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Factors influencing the loss of pesticides in drainage from a cracking clay soil

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Abstract

An experiment was established on plot lysimeters in autumn 1989 to examine the loss of pesticides from a cracking clay soil. Emphasis was placed on the movement of two autumn/spring-applied herbicides with contrasting properties — isoproturon and mecoprop. The first major drainflows in autumn/winter were important for the transport of these herbicides. During the dry autumns of 1989 and 1990, the development of substantial subsoil cracks led to rapid vertical movement of water, through the soil-cracks to the drainage system, before field capacity was reached. Isoproturon was detected in the resultant drainflow at concentrations of up to 50 $\mu g\ l^{-1}$, well above the EC Directive for potable waters. Mecoprop was not detected. Measurements of herbicide degradation in soil indicated that isoproturon was rather persistent and hence available over many months for transport to the drainage system. In contrast, the long delay between application and the onset of drainflow, combined with the much faster degradation of mecoprop, resulted in this herbicide not occurring in drainflow. Although the site was some distance from a supply point for potable water, the loss of such concentrations of isoproturon in the early drainage flush could have undesirable consequences for water supplies and for the ecology of adjacent water courses.

1. Introduction

In recent decades there has been a general increase in the use of fertilisers and pesticides in the UK (Orson, 1987). Today, some 360 pesticide active ingredients are registered for use in the UK. The widespread use of pesticides, especially of

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herbicides which constitute approximately 70% of the 25 000 tonnes of pesticides used annually in the UK (Davis et al., 1991), has led to their occurrence in surface and groundwaters (Lees and McVeigh, 1988; Department of the Environment, 1991). The introduction of the EC Directive on potable water (the maximum permitted concentration of 0.1 $\mu g\ l^{-1}$ for a single pesticide, Anon., 1980) and the requirement for data both to support applications for pesticide approval and to review existing approvals (Tooby and Marsden, 1991) have led to the need to examine the fate and behaviour of pesticides in soils and water and to identify the potential transport mechanisms involved.

Although the loss of nitrate to bodies of water has been researched, extensively with reviews by Wild and Cameron (1980) and Winteringham (1980) identifying the principal mechanisms involved, information on the transport mechanisms for pesticides is less readily available. In particular, the ability to predict the movement of pesticides through clay soils, especially those soils prone to cracking, depends on factors other than those properties specific to the product, such as sorption or degradation (Tooby, 1992). With some 30% of UK cereals grown on clay soils, many of which are drained (Cannell et al., 1984) and receive several agrochemical applications per annum, this is an area requiring investigation. Although many studies have been conducted in other countries, particularly in the United States (Hall et al., 1989; Monke et al., 1989), the different conditions both in terms of climate and soil type have led to the development of research programmes to investigate these factors in the UK.

This paper describes a study to investigate the way in which soil, weather and drainage factors influence the movement of two key herbicides, isoproturon and mecoprop.

2. Experimental details

2.1. Site

The site at Brimstone Farm, Oxfordshire (Grid Reference 248 947) was established in 1978, and is located on a pelo-stagnogley (Avery, 1980) of the Denchworth series. This soil type is characterised by a large clay fraction (60% at < 2 μm in the subsoil) and the presence of a thick, slowly permeable, subsoil horizon (Avery, 1980). Values of subsoil conductivity, typically ranging from 0.1 to 1.0 m day^{-1} (Goss and Youngs, 1983), are very dependent on soil cracking. The site, with an altitude of about 130 m above Ordnance Datum (AOD) and an average annual rainfall of 686 mm, is representative of many cereal-growing areas of central England. Historical details of the site, its uniformity and the methods of hydrological separation for the plot lysimeters have been reported by Cannell et al. (1984). In earlier experiments, the effects of cultivations and drainage on the movement of excess water through the heavy clay soil and on the transport of nitrate were investigated utilising 20 continuously cropped plots, half of which were drained (Cannell et al., 1984; Harris et al., 1993). Crop residues were burnt in previous years.

2.2. Plot layout

Isolation of each 0.2 ha plot lysimeter was provided by polythene barriers to a depth of 1.1 m down the 2% slope and by interceptor drains (with permeable backfill to the ground surface) across the slope (Fig. 1; Harris et al., 1993). The original site utilised 20 plots, as described above. To facilitate the new experimental design based on 13 plots, several of the undrained plots were drained for the first time in 1988. The drainage system consisted of a single pipe drain at the bottom of each plot, at 0.9 m depth, located in a 0.1 m wide trench with permeable backfill to within 0.35 m of the ground surface. A

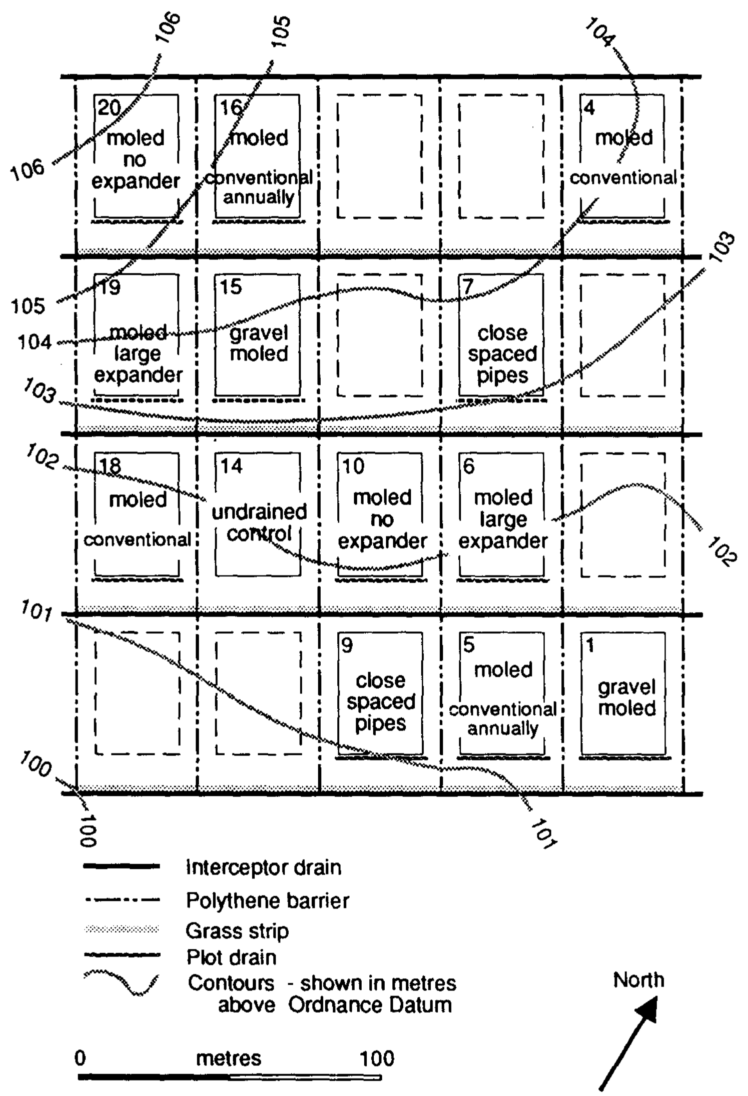

Fig. 1. Site plan showing layout of plots and drainage treatments.

secondary drainage treatment, with attendant cracking, was drawn at 0.55 m depth, at right angles to the pipe drain, down the plot slope (Cannell et al., 1984).

2.3. Drainage treatments

There were six drainage regimes (with twofold replication) and an undrained control (Fig. 1). Superimposed on the drainage regimes were variable cropping systems aimed primarily at manipulating the organic matter turnover to support a companion trial on minimising nutrient losses. Key features of the hydrological and cropping treatments are given below and are summarised in Table 1.

(1) Gravel-filled mole drainage plots (Plots 1 and 15) were under a grass ley receiving no herbicides from autumn 1988 to autumn 1991. These plots provide data on the effect of stable 'mole channels' and the carry over of residues of isoproturon from previous applications.

(2) Conventional mole drainage plots (Plots 4 and 18) were in winter cereals, sown by tine cultivation, until harvest 1990 when winter beans were sown after ploughing. Crop residues were burnt on this plot.

(3) Large-expander mole drainage plots (Plots 6 and 19) had a continuous cereal cropping in a winter oats/winter wheat rotation; crop residues were incorporated by ploughing. These plots provide data on the effects of incorporating crop residues on herbicide loss, which will be of interest now that burning is restricted in the UK.

(4) Frequent mole drainage plots (Plots 5 and 16) and close-spaced, 0.035 m diameter, shallow pipe drainage plots (Plots 7 and 9) included spring cropping in 1988/1989 and 1990/1991. In both years, one pair of plots was in bare fallow prior to spring cropping and one pair had a winter cover crop prior to spring cropping. Crop residues were burnt after harvest. Both treatments were likely to provide opportunities for rapid water movement through the soil profile.

Table 1
Drainage and crop rotations for harvest years 1989–1991

Secondary treatment Plot no.	1989	1990	1991
Moled gravel-filled Plots 1, 15	Grass ley	Grass ley	Grass ley
Moled conventional Plots 4, 18	Winter oats	Winter wheat	Winter beans
Moled large-expander Plots 6, 19	Winter oats	Winter wheat	Winter wheat
Moled annually Plots 5, 16	Bare fallow/ spring wheat	Winter barley	Forage rape/ spring beans
Close-spaced pipes Plots 7, 9	White mustard/ spring wheat	Winter barley	Bare fallow/ spring beans
Moled no-expander Plots 10, 20	Winter oats	Winter wheat	Winter wheat
Undrained control Plot 14	Spring oats	Winter wheat	Winter wheat

(5) No-expander mole drainage plots (Plots 10 and 20) were continuously cropped with a winter oats/winter wheat rotation but, in contrast to the large-expander mole drainage treatment (3), residues were burnt before incorporation by ploughing. Mole drainage channels drawn without an expander are less likely to create an effective crack structure.

(6) An undrained plot (Plot 14) was retained to investigate the effect of no subsoil drainage on the transport of herbicides.

The gravel-filled mole drainage and close-spaced pipe drainage represented a semi-permanent system in which the crack structure introduced at the time of installation could be maintained only by the natural swell/shrink processes of clay soils. These treatments provided a contrast to 'conventional' mole drainage systems where the crack structure would be renewed, typically every 3 to 4 years, during re-installation of the secondary drainage.

On all treatments except treatment (3), residues were burnt and the ash was incorporated within 36 h with a light harrow; no further disturbance occurred prior to the passage of the seed drill and a light harrow to cover the seed.

2.4. Herbicides

The herbicides studied were isoproturon, a phenylurea, and mecoprop, an aryloxyalkanoic acid; both of these are widely used (Davis et al., 1991) and have been reported as contaminants in surface water sources in the UK. These herbicides were applied as part of a typical cropping programme (Table 2).

2.5. Hydrological monitoring

On each plot, surface runoff was collected in a single plough furrow, drawn across the full width of the plot, just downslope of the plot drain (Harris et al., 1993). Surface runoff and flow from the drainage systems were carried in sealed pipes to V-notch

Table 2
Applications of target pesticides from harvest years 1988–1991

Date applied	Pesticide	Trade name	Active ingredient ($g\,ha^{-1}$)	Plots
19/04/1988	Mecoprop	Swipe 560EC	2240	All plots
08/02/1989	Mecoprop	Swipe 560EC	2240	4, 6, 10, 14, 18, 19, 20
22/05/1989	Mecoprop	Swipe 560EC	1792	5, 7, 9, 16
19/07/1989	Mecoprop	Swipe 560EC	1344	14 only
15/11/1989	Isoproturon	Arelon	2488	All plots except 1, 15
11/03/1990	Mecoprop	Musketeer	1170	All plots except 1, 15
11/03/1990	Isoproturon	Musketeer	1625	All plots except 1, 15
08/10/1990	Isoproturon	Arelon WDG	2448	6, 10, 14, 19, 20
08/10/1990	Mecoprop	Isocornox	2394	6, 10, 19, 20
10/04/1991	Mecoprop	Musketeer	1170	6, 10, 14, 19, 20
10/04/1991	Isoproturon	Musketeer	1625	6, 10, 14, 19, 20

weir chambers located in the grass discard areas (Fig. 1) between the plots. The weirs were equipped with dual autographic and logged recorders to measure the rate of flow. The flow-recording system was linked to the water samplers, with extraction from a 'U' bend reservoir prior to the weir chamber. The water table response to rainfall was monitored by autographic water table meters installed in open auger-holes on each plot (Armstrong, 1983).

2.6. *Water sampling procedures*

Monitoring of pesticides in water samples was begun in autumn 1989. Water samples were collected primarily from the plot drainage pipes although occasional samples were included from the surface-layer flow collectors. In this first year, samples were taken sequentially through separate bulkhead connectors in the 'U' bend reservoir and were bulked from smaller samples (typically 50–100 ml) collected by the automatic water samplers. The samples were drawn through polythene tubing and passed, via rubber tubing and polypropylene connectors, into evacuated 500 ml glass bottles. The glass bottles were initially in factory condition and thoroughly washed in tap water thereafter before use.

Water sampling was based initially on a semiautomatic time-based sampler so that few data were available on the variations over individual rain events. The baseline monitoring was considerably extended in the spring of 1990 and from the second winter (1990/1991) using several programmable samplers with flow-related triggering to provide the opportunity for detailed sampling during storms. These additional samplers delivered single samples through teflon tubing direct to new darkened-glass bottles on each occasion as described by Harris et al. (1991). The water samplers were initiated automatically when float switches reached preset levels. At each location, a data logger was linked to the water sampler to record sampling times. The logged data were regularly downloaded using a hand-held Psion computer. When the required samples had been taken, the glass bottles were sealed with a plastic cap with inert inner seal and then stored at 4°C until extraction.

2.7. *Soil sampling procedures*

The large-expander mole drainage treatment (Plot 6), which received isoproturon and mecoprop on 8 October 1990 (Table 2), was sampled using a steel corer with an aluminium split liner. Soil cores (length 0.9 m, diameter 0.075 m) were removed immediately prior to the application, and at intervals up to 16 weeks thereafter. Cores were divided into eight sections (0–0.025, 0.025–0.050, 0.05–0.10, 0.10–0.20, 0.20–0.30, 0.30–0.45, 0.45–0.60 and 0.60–0.90 m) with corresponding sections from four replicate cores generally being combined. Soil samples were frozen (−15°C) until they were analysed. Subsamples (10 g) were used to measure water content with drying at 110°C.

2.8. *Analysis of herbicides in water*

Details of the extraction procedure employed for the water samples are given by Harris et al. (1991). Extracts of the water samples were stored at −18°C prior to analysis. Isoproturon was determined by reverse-phase high performance liquid chromatography (HPLC) with a diode-array detector. The limit of determination for isoproturon was 0.1 $\mu g\ l^{-1}$ (the EC maximum permitted concentration for a single pesticide in potable water (Anon., 1980)). The identity of isoproturon in samples was confirmed by the UV spectrum.

Mecoprop was converted to a pentafluorotoluene derivative (Anon., 1986) and the concentration determined by gas chromatography (GC) with an electron-capture detector. The limit of detection for mecoprop varied between 0.2 and 0.5 $\mu g\ l^{-1}$ and the identity could be confirmed by mass-spectrometry.

Analytical quality assurance was provided by recovery experiments utilising known amounts of pesticide. Data from other experiments suggested that the range of concentration could be from < 0.1 to > 1000 $\mu g\ l^{-1}$. The recovery procedure adopted was to extract a sample of water and then retain the water sample extracted; this was then spiked with 2 $\mu g\ l^{-1}$ of pesticide and extracted again as a separate 'recovery' extract. This procedure was not ideal as water samples used for the recovery would have been 'cleaned' by the initial solvent extraction but the method represented a practical working compromise. Average recoveries of isoproturon and mecoprop were 73% and 58%, respectively. The results reported were not corrected for recovery (see page 247).

The stability of isoproturon and mecoprop in water samples stored at 4°C was demonstrated by Harris et al. (1991). No significant reduction in the concentration of isoproturon was found after 3 months. Unfortunately the data for mecoprop were incomplete owing to analytical difficulties with the method. However, similar experiments (D.J. Mason, Personal Communication, 1993) have shown no significant reduction of mecoprop concentrations in water drained from sandy soils and stored in a cold room for up to 56 days.

2.9. *Analysis of herbicides in soil*

Duplicate samples of soil were extracted with acetone:aqueous ammonium carbonate; this extract was partitioned with dichloromethane to remove isoproturon, and then acidified with concentrated hydrochloric acid and extracted with dichloromethane to remove mecoprop. The isoproturon extract was purified on a silica Sep-pak cartridge, and the extracts then analysed by HPLC using a column of Lichrospher RP 18. Spectrophotometric detection was at 232 nm. Recoveries of isoproturon and mecoprop by these methods were 97.1% and 87.5%, respectively, and all results were corrected for recovery; the limits of determination were 0.05 mg kg^{-1} and 0.1 mg kg^{-1} of soil, respectively.

3. Results

3.1. *Weather patterns and drainage*

Throughout the period from harvest 1988 to harvest 1991, rainfall was generally

Table 3
Monthly rainfall recorded at Brimstone Farm compared with the long-term average (latter data from Lechlade, 6 km to the northwest)

Month	Rainfall (mm)			
	1988/1989	1989/1990	1990/1991	Long-term average
August	44.5	32.3	20.9	74
September	37.8	26.6	26.6	57
October	42.5	66.8	42.5	63
November	27.9	37.7	21.8	68
December	16.4	130.2	50.8	65
January	36.8	73.0	66.2	60
Febraury	67.6	104.8	16.8	45
March	50.6	16.8	48.5	46
April	65.2	27.3	57.2	44
May	10.6	9.1	6.9	60
June	41.6	45.9	79.2	51
July	32.2	15.3	62.6	53
Total	473.7	585.8	500.0	686

less than average. In the first winter, rainfall during the period November 1988 to January 1989 was only 40% (Table 3) of the long-term mean and this limited the development of the water table on most plots. In the following year, heavy rainfall in mid-December produced flow from all the plot drains, although the water table did not rise above the drains until mid-March. Mid-winter responses were therefore dominated by crack flow, with water movement to the mole drainage channels occurring through the major macropores. However, although differences in response were apparent between the secondary drainage treatments, the drainflow on the conventional mole drainage plots was broadly similar to that observed on the site in earlier experiments (Harris et al., 1993). Generally, peak drainflows were recorded approximately 2 h after peak rainfall, with a gradual reduction in the peakiness of the hydrograph with time consequent upon deterioration of the mole drainage channels. In the winter 1989/1990, the most responsive systems were the gravel-filled mole drainage and the large-expander mole drainage, which recorded hydrograph peaks in excess of the no-expander mole drainage and close-spaced pipe drainage. The drainflow response from the annual mole drainage treatment was slightly slower than from conventional (4 year cycle) mole drainage.

By winter 1990/1991, further deterioration had occurred in some drainage treatments. The continued deterioration of the mole drainage channels in the no-expander treatment resulted in low drainage peaks whereas, in contrast, the close-spaced permanent pipes became the most responsive system (Fig. 2). The highest excess winter rainfall was removed through the close-spaced pipe drainage system which best intercepted the crackflow drainage. The bare fallow prior to spring beans may have accentuated the differences in drainflow.

The responses observed largely conformed to those expected. In particular, the

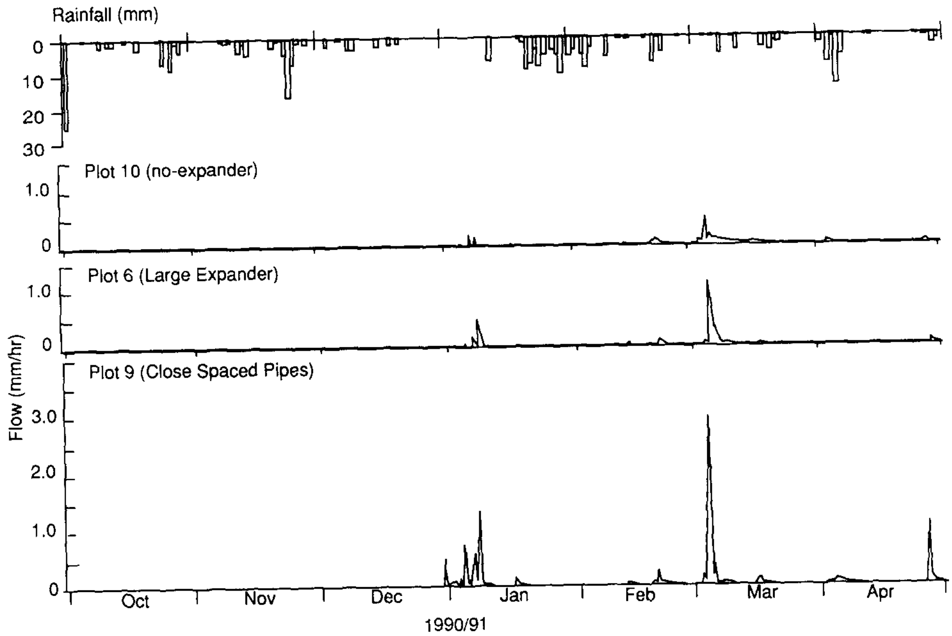

Fig. 2. Comparison of drainflow responses, no-expander and large-expander mole drainage and close-spaced pipes, in winter 1990/1991.

novel drainage systems of gravel-filled mole drainage and close-spaced pipe drains remained very responsive and transmitted water rapidly from the top soil to the pipe-drains, with good connection being maintained between topsoil and subsoil.

3.2. Secondary drainage treatments

Representative sections of the mole drainage treatments installed in autumn 1988 were first examined in March 1989. All the channels had decreased in cross-sectional area, typically by 40%. The condition of the mole drainage channels and the novel treatments was examined again in July 1990; it was evident that the dry summers of 1989 and 1990, with associated deep cracking, had by then resulted in a deterioration of the mole drainage channel itself. In particular, infilling of the mole drainage channels by topsoil had occurred causing partial blockages. However, the condition of the gravel-filled mole drainage channels and close-spaced pipes remained good with no evidence of substantial blockage of the slots in the latter system.

3.3. Herbicide loss in drainflow

Water samples taken over the drainage season 1989/1990 covered the period from the first autumn drainflows through the following winter. The samples were analysed for both isoproturon and mecoprop but initial difficulties in the analysis for mecoprop resulted in only limited data in this first year. Frequent samples were

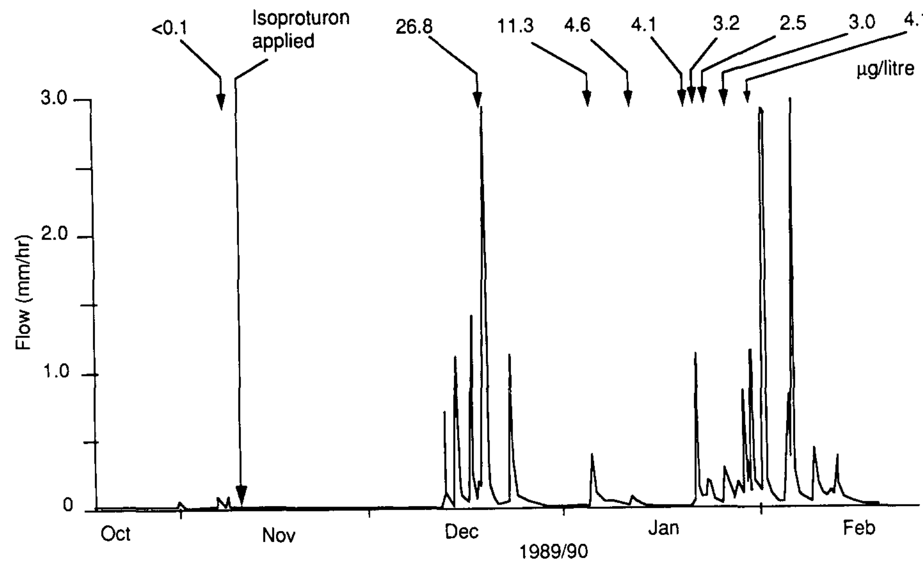

Fig. 3. Drainflow and loss of isoproturon (applied 15 October 1989), October–February 1990, large-expander mole drainage (Plot 6).

also taken in the first drainflow event following the application of spring herbicides; these samples were analysed for isoproturon only.

Only isoproturon was detected in bulk samples, and occurred at concentrations of up to 54 $\mu g\ l^{-1}$ in the first drainflow after autumn application in November 1989. Concentrations subsequently fell rapidly to residual winter levels around 3 $\mu g\ l^{-1}$ in most treatments (Fig. 3, Table 4).

Slightly higher concentrations of isoproturon were seen over a small rainfall event in mid-January (Table 4) in contrast to very high concentrations of up to 600 $\mu g\ l^{-1}$ in a similar event (drainflow 0.5 mm) after a further application of isoproturon in March 1990. No mecoprop was detected. The estimated loss of isoproturon through the drainage system between autumn application and the end of February 1990 was 11.5–12.5 g ha^{-1} on most treatments (Table 4); this represents 0.5% of the herbicide applied. The highest loss was found in the close-spaced pipes drainage (22 g ha^{-1} or 1.0% of the herbicide applied); these larger losses presumably resulted from rapid drainage and the limited soil-water contact time. Loss from the grass ley treatment was less than 1 g ha^{-1}. In winter 1990/1991, herbicide losses were monitored in the first flush event (25 December–10 January). This drainflow resulted from rapid water movement through the macropores. This was intercepted by the mole drainage channels; a water table above drain depth was not evident on most plots until March 1991.

With the large-expander mole drainage (Plot 6), concentrations of isoproturon were 30 $\mu g\ l^{-1}$ at the start of drainage and fell rapidly to only 3 $\mu g\ l^{-1}$ after 10 days (Fig. 4). With no-expander mole drainage (Plot 10), a similar reduction in isoproturon concentration was seen, this falling from 40 $\mu g\ l^{-1}$ to nearly 10 $\mu g\ l^{-1}$

Table 4
Concentrations and amounts of isoproturon lost in winter drainflow from different drainage regimes in 1989/1990

Drainage systems	Response type	Autumn flush ($\mu g\, l^{-1}$)	January event ($\mu g\, l^{-1}$)	Residual period ($\mu g\, l^{-1}$)	Winter loss ($g\, ha^{-1}$)
Moled gravel-filled	Fast	< 3	< 0.4	< 0.1	0.8
Moled conventional	Fast	6–33	2–5	1–3	12.2
Moled large-expander	Fast	13–27	2–4	1–4	12.3
Moled annually	Fast	21–41	1–4	1–5	11.5
Close-spaced pipes	Medium	37–54	4–7	2–6	21.9
Moled no-expander	Slow	31	1–4	< 0.1	12.2

in the same period before recovering to 30 $\mu g\, l^{-1}$ (Fig. 5). Both plots lost less than 0.2 g ha^{-1} of isoproturon in this period. In contrast with close-spaced pipe drainage (Plot 9), where isoproturon losses were the result of carry-over from the previous season (mid-November 1989, Table 2), concentrations exceeded 30 $\mu g\, l^{-1}$ with a total loading of 2.1 g ha^{-1} over the 18 day period (Fig. 6). However, on this plot both chemographs and bulk samples showed a very rapid fall in the isoproturon concentration.

Examination of the isoproturon chemographs showed a dilution effect over the hydrograph. After the first runoff/leaching event, the concentration in drainflow from all plots fell over the period of rapid water flow before rising in the recession period. By comparison, mecoprop was not found above the detection limit on these three plots in samples taken over the first drainflow flush. Surface layer flow was limited on

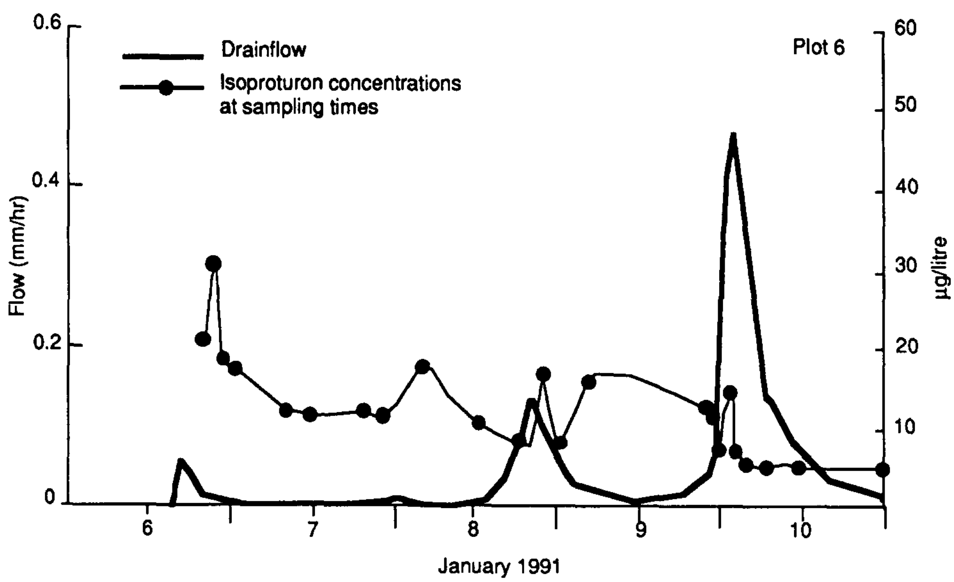

Fig. 4. Loss of isoproturon (applied 8 October 1990) for large-expander mole drainage (Plot 6) in the first winter drainflow, January 1991.

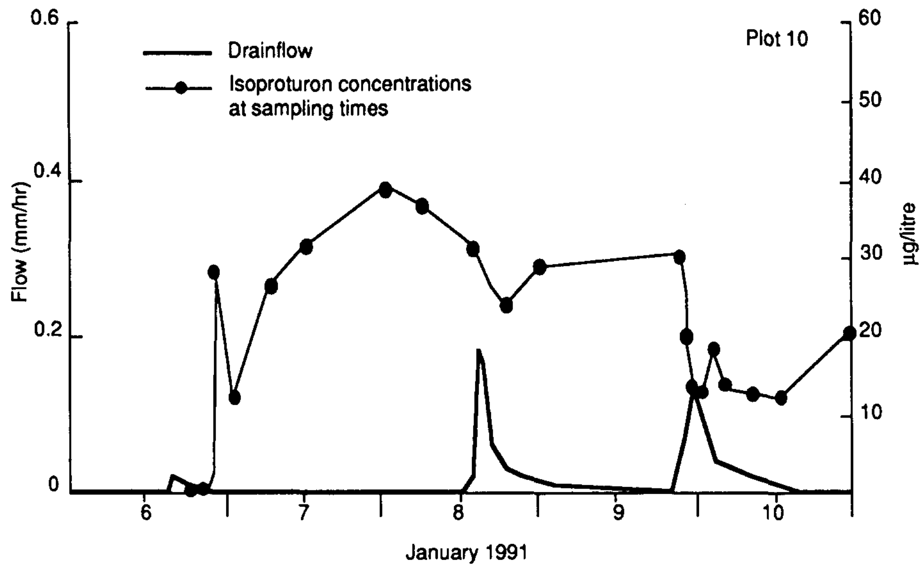

Fig. 5. Loss of isoproturon (applied 8 October 1990) for no-expander mole drainage (Plot 10) in the first winter drainflow, January 1991.

all plots owing to the dry weather. In addition, problems with the flow collecting system on the undrained plot in winter 1989/1990 restricted opportunities to collect samples. However, samples of surface layer flow from both drained and undrained plots showed isoproturon concentrations > 100 $\mu g\ l^{-1}$; this was well above those found in the drainage water. For example, samples taken in the drainage event on 8 January 1991 on the no-expander mole drainage treatment showed peak isoproturon concentrations of 160 $\mu g\ l^{-1}$ in the surface layer compared with 39 $\mu g\ l^{-1}$ in drainflow and 107 $\mu g\ l^{-1}$ in surface layer flow from undrained land.

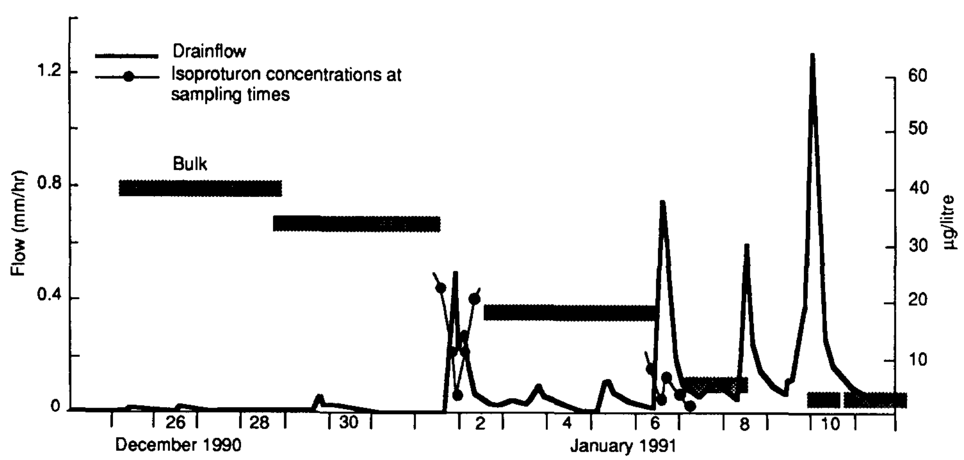

Fig. 6. Loss of isoproturon (applied 11 March 1990) for close-spaced pipes drainage (Plot 9) in the first winter drainflow, December 1990–January 1991.

The analytical results confirmed that the quality assurance procedures adopted for water samples were satisfactory. Mecoprop was not found in any sample; the recovery of isoproturon was good and the variability at such low concentrations makes it not meaningful to apply correction for recovery.

3.4. Herbicide in soil

The breakdown of isoproturon and mecoprop in the Brimstone Farm soil was measured in laboratory incubations, under different temperature and moisture regimes, and followed first-order kinetics (P.H. Nicholls and A.A. Evans, unpublished work). Under typical autumn/early winter conditions of 10°C and a moisture content 80% of field capacity (determined using soil taken from the site at field capacity, which contained 29.2% water by weight), half-lives were 55 days and 4.5 days for isoproturon and mecoprop, respectively. The degradation rates were markedly slower in drier soils and at lower temperatures; a 10°C lowering of the soil temperature typically caused a two to threefold increase in half-life. Sorption in the Brimstone topsoil was linear with coefficients (Kd) of 2.9 l kg^{-1} and 0.6 l kg^{-1} for isoproturon and mecoprop, respectively (method of Nicholls and Evans, 1991).

Soil cores taken in early October 1990 from the large-expander mole drainage system (Plot 6) and the no-expander mole drainage system (Plot 10) immediately before the autumn herbicide application indicated that small concentrations of isoproturon were present to 200 mm depth. These represented carry-over of 14% from previous applications, the most recent of which was in mid-March 1990; mecoprop applied at the same time was not detected. Samples over the 4 months from October 1990 were used to measure the distribution of both compounds. Neither compound had leached appreciably to depth (Fig. 7), and the lack of movement of the weakly sorbed mecoprop was due to the low rainfall in the 2 months after application. Mecoprop was not persistent with little remaining after 56 days (by late

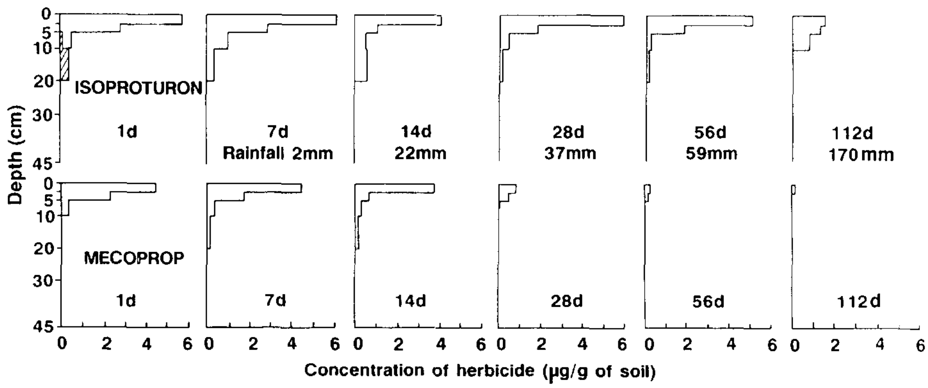

Fig. 7. Persistence and distribution of isoproturon and mecoprop on large-expander mole drainage (Plot 6) following application (8 October 1990). Concentrations are based on dried soil; hatched area at day 1 indicates carry-over of isoproturon.

November) whereas some 35% of the isoproturon applied was still present after 112 days (end of January 1991).

The 2 month period over which the mecoprop was very largely degraded in the soil coincided with the dry autumn 1990 when neither surface flow nor drainflow occurred (Fig. 2). In contrast, isoproturon was more persistent and present in soil at the onset of drainflow (late December 1990) and for the remainder of the major drainflow period to mid-January 1991.

4. Discussion

The need for subsurface mole drainage in UK clay soils used for arable cropping has been well documented. Trafford and Oliphant (1977) reported that mole drainage channels at 2 m spacing were required to maintain a water table at a depth of 500 mm below the soil surface within 24 h of the cessation of rainfall. Under such conditions, a yield benefit of 10% could be expected compared with similar undrained land (Armstrong, 1978). Other work by Cannell and Belford (1982) has demonstrated that there is likely to be crop loss if waterlogging occurs at the time of germination and tillering.

For effective removal of excess water through a mole drainage system, the development of good crack structure is essential (Spoor and Ford, 1987). In mole drained soils, the structure introduced by the passage of the mole bullet can coexist with that developed during the winter/summer shrink and swell process (Harris et al., 1993) and can lead to rapid water movement through the soil profile in the absence of a water table. This process was evident during this study at Brimstone Farm and provided the opportunity for rapid movement of herbicides to the drainage system.

Although the deterioration of the mole drainage channels in this study was slightly greater than that seen previously on this site (Harris et al., 1992a), resulting principally from topsoil infill owing to the very dry weather, the drainage system remained effective over the study period. The only exception to this was with the no-expander mole drainage where the ability to intercept water, especially that transmitted via the macropores, was reduced, resulting in less drainflow.

Comparison of the alternative drainage systems (secondary drainage spacing of 2 m) at Brimstone Farm demonstrated that manipulation of the soil-water regime was possible by relatively small changes in the drainage approach. The novel treatment of gravel-filled mole drainage, most widely used in peat soils where channel stability is often poor (Galvin, 1983), maintained an effective mole drainage channel and an adequate connection with the soil surface over the 4 year study period. This system and the close-spaced pipes maintained the most responsive drainage and so created the opportunity for rapid herbicide transport in the drainflow. The long-term viability of these drainage treatments, in particular the maintenance of adequate soil structural cracks to transmit water under wetter winter conditions, could not be tested in this experiment.

In the drier-than-average weather experienced in these experiments, much of the winter drainflow occurred before the soil reached field capacity. This flow passed rapidly through soil structural cracks connecting the topsoil with the drainage system. Similar observations of bypass flow have been reported by many workers (Bouma et al., 1979; Bouma, 1981; Beven and Germann, 1982) and such flow can play an important role in water movement in structured clay soils. The loss of isoproturon occurred mainly under such conditions.

The monitoring of pesticide losses in undisturbed monolith lysimeters (diameter typically 0.8 m) is a valuable technique, particularly for sandy soils, and is used to identify the effect of management treatments on pesticide losses (Kordel et al., 1991; Yon, 1991). By establishing 0.2 ha field plot lysimeters on the clay soil at Brimstone Farm, the problem of shrinkage and swelling of the soil, which can create either poor or preferential water movement in monoliths (Leake, 1991), was overcome. However, pesticide losses observed in these lysimeters are likely to be much higher than the resulting concentrations in rivers because of the subsequent processes of dilution, sedimentation, removal by vegetation and degradation during the transport process (Leonard, 1990).

Peak concentrations of isoproturon in winter drainflow in these experiments were typically in the range 10–50 $\mu g\ l^{-1}$; in contrast, mecoprop was not detected although applied at the same time as isoproturon. Concentrations of isoproturon in the limited spring drainflow (0.5 mm drainflow) were up to 600 $\mu g\ l^{-1}$. Only isoproturon was found in the limited autumn/winter surface layer flows; peak concentrations (> 100 $\mu g\ l^{-1}$) observed from both drained and undrained land were notably higher than those seen in drainflow. Similar high peak concentrations of isoproturon have been found in surface layer flows in a further study using plot lysimeters on a clay soil (Harris et al., 1992a).

Several other UK studies have reported the presence of isoproturon and/or mecoprop in surface waters (Croll, 1986; Lees and McVeigh, 1988; Harris et al., 1991; Department of the Environment, 1992), with diffuse loss from agricultural land often cited as the likely source (Brooke and Matthiessen, 1991; Gomme et al., 1991; Williams et al., 1991: Harris et al., 1992b). In these catchment-based studies, peak concentrations from diffuse agricultural contamination are generally in the range 1–3 $\mu g\ l^{-1}$, although Brooke and Matthiessen (1991) observed mecoprop at 12 $\mu g\ l^{-1}$ in streamwater during a runoff event approximately 30 h after spraying.

Brooke and Matthiessen (1991) measured mecoprop concentrations in the top 1.0 m of the soil and also estimated them using a fugacity model (Mackay and Paterson, 1981). Most of the mecoprop decayed within 1 month of application. These results support those from Brimstone Farm where rapid degradation of mecoprop was observed both under laboratory conditions and in the field with substantial loss after 14 days and almost complete loss by 56 days. As the first drainflow was unfortunately not recorded in this experiment until 30 days after application of mecoprop in 1989 and nearly 2 months in 1990, it was reassuring to observe that mecoprop was not detected in the drainflow water. In contrast, the slower degradation observed for isoproturon resulted in substantial quantities of isoproturon remaining in the topsoil after 56 days in 1990. There was thus a risk that isoproturon could be transported to the drainage waters; this was confirmed by the isoproturon concentrations observed.

During the winter 1990/1991, isoproturon was essentially only present in the top

200 mm of the soil profile. The detection limits were higher in soil than in water, but none the less 10 $\mu g\ l^{-1}$ of isoproturon in soil-water would have given detectable amounts in soil; these were not observed in the deeper soil layer and so the loss of this herbicide to drainflow must have resulted from transport through the crack structure or macropores rather than by leaching through the body of the soil. Further evidence of such transport and of the importance of soil-water contact time was provided by the close-spaced pipe system at Brimstone Farm; once a herbicide was carried downwards to the subsoil, soil-water contact and hence sorption of the compound by soil was restricted by the water transmission through the plastic conduits. Such transport is in contrast to mole drainage where water moving through the irregularly shaped mole drainage channels remains in contact with the soil. Isoproturon concentrations in drainflow from the close-spaced pipes drainage were higher than those observed from other drainage systems; this resulted in a total loss of just 1% of the applied isoproturon in winter 1989/1990 compared with 0.5% for other treatments. Similar losses have been reported by Wauchope (1978). Most applied herbicide is degraded and mineralised or incorporated into the soil organic matter; a small amount is taken up by the crop. The remaining tiny proportion lost by leaching resulted in concentrations above the EC Directive on potable water (Anon., 1980).

Isoproturon residues, present as carry-over from one season to the next, were little moved into drainflow and a winter loss of 0.8 g ha^{-1} was observed compared with 12 g ha^{-1} on most other drainage systems where isoproturon had been applied during that season. None the less, these findings are important as they demonstrate that concentrations above the EC Directive for potable water (maximum concentration of 0.1 $\mu g\ l^{-1}$ for an individual pesticide) can occur in drainflow for at least one season after the last application. Similar data have been reported for isoproturon by Harris et al. (1992a) in the first season of fallow set-aside.

The high concentrations of isoproturon seen in surface flow at Brimstone Farm, and also reported by Harris et al. (1992b) for plot lysimeters on a second clay site, support the case for maintaining drainage systems in clay soils in such a way as to minimise surface flows. However, because drainage of clay soils can encourage the development of enhanced soil cracking, i.e. in addition to the normal shrink/swell processes, the potential for loss of certain pesticides via drainflow is increased by such drainage. From this work it is suggested that consideration should be given to finding a balance between effective drainage and water table control, so reducing opportunities for rapid movement of water and chemicals through the soil. Drainage systems that increase the residence time of pesticides in soil, particularly in the period immediately after application and prior to field capacity being reached, will provide greater opportunities for degradation of pesticides and consequent reduction of contamination of surface waters.

5. Conclusions

(1) The alternative secondary drainage systems manipulated soil-water movement

in the heavy clay soil. Close-spaced pipe drainage and gravel-filled mole drainage treatments provided very effective drainage and transmitted water rapidly from the topsoil to the subsoil. Mole drainage channels drawn without an expander were less stable than conventional mole drainage and resulted in lower drainflow peaks.

(2) Macropore movement of water was very important; under the dry winter conditions examined, this macropore flow resulted in drainflow occurring several months before field capacity was reached.

(3) Isoproturon was degraded slowly with 35% of applied isoproturon persisting after 4 months. As a consequence, isoproturon was detected at concentrations of 50 $\mu g\ l^{-1}$ in the first drainflow. Some carry-over of isoproturon also occurred from previous seasons and this could result in some contamination of water courses.

(4) Most mecoprop had been lost by degradation from the topsoil within 56 days. Under the dry conditions observed in this experiment, drainflow first occurred 2 months after application, by which time little mecoprop remained. The absence of mecoprop in this drainflow confirmed the importance of the rate of degradation in influencing the potential for contamination of surface waters by mecoprop.

(5) Neither isoproturon nor mecoprop was detected in appreciable quantities at depths below 200 mm in the soil, indicating that any findings of these pesticides in drainage water were the result of rapid movement through soil cracks. Most loss of isoproturon to drainflow occurred as a result of bypass flow through the crack structure before the soil was wetted up.

(6) Concentrations of isoproturon were higher in surface flow than drainflow. It is proposed that soil drainage which minimises both surface flow and rapid bypass flow to the drainage system would be the best compromise.

(7) Total amounts of isoproturon in drainflow were a tiny proportion of that applied; generally 0.5% of that applied the previous autumn was lost in the following winter.

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