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# **5: Pesticide Leaching in Phase II**

# **Rothamsted Research**

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# 5. PESTICIDE LEACHING IN PHASE II

#### 5.1 BACKGROUND

As sub-surface drainage and soil structure development influence the leaching of nitrate in the soil of Brimstone Farm, they may also influence losses of pesticide residues. Both surface flow and rapid water movement through soil cracks and other macropores may increase pesticide residue losses because of limited contact with the soil and therefore less opportunity for adsorption and/or degradation. Various crop management strategies, such as straw incorporation, and different types of soil drainage are also likely to affect losses of pesticides.

#### 5.1.1 Objectives

- 5.1.1.1 To develop soil drainage and crop management strategies for minimizing leaching and runoff of pesticides.
- 5.1.1.2 To provide data for validating and improving models of pesticide movement.

# 5.2 EXPERIMENTAL DESIGN

The six pairs of plots with different drainage treatments and cropping systems utilized in Phase II had the following potential implications for leaching of pesticide residues:

- a) Plots 1 and 15 (gravel-filled mole drains) indicated the effects of organic matter turnover on leaching of pesticide residues and the carry-over of pesticides applied in Phase I, as the grass leys on these plots in Phase II received no pesticides between autumn 1988 and autumn 1991.
- b) Plots 4 and 18 (conventional mole drains) indicated the effects of straw burning in conjunction with tine cultivation on pesticide leaching in the first two years of Phase II. The incorporation of winter beans into the cropping cycle in 1990/91 then provided an opportunity to study losses of simazine.
- c) Plots 6 and 19 (large expander mole drains) had crop residues incorporated and so offered a contrast to Plots 4 and 18. This is important now that burning of residues is restricted in UK. The large expander mole drains allow rapid water movement from topsoil to subsoil, which may accelerate pesticide leaching.
- d) Plots 5 and 16 (closely spaced mole drains) and Plots 7 and 9 (closely spaced 35 mm diameter shallow pipes) had spring cropping programmes following winter cover crops and fallow in 1988/89 and 1990/91. Both drainage treatments encouraged rapid water movement through the soil profile, and the pipes minimized soil water contact time, which may be the worst situation for leaching of some pesticides in a clay soil.

Date	Trade name	Pesticide	Active Ingred.	Plots
(1988-89)			14/1101	
08-02-89	Swipe 560EC	Ioxynil	280	4,6 10,14,
				17,18,19,20
		Bromoxynil	280	
		Mecoprop	2240	
	New 5C	Chlormequat	1612	
	Cycocel	Chloride		
	Bayfidan	Triadimenol	125	
09-02-89	Cleansweep	Paraquat	300	5,7,9,16
		Diquat	300	
26-04-89	Cleansweep	Paraquat	5000	14 Only
		Diquat	500	
17-05-89	Mantrac	Manganese		4,6,10,17,18,19, 20,
22-5-89	Swipe 560EC	Ioxynil	224	5,7,9,16
		Bromoxynil	224	
		Mecoprop	1792	
	Bayfidan	Triadimenol	125	
04-07-89	Bayfidan	Triadimenol	125	5,7,9,16
19-07-89	Swipe 560EC	Mecoprop	1344	14 Only
		Ioxynil	168	
		Bromoxynil	168	
08-08-89	Roundup	Glyphosate	540	5,7,9,16
(1989-90)				
13-10-89	Grammoxone 100	Paraquat	800	14 Only
17-10-89	Avadex BW	Triallate	2160	All plots except 1,15
15-11-89	Decis	Deltamethrin	5	All Plots
	Arelon	Isoproturon	2488	
11-03-90	Cosmic FL	Carbendazim	160	All plots except 1,15
		Tridemorph	360	
		Maneb	1280	
	Musketeer	Isoproturon	1625	All plots except 1,15
		loxynil	325	
		Mecoprop	1170	
14-03-90	New 5C	Chlormequat	1129	4,6,10,1418,19,20
	Cycocel	Chloride		
09-04-90	Terpal	2-Chloroethyl-	310	5,7,9,16,17
		Phosphonic Acid		
		Mepiquat-	610	
		Chloride		
01-05-90	Mantrac	Manganese		
31-05-90 (1990-91)	Tilt Turbo 375EC	Propiconazole	125	All plots except 1,15
		Tridemorph	250	
08-10-90	Grammoxone 100	Paraquat	300	6,7,9,10,14,17,19,20
	Arelon WDG	Isoproturon	2448	6,10,14,17,19,20
	Iso Cornox 57	Mecoprop	2394	6,10
16-10-90	Gesatop 500 FW	Simazine	1150	4,8,12,18
06-11-90	Decis	Deltamethrin	5	All Plots
16-01-91	Librel CMX	Iron	100	All Plots
		Copper	50	

Table 13. Applications of pesticides to Brimstone plots, Phase II.

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100

Manganese

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Table 13. Cont.

Date	Trade name	Pesticide	Active Ingred. (g/ha)	Plots
27-03-91	New SC	Chlormequat	1129	6 10 14 17 19 20
21-03-71	Cycocel	Chloride	1127	0,10,14,17,19,20
10-04-91	Musketeer	Isoproturon	1625	6 10 14 17 19 20
	mashereer	Iovvnil	325	0,10,14,17,17,20
		Mecoprop	1170	
	Sportak	Prochloraz	399	6 10 14 17 19 20
	Alpha	Carbendazim	150	0,10,11,17,17,20
	Aventox SC	Simazine	216	57916
	11101101100	Triatezine	1509	·, · , · , · · · · ·
	Grammoxone 100	Paraquat	800	57916
17-05-91	Decis	Deltamethrin	7.5	4 5 7 9 16 18
01-07-91	Bravocarb	Chlorothalonil	900	4 5 7 9 16 18
		Carbendazim	200	
10-07-91	Tilt Turbo 375EC	Propiconozole	125	6,10,14,19,20
		Tridemorph	250	-,,,
05-09-91	Grammoxone 100	Paraguat	800	1.15
(1991-92)		*		
09-10-91	Arelon WDG	Isoproturon	2448	All Plots
	Grammoxone 100	Paraguat	300	All Plots
	Iso Cornox	Mecoprop Salt	2394	
29-10-91	Iso Cornox 57	Mecoprop Salt	2394	Rest Of Plots
	Decis	Deltamethrin	5	All Plots
05-04-92	Musketeer	Isoproturon	625	All Plots
		Ioxinil Salt	325	
		Mecoprop Salt	1170	
	Sportak	Prochloraz	399	All Plots
	Alpha	Carbendazim	150	
29-04-92	Terpal	Mepiquat Chloride	610	All Plots
		2- Chloroothulphaeph	310	
		noid		
10.05.02	Tilt Turbo	Propioopazola	125	All Diote
17-03-72	The Turoo	Tridemorph	285 7	All Flots
17-07-02	Roundun	Glumbosate	265.7	All Diote
11-01-72	Ethokem	Polyethanoxy-	200	All Flots
(1992-93)		anyianine		
05-09-92	Scythe	Paraquat	600	All Plots
19-03-93	Grammoxone 100	Paraquat	400	All Plots
	Agral	Dichloride Salt	360	All Plote
30-04-93	Starane?	Flurosonvr	150	All Plots

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e) Plots 10 and 20 (no-expander mole drains) grew continuous winter cereals, the burnt residues of which were incorporated by ploughing. As this type of mole channel was vulnerable to collapse in Phase I and offers slower movement of water than others, it may influence pesticide leaching by increasing the residence time in the soil.

An additional plot (14) was retained as an undrained control. This allowed the effect of increased flow in the surface (cultivated) layer on movement of pesticide residues to be measured. Table 13 gives the applications of pesticides to these plots in 1988-1991.

# 5.3 DATA COLLECTION

#### 5.3.1 Water sampling

In the first year (1989/90) water samples were bulked from the small samples collected for nitrate analysis by the automatic vacuum water samplers (Fig. 5). This gave few data indicating variations within individual rainfall events, such as the initial response, the period near peak flow and the hydrograph recession. Monitoring was extended in the spring of 1990 and the second winter (1990/91) to give more intensive sampling over storm events. Two EPIC programmable samplers with flow-related trigger systems were added to the site facilities in autumn 1990, and a further five were installed in summer 1991 for work in the third winter. The programmable samplers delivered single samples of larger volume  $(1-2\frac{1}{2}1)$  direct to darkened glass bottles through teflon tubing.

#### 5.3.2 Analysis for pesticide residues

The work at Brimstone Farm in Phase II complements other UK research on leaching of pesticide residues. Those studied were the herbicides isoproturon, mecoprop and simazine, and the fungicides triadimenol, prochloraz and propiconazole, many of which have been found in surface water courses elsewhere.

Analyses were done by the MAFF CSL Pesticide Analysis Group. Water samples were stored in a cold room, the delay before extraction being < 14 days. One-litre samples were mixed with sodium chloride and hydrochloric acid, and pesticides were extracted with dichloromethane, which was then filtered through anhydrous sodium sulphate and evaporated to dryness under dry nitrogen. The residue of extracted pesticides was then dissolved in 1 ml methanol and divided into two 0.5 ml portions, which were stored at  $-18^{\circ}$ C prior to analysis.

For determination of isoproturon, simazine, triadimenol, prochloraz and propiconazole the extract was used directly, but for determination of mecoprop a 0.5 ml portion was converted into a pentafluorotoluene derivative.

Concentrations of isoproturon and simazine were determined by reverse phase high performance liquid chromatography (hplc) using a photodiode array detector. Concentrations of fungicides were determined by gas chromatography (gc) using a nitrogen-phosphorus detector. The mecoprop derivative was determined by gas chromatography-mass spectrometry (gc-ms). The limits of detection were less than the EC maximum permitted concentration  $(0.1 \ \mu g/l)$  for a single pesticide in drinking water

(Anon. 1980), but greater than this for mecoprop. The identity of any pesticide found in drinking water by hplc using the photodiode array detector was confirmed by comparing ultraviolet spectra with those of known standards; those determined by gc were confirmed by gc-ms or by reanalysis using a column of different polarity.

# 5.4 WEATHER PATTERNS AND DRAINAGE

Because the weather was unusually dry from November 1988 to January 1989, the typical winter water table position (above the drains) was not reached until mid-March 1989 on some plots. Drainflow was intermittent in these conditions and was influenced by the different secondary drainage treatments. However, in February 1989 the rainfall was 150% of the long-term mean for the month; this resulted in considerable variation in drainflow, though with little difference in peak flow rates between the drainage treatments except that the no-expander mole drains gave lower peak flows and longer drainflow recessions.

Heavy rainfall early in the second winter (1989/90) produced drainflow on all plots by mid-December, but the water table again did not rise above the drains until mid-March. As in 1988/89, mid-winter responses were dominated by crack flow. Peak flows occurred approximately 2 hr after peak rainfall, but there was a gradual decrease in the peakiness of some hydrographs because of deterioration of the mole channels. The most responsive systems were the gravel-filled and large expander mole drains, which gave hydrograph peaks greater than those of the no-expander mole drains and closely spaced pipes.

By the third winter (1990/91) further deterioration of the no-expander mole drains resulted in slow runoff so that the closely spaced pipe system then became the most responsive (Fig. 16). However, the bare fallow may have increased the runoff from the plots with closely spaced pipes (7 and 9).



Fig. 16 Comparison of drainflow (mm/hr) between no-expander, large expander and close spaced drainage treatments, winter 1990/91. Arrows show major rainfall events

#### 5.4.1 Deterioration of secondary drainage treatments

In March 1989 all the mole drains had decreased in cross sectional area by about 40%, which was a slightly greater first year deterioration than was seen in Phase I. By July 1990 they were partly infilled with topsoil as a result of deep cracking during the dry summers of 1989 and 1990. However, the gravel-filled channels and closely spaced pipes were still in good condition.

# 5.5 RESULTS

# 5.5.1 Winter 1989/90

Approximately 120 samples over this winter drainage season were analysed for the three fungicides and for isoproturon but not for mecoprop because of initial difficulties in detecting this herbicide. None of the samples contained any of the fungicides in amounts greater than the detection limit. Isoproturon occurred in concentrations > 50  $\mu$ g/l in the first drainflows after autumn application, and then declined to give typical winter concentrations of about 3  $\mu$ g/l in most treatments. After several days of rain in mid-January (total 15 mm) a further 2 mm event increased peak drainflow to 0.2 mm/hr and increased isoproturon concentrations to 2-7  $\mu$ g/l.

After spring applications of herbicide, much greater isoproturon concentrations up to  $600 \ \mu g/l$  occurred in a similar small drainflow event following 13 mm rain (Table 14).

Table 14. Concentrations of isoproturon ( $\mu$ g/l), 1989/90 from slow, medium and fast runoff responses through the drainage system.

Drainage treatment	Response type	Autumn flush	January event	Residual loss	Spring event
Large expander/ annual mole drainage	(Fast)	10-35	2-7	3	550
Close spaced pipes	(Medium)	35-50	4-7	3-6	600
No-expander mole drainage	(Slow)	3	3	< 0.1	550

Winter loadings of isoproturon losses in runoff, obtained by integrating flow totals for each bulk sampling period with the concentrations for that period, were equivalent to 11-22 g/ha, or 0.5-1.0% of the herbicide applied in autumn. The largest loading was from the closely spaced pipe treatment, suggesting that the limited soil-water contact time associated with this treatment increases losses.

#### 5.5.2 Winter 1990/91

The first drainflow event in this winter occurred between December 25 and January 10, and resulted from rapid water movement through macropores, as water tables did not

rise above mole drain level until March 1991. Isoproturon concentrations were high at the start of drainage, but declined rapidly over a few days. Isoproturon could not be detected in the soil below a depth of 20 cm, indicating the role of macropore flow in the isoproturon reaching the mole drains at 55 cm depth. In Plot 9 where the last applications had been in the previous winter, concentrations were almost as high as on plots where isoproturon was applied in autumn. Neither mecoprop nor the target fungicides were above the detection limit in this period.

Comparison of drainflow hydrographs and isoproturon chemographs often showed a dilution effect after the first leaching event; the concentrations on all plots decreased over periods of rapid water flow through the macropores, but increased in the hydrograph recession periods when more of the flow was through smaller soil pores. However, no dilution effect was seen in the single chemograph obtained for simazine. The dilution effect for isoproturon is similar to than for nitrate at Brimstone Farm (Fig. 17). This suggests that the two are leached in similar ways when macropore flow dominates the drainflow, so that models for nitrate movement may be applicable to leaching of isoproturon.



Fig.17. Drainflow (mm/hr), losses of isoproturon (µg/l) and nitrate (mg/l), early January 1991, Plot 10 (no-expander mole drainage treatment).

Little surface layer flow occurred in Phase II, so few samples were analysed. However, results for isoproturon losses show that very high concentrations can occur. Work by Water Research Centre, Medmenham, on samples of surface layer flow from the undrained Plot 14 collected over the period between application on November 15, 1989 and cessation of flow on March 1, 1990, indicated a total loading of about 13% of the amount applied.

#### 5.6 DISCUSSION OF RESULTS

The first two years' results of Phase II showed that the leaching losses of some pesticides in clay soils can be modified by the type of secondary drainage system used. Winter isoproturon loadings from the closely spaced pipes treatment, which decreases soil-water contact time, were nearly twice those of other drainage types, and rapid surface layer flow or macropore water movement also seemed to increase isoproturon leaching.

The decreased autumn rainfall in 1989 and 1990 resulted in delays of nearly two months between the autumn application of herbicides and the first leaching losses in drainflow. This probably accounts for the absence of mecoprop in the drainflow; although this is more mobile than isoproturon on the basis of its octanol-water partition coefficient (Worthing and Hance 1991), confirmed by sorption measurements, it is degraded more rapidly. Isoproturon persists not only through this two month period but also from year to year in sufficient amounts to produce runoff containing many times the EC drinking water limit. The measured concentrations in runoff do not take into account the opportunities for further degradation in the transport of pesticides to surface waters or the impact of dilution from other water sources containing less pesticide residues. However, the clay plot lysimeters of Brimstone Farm do allow the effects of soil structure and different secondary drainage treatments on pesticide leaching to be evaluated in a way that is realistic to the commercial farmer. They also provide data to develop and evaluate predictive models of pesticide leaching based upon soil physical and physicochemical properties.