MINISTRY OF AGRICULTURE, FISHERIES AND FOOD **CSG 15**

Research and Development

Final Project Report

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Project title	Brimstone Farm III : Systems to minimise the leaching of pesticides to drainage water from a structured clay soil
MAFF project code	**PL0502**
Contractor organisation and location	IACR-Rothamsted Department of Biological and Ecological Chemistry Harpenden, Herts, AL5 2JQ
Total MAFF project costs	£ 464,675
Project start date	01/04/98
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Executive summary (maximum 2 sides A4)

Much of the surface water in lowland Britain is used for drinking water, and so the contamination of rivers by traces of pesticides is a matter of potential concern. This contamination can arise both from point sources such as spillages and diffuse sources such as the presence of pesticides in field drainage. Heavy clay soils are often drained, as at Brimstone Farm, and the preferential flow pathways so created can allow traces, even of pesticides that are strongly sorbed to soil, to reach drainage. Such contamination of drainage can vary greatly from year to year for reasons that were not understood. This programme of research at Brimstone Farm, collaborative with ADAS and the BAA and itself organised within a larger grouping of MAFF-funded cracking-clay projects, has attempted to identify the factors involved in pesticide movement to drainage and so to propose ways to mitigate this problem.

Our project within this wider programme has investigated the role of pesticide sorption and degradation in soil on these losses. This includes the development and use of computer simulation with the Pesticide Leaching Model (PLM) to investigate the factors influencing the year-to-year variations.

Pesticides spanning a range of physicochemical properties (particularly sorption to soil and degradation rate) have been applied at Brimstone Farm since 1990. One compound, isoproturon, has been applied every year; this is a widely used herbicide in cereals, and following autumn application is often the main contaminant amongst pesticides in rivers in arable areas. Isoproturon is moderately sorbed (K_d 2.9) and moderately persistent in this clay soil, as observed earlier in two seasons' field measurements and in three series of laboratory incubations (the last in 1997) that provided the input parameters for PLM and other collaborative modelling. However, in 1998, Allan Walker studying spatial variability across the plots, rather than bulked randomised soil samples, found 'hot spots' of degradation of isoproturon indicative of microbial adaptation. These findings were confirmed in a joint Rothamsted-HRI study. To assess the impact of this new situation on the drainage findings, field measurements of isoproturon behaviour (using analysis of bulked core samples) were made on three plots following application in February 1999. About 50% of the isoproturon was lost rapidly despite the winter temperatures, and then losses slowed to those typically observed previously. This was interpreted as caused by rapid losses in the 'hot spots' with the normal breakdown elsewhere. Though this new behaviour complicates comparison of current drainage losses with previous years, isoproturon is still persistent enough to give useful results. Chlorotoluron, a very similar herbicide, has also been used on the plots; recent tests showed it to be three to four times more persistent than isoproturon and showed no lag phase kinetics, though across 12 soil samples the breakdown rates of isoproturon and chlorotoluron were closely correlated.

The modelling studies indicated that degradation is not a primary factor in determining drainage losses, insomuch as the predicted variation in the amount of pesticide remaining at the first drainage event was much less than the year-to-year variation in pesticide concentrations in drainage. The PLM studies, produced as a report, indicated the difficulty of predicting macropore flow processes for trace amounts of pesticides, in essence because the parameters for macropore flow and the associated lack of sorption equilibrium are difficult to define.

All the findings from this and associated projects have recently been brought together and summarised, and the main conclusions are listed below:

- The pesticide properties that minimise pesticide contamination in drain flow are high K_{oc} (i.e. sorption to organic carbon in soil) and low application rate.
- For moderately sorbed pesticides (e.g. isoproturon), early application of autumn herbicides would appear beneficial on heavy clay soils as this gives more time for sorption to reduce availability before the first leaching event; however, there may be important agronomic reasons to delay application.
- Other agronomic practices (fine tilth, spacing of mole drains, use of soil sealants, shallow incorporation of pesticide) have only a small and often inconsistent influence on pesticide losses, though very rapid drainage may exacerbate such losses.

Scientific report (maximum 20 sides A4)

The Brimstone Farm experiment has examined the factors determining the movement of pesticides to drainage in a cracking clay soil. This work started in 1990 and was formally expanded in 1993 leading to the present phase 1997/2000. The site is run jointly by IACR-Rothamsted and ADAS, and the whole programme has also involved several other contractors and advisors coordinated by a Steering Committee to Minimise Pesticide Leaching to Drainage overseen by MAFF CSG. In this report, we discuss our research within this large-scale collaborative programme together with the overall conclusions that have been drawn from the programme as a whole. It should be noted that most of the detailed results from the field experiment and computer simulations have been prepared into reports for MAFF, and these need to be used as the primary data source. Publications already out or pending will present the salient points but cannot include all the detailed flow measurements and individual pesticide analyses.

The Brimstone Farm site in Oxfordshire (Cannell *et al*., 1984; Harris *et al*., 1994) is a heavy structured clay (60% <2µm) of the Denchworth series, having pH ~7.0 (0.01M $CaCl_2$) and containing 4.5% organic matter. The site receives an average annual rainfall of 686 mm and is representative of many cereal-growing regions of central England. There are 20 hydrologically isolated plots of 0.19 ha each, of which 16 were used in this research. The field has a gentle slope, and the plots are drained by mole or pipe drains at 60 cm deep leading into collector drains and below which the sub-soil is largely impermeable.

The field experiments were based upon autumn application of pesticide (primarily herbicides) to winter cereals, since it was thought that movement of compounds over the winter period into drainage was a more important source of contamination of surface waters than spring applications. The usual crop was winter barley, with oats used as a break crop to limit damage by the take-all fungus. A range of pesticides was tested from 1993-2000 with isoproturon being used annually as the standard main compound to allow year-to-year comparisons. Isoproturon is a herbicide widely used in cereals to control blackgrass and other weeds; being moderately sorbed by soil and moderately persistent, it has become often the main pesticide contaminant in lowland rivers with concentrations of 1 to 3 µg/l. This is substantially in excess of the EU drinking water limit of 0.1 µg/l for an individual pesticide, and so the water companies have to do additional clean-up before surface waters meet this criterion and can be piped for domestic use.

In order to understand what determines the losses of pesticide to drainage at this site, the following factors were investigated in the field:

1. Pesticides spanning a wide range of physicochemical properties (pKa and lipophilicity expressed as 1-octanol/water partition coefficients, K_{ow}).
2. Agronomic practices (application timing, tilth, use of soil sealant).
3. Drainage practices (slowing drainage with raised U-bends, mole spacing and re-moling).
4. Use of sorbents in the moles.

Following autumn application of pesticides, drainage was collected automatically from the plot collector drain and this was done over each of the first four major drainage events insomuch as these could be ascertained. In certain dry winters such as 1995/96, very little drainage occurred; in contrast, autumn 1998 was so wet that the pesticide could not be applied until February 1999. The drainflow was subsampled to give coverage over each event, and these were analysed for pesticides by extraction and high-pressure liquid chromatography.

In order to interpret the drainage results, we made additional field, lysimeter and laboratory measurements. These included:

1. Dissipation in the field of the pesticide (isoproturon examined in winter 1999).
2. Lysimeter leaching.
3. Degradation of pesticide in soil under controlled conditions of temperature and soil moisutre.
4. Pesticide sorption to the Brimstone Farm soil.
5. Pesticide sorption to the sorbent (Jimsorb) placed in the mole drains.

The pesticides tested from 1993-2000 are listed in Table 1 together with their properties. Triasulfuron, being a weakly sorbed and moderately persistent compound, is not approved for autumn use and was chosen for use in this way as an investigative approach only. The fungicides prochloraz and propiconazole together with the herbicide pendimethalin were the most lipophilic and so most strongly sorbed by soil. The degradation and sorption measurements provided the parameters for use in the computer modelling studies done subsequently both by us and other collaborators.

Table 1. Pesticide properties, application rates and usage

Pesticide[1]	Sorption Kd (1 kg^{-1})	Half-life[2] (days)	Full rate[3] (g ha^{-1})	Applied to core plots						
				1993/94	1994/95	1995/96[4]	1996/97	1997/98	1998/99	1999/00
Triasulfuron (h)	0.43	122	7.5	-[3]						
Mecoprop (h)	0.6	3.6	2400		-	-	-	-	-	-
Isoproturon (h)	2.9	75	1500							
Chlorotoluron (h)[5]	(2.9)	117	1500	-					-	
Propiconazole (f)	19.2	(>100)	250	-	-[6]	-	-	-	-	-
Prochloraz (f)	75	(>100)	405	-[6]	-	-	-	-	-	-
Pendimethalin (h)	88	619	2000		-	-	-	-	-	-

[1] Herbicide (h) or fungicide (f).
[2] Half-life in Brimstone Farm soil at 80% field capacity and 10ºC; values in brackets are estimated. Note that isoproturon is now less persistent.
[3] Full rate for isoproturon and chlorotoluron was 2500 g ha^{-1} prior to 1996/97.
[4] Winter oats, isoproturon and chlorotoluron applied at 250 g ha^{-1} to avoid damage.
[5] Chlorotoluron was applied only as a later treatment to the growing crop.
[6] Applied in these years to the four pilot plots only.

Losses of pesticide to drainage

These samples were selected by ADAS and analysed mainly by CSL. The results have been published in annual reports, and also to a limited extent in publications (Bromilow *et al*., 1998; Jarvis *et al*., 1995). The lipophilic compounds which showed strong sorption to soil (Table 1) (pendimethalin, prochloraz, propiconazole) appeared only at low concentrations in drainflow, typically 1 µg l^{-1} or less. The moderately sorbed isoproturon in some years gave concentrations >300 µg l^{1} in the first drainflow event, though concentrations in subsequent events were much less in most years except for 1993/94. This effect was much greater than could be accounted for by degradation in soil between events. Year-to-year variation was very great, and little isoproturon was found in the dry winters with limited drainage; even so, losses were generally <2% of applied. Losses of the weakly sorbed triasulfuron varied less from year to year, typically being about 5% of applied; concentrations however were never more than a few µg l^{-1} due to the very low application rate. Taken together with lysimeter results reported previously from Rothamsted and SSLRC, it was concluded that maximising the time between application and the first drainflow minimised drainage losses for the more sorbed compounds, presumably by favouring a more complete sorption equilibrium.

Pesticide degradation

An important finding was that, after several years of annual isoproturon application, 'hot spots' of isoproturon degradation could be found in the plots. First noted by Dr. A. Walker, a joint study confirmed the rapid breakdown of isoproturon in soil samples taken from point sources across several plots. Such behaviour is typical of microbial adaptation, and an example is given in Figure 1.

Figure 1. Effect of position within plot on degradation of isoproturon in Brimstone Farm topsoil incubated at 15°C (Plot 20)

This led us to reexamine isoproturon persistence in the field. Following application to Plots 6, 17 and 20 on 12 February 1999, analysis of soil cores showed quite a rapid loss of isoproturon until about 50% remained (assessed using randomised bulk sampling) followed then by slowing losses (Figure 2).

This is interpreted as showing initial rapid loss due to the microbial 'hot spots' followed by degradation elsewhere at a rate typical of that observed previously.

Figure 2. Persistence of isoproturon applied (0.25 kg/ha) at Brimstone Farm on 12 February 1999

Chlorotoluron is closely related to isoproturon and was used on some plots as a late application to examine the effect of, for example, soil moisture conditions at application. To see if the microbial populations able to degrade isoproturon were also able to degrade chlorotoluron, then two compounds were co-incubated in new subsamples of the point soil samples used previously. The breakdown of chlorotoluron showed no lag phase and followed first-order kinetics (Figure 3),

Figure 3. Effect of position within plot on degradation of chlorotoluron in Brimstone Farm topsoil incubated at 15°C (Plot 20)

and was some three to four times slower than that of isoproturon. However, breakdown rates of the two compounds were closely correlated in the 12 soil samples tested (Figure 4).

Figure 4. Correlation between rate of breakdown of isoproturon and of chlorotoluron in Brimstone Farm topsoil incubated at 15°C

<u>Use of a sorbent to decontaminate drainage</u>

Laboratory tests were done to measure the sorption of pesticides by Jimsorb, a carbonaceous by-product from china-clay production which had been used as a fill in two mole drains at Brimstone Farm. Sorption from water increased with time and strongly increased with increasing lipophilicity (Figure 5). For acidic herbicides, sorption was higher at pH 5 than pH 7, but was always weak as these herbicides would be substantially dissociated even at pH 5.

Figure 5. Sorption of four herbicides from water (initial concentration 1.0 µg/ml) by Jimsorb

These measurements were used as parameters in a modelling exercise to appraise the likely efficacy of such an approach in cleaning drainflow (Addiscott and Bromilow, 2000). This concluded that used as a 1-m plug at the end of the mole drains, Jimsorb would not be sufficiently sorptive to hold back compounds such as isoproturon. However, used as a mole drain fill, it would substantially mitigate losses of such compounds (and may be 'self-cleaning' by encouraging microbial degradation over the summer), though not of the more weakly sorbed acidic herbicides. The field trials, though limited, largely bore out these conclusions.

<u>Computer modelling</u>

Drainage results from 1990 to 1998 were investigated using the macropore flow model PLM (Hall and Nicholls), and the conclusions presented in a MAFF report (Nicholls, 2000). Isoproturon, chlorotoluron, triasulfuron and pendimethalin were simulated for 8, 1, 4 and 1, respectively, winter seasons after autumn application, using results from three different plots with conventional mole drains and one that held close-spaced drains. Although PLM was designed to simulate concentrations of pesticide that reach drainage waters by preferential flow in structured soils, concentrations of herbicide in drainage water at Brimstone Farm could only be simulated after extensive calibration of the model. A facile three-step calibration procedure was devised. Firstly, the time of onset of the first drainage event was calibrated by adjusting the initial soil-water deficit. Secondly, the amount of water drained was calibrated by adjusting the proportion of water moving to drains. Thirdly the % 'fast' pores parameter could be used to calibrate the concentration of herbicide.

In some years such as 1994/95 and 1995/96, there was little observed leaching of isoproturon. Additionally, concentrations of isoproturon often declined rapidly after the first event. Such decline could not be explained by rates of degradation alone.

Quite often isoproturon was detected at Brimstone Farm in drainage water under base-flow conditions. At Brimstone Farm the drains flow after the water table rises to the level of the drains and that may cause the entry of solute into drains under base-flow conditions. PLM does not simulate a water table and did not simulate high concentrations of herbicide under base flow conditions.

Model parameters derived to calibrate the isoproturon tended to over-predict concentrations of pendimethalin and under-predict those of triasulfuron. This indicates that susceptibility to transport by preferential flow may be inversely related to sorption.

<u>Conclusions</u>

The overall findings of the various projects at Brimstone Farm (MAFF projects PL 0501-03, PL 0521 and PL 0524) have been summarised. The reported project was designed to assist interpretation of the series of collaborative projects, and so the summary prepared by the Steering Group for MAFF provides the conclusions from all this research. These conclusions are appended below:-

Management Practices to Reduce Pesticide Leaching

Summary findings from MAFF projects PL0501-03, PL0521 and PL0524

Processes influencing pesticide losses by macropore flow

- A review of current and historical results from Brimstone Farm shows time from application to first drainflow event to be the dominant factor in determining concentrations and losses in drainflow of a moderately mobile, moderately persistent herbicide (isoproturon).
- The decrease in concentrations and losses of isoproturon in drainflow with increasing time from application to event is significantly greater than would be expected from degradation alone. The reasons for this are unknown, but availability for leaching may be additionally influenced by diffusion into the soil matrix, time-dependent sorption or other processes.
- Wet or dry moisture conditions in upper soil layers prior to, or shortly after, application had no consistent effect on losses of isoproturon to drains either at Brimstone Farm or in lysimeter experiments with the Brimstone soil. However, rainfall from application influenced the occurrence of drainage and thus the overall winter loss of isoproturon.
- Shallow incorporation of isoproturon in Brimstone soil did not affect losses to drainage either in the field or in lysimeters. This suggests that soil surface processes such as rain splash and runoff are not influential.

Influence of pesticide properties

- In most seasons, losses of isoproturon occurred predominantly in the first drainflow event. There was an exception to this in 1993/94 when movement was observed for a number of events, but the reasons for the differences in behaviour are not clear. Total losses varied greatly from year to year, but rarely exceeded 2% of applied.
- Losses of a more mobile and moderately persistent compound (the acidic herbicide triasulfuron) were much less dominated by time from application to drainage event. Losses were generally observed over a number of successive events, and were more consistent year-on-year, averaging about 5% of applied.
- Losses to drainage, expressed as a proportion of the amount applied, decreased with increasing Koc, with only traces (generally <0.05%) of strongly sorbed pesticides (propiconazole, prochloraz and pendimethalin) reaching drainflow.

Agronomic practices

- Generation of a fine tilth reduced concentrations and losses of isoproturon in drainflow from lysimeters (containing the Brimstone soil) by approximately 33% relative to a standard agricultural tilth. Laboratory experiments suggest that an effect in decreasing the time to reach sorption equilibrium may be wholly or partially responsible. Successful generation of a fine tilth on heavy clays depends upon field conditions and cannot be guaranteed in a particular season.
- The proportion of applied pesticide lost to drainage appeared essentially independent of the rate of application.

- More efficient drains tended to exacerbate pesticide losses at Brimstone Farm.
- Limited experiments suggest that the use of a soil sealant may have a small positive effect on reducing drainage losses but insufficient work has been performed to make this conclusion definitive.
- Restricting drainage effectiveness by adding an inverted U-bend to the drainage outfall achieved the desired effect of holding water in the soil profile for longer, whilst still permitting drainage under high rainfall, saturated conditions. This reduced losses of isoproturon by up to 25%.
- Widening of mole drainage channel spacings was examined as a practical interpretation of the U-bend restrictive drainage approach. However, this did not produce an observable reduction in pesticide loss.
- Jimsorb (a granular mineral sorbent) placed in selected mole channels was very effective in removing isoproturon and other non-ionic herbicides from drainflow, but not acidic herbicides such as triasulfuron. However, laboratory tests and modelling

suggested that Jimsorb is unlikely to be reliably effective as a short-plug system in the drains under normal commercial agricultural practice.

Modelling

- Current preferential flow models give robust simulation of the hydrology of heavy clay soils. However, they are unable to simulate the rapid decrease in availability for leaching beyond that due to degradation. Pesticide behaviour (sorption, degradation, diffusion *etc*.) in the different structural regions of soil and partitioning into flow from the soil matrix and macropore linings are not well characterised or described.

Enhanced breakdown of isoproturon

- Accelerated degradation of isoproturon in particular parts of a field has been demonstrated at Brimstone Farm and a number of other sites. Accelerated degradation deviates strongly from first-order kinetics and rather shows an initial lag period followed by rapid degradation. Sites with accelerated degradation are strongly correlated with higher soil pH. Losses in the field in 1999 were initially fast and then slowed, indicating rapid breakdown in the 'hot spots' followed by the typical original behaviour elsewhere. Bacteria with the ability to rapidly degrade isoproturon have been isolated from soil. Breakdown of chlorotoluron was four times slower than that of isoproturon and did not show a lag phase; however, soils able to degrade isoproturon rapidly also gave the fastest degradation of chlorotoluron.

- Latest evidence suggests that isoproturon may no longer be stable in drainage water taken from Brimstone Farm where continuous application has been made for at least thirteen years. This contrasts with the start of the study and with results from lysimeters recently taken from Brimstone Farm, where the compound was shown to be stable in drainage water.

Conclusions

- The pesticide factors that minimise pesticide concentrations in drainflow are high Koc, short half-life in soil and low application rate.

- For moderately sorbed compounds (e.g. isoproturon), early application of autumn herbicides would appear beneficial on heavy clay soils anticipating as long a period as possible before drain flow commences. However it is recognised that there are also important agronomic reasons to delay application.

- Re-moling should not be carried out more often than necessary as this is likely to enhance pesticide losses.

- Other agronomic practices, such as fine tilth, generally have a lesser influence on pesticide losses and may not be viable within commercial agricultural systems.

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