.70
chlorfenvinphos	•		17	1,10	7.	0.40
dieldrin	*		14	0.90	6	0.40
diuron	*		6	0.40	5	0.30
endosulfan total (a+b)	*		6	0.40	5	0.30
MCPA	*		4	0.30	5	0.30
dichlorvos	*	0.34	10	0.70	4	0.20
2,4-D	*		3	0.20	4	0.20
chlorotoluron	*				3	0.20
azinphos-methyl	*	0.06	2	0.10	2	0.10
atrazine & simazine	- <b>*</b>	0.06			2	0.10
isoproturon (IPU)	*		16	1.10	10	0.06
total DDT	*	0.14	1	0.06	1	0.06
ppDDT	*	0.06	1	0.06	1	0.06
fenitrothion	*	0.03	1	0.06	1	0.06
hexachlorobenzene	*	0.03	1	0.06	1	0.06
methiocarb	• 1994 I		1	0.06	1	0.06
mecoprop	*		1	0.00	. 1	0.06
malathion	*	0.06			1	0.06
triazophos	*			[	1	0.06
endrin	•	1	5	0.34		
isodrin	*		5	0.34		
tecnazene	*		2	<u> </u>	·	
pentachlorophenol	*	0.09	1	0.06		
aldrin	•	1	1	0.06		
trifluralin	*	1	1	0.06		
total drins	*	0.26	· · · · · ·		†	

\* Data no longer held

Table 3 - Reasons Given for Sheep Dip Pesticide EQS Failures 1995 (numbers of sites)

Region	Diazinon	Propetamphos	Cypermethrin	Reason
Anglian	2	-	-	Dipping suspected
Midlands	13	5	3	3 due to sheep dipping, 7 to industry, 5 neither, 6 unknown
North East	8	3	21	Wool industry
North West	-	1	-	Wool industry
Southern	-	-	2	Chemical manufacture
South West	2	3	-	Wool industry
Thames	7	-	-	Sheep dipping suspected
Welsh	2	2	-	1 due to dip spill, 3 dipping activities suspected



