Institute of Hydrology

Report No. 129

Rosemaund pesticide transport study 1987-1993

Natural Environment Research Council

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Contents

Executive summary

1. This document summarises the results, conclusions and recommendations of a pesticide translocation research project carried out over the period 1987 to 1993 at ADAS Rosemaund Research Centre (formerly ADAS Rosemaund EHF) in Herefordshire. The main purpose of the project was to monitor the water-borne transfer of pesticides from agricultural fields into the stream draining the Rosemaund catchment, in order to provide a better understanding of pesticide translocation, and to allow the development and validation of improved computerised models of translocation processes and environmental pesticide exposure.

2. The project was a collaboration between ADAS Rosemaund Research Centre (ADAS Rosemaund), the Building Research Establishment (BRE), the Institute of Hydrology (IH), the Ministry of Agriculture, Fisheries and Food's Directorate of Fisheries Research (MAFF), the National Rivers Authority (NRA), the Soil Survey and Land Research Centre (SSLRC), the Soil and Water Research Centre of ADAS, and the Universities of Essex and (latterly) Birmingham. The main funding agencies were the Department of the Environment, the Ministry of Agriculture, Fisheries and Food, the National Rivers Authority and the Natural Environment Research Council.

3. ADAS Rosemaund was chosen for this work because the farm neatly occupies a complete small water catchment, giving the project good knowledge of all agrochemical inputs. Furthermore, it can be considered as a 'worst case' catchment for the translocation of pesticides to surface waters, because rainwater is able to move rapidly via so-called by-pass flow through soil macropores into an extensive network of field-drains, and thence to the stream. Due to the presence of impervious underlying rock strata, little water moves down into the aquifer beneath the catchment. It should be noted that a hydrological regime of this type is far from rare: approximately 32% of UK soils are dominated by by-pass flow (Boorman *et al.*, 1995), so the results have implications for a large number of catchments.

4. This report only presents a brief summary of the data collected by the project. The complete dataset is archived in four unpublished reports (Bird *et al.*, 1991; Hack, 1991; Hack, 1994; Mitchell, 1995) and much of the information has been published in the scientific literature (Brooke and Matthiessen, 1991; Williams *et al.*, 1991a; Williams *et al.* 1991b; Carter and Beard, 1992; Matthiessen *et al.*, 1992; Di Guardo *et al.*, 1994b; Matthiessen *et al.*, 1994; Matthiessen *et al.*, 1995; Turnbull *et al.*, 1995a; Turnbull *et al.*, 1995b; Williams *et al.*, 1995).

5. In essence, the project aimed to study the pesticide concentrations in soil and water that resulted from the normal use of agrochemicals on arable crops at Rosemaund farm. The pesticides were applied by tractor-mounted sprayers, as nearly as possible according to good agricultural practice, and over the lifetime of the project included a total of 19 herbicides, fungicides and insecticides from most of the major pesticide groups. Most effort went into monitoring those substances already known to be prone to leaching, but significant attention was also given to some pesticides traditionally assumed to be immobile in soil. The majority of the monitoring work involved regular manual sampling and pesticide analysis of soil and soil water from treated fields, together with rainfall-driven automated sampling of water in field drains and in the stream into which they discharge. As resources allowed, bioassays of stream water and sediments were also conducted from time to time to evaluate the potential biological impact of the translocated residues on stream fauna.

6. The project found that the majority of pesticide (generally more than 99% of that applied) stayed in the soil and degraded there. Most of the translocation to the stream occurred in a few hours immediately after significant rainstorms (>10 mm in 24 hours) in the months November - April, and was almost exclusively via by-pass flow to the field drains, although one cannot exclude overland flow and seepage as infrequent contributory factors. If one defines a pesticide translocation event as the concentration profile of a single pesticide through the hydrograph at a given location, then 123 such events were monitored in the field drains and stream during the course of the study. In 11 cases pesticides were either absent or the maximum concentrations were below the level of detection; higher concentrations generally dropped back below those limits within about 12-24 hours. Peak concentrations were over 10 $\mu g\ l^{-1}$ during 25 events, in the range 1-10 $\mu g\ l^{-1}$ during a further 48 events, and below 1 $\mu g\ l^{-1}$ during the remaining 50 events. In 90 events, the flow-weighted mean concentration exceeded 0.1 $\mu g\ l^{-1}$, the EC Drinking Water Directive limit for individual pesticides in drinking water. Concentrations in the field drains were

generally higher than in the stream, but up to 68 μg l^{-1} was nevertheless observed in the stream.

7. Although the application rates of the pesticides and their properties (notably water solubility, soil half-life and soil organic carbon adsorption coefficient) played some part in determining the concentrations that appeared in the stream, it appears that the hydrological regime in the soil was the dominant factor. That application rates and properties were of relatively low significance is illustrated by the strongly soil-adsorbed insecticide deltamethrin, which was applied at only 5 g ha^{-1}, but which was nevertheless found to peak in the stream at 1.9 μg l^{-1}. Similar observations were made for the other three pesticides studied (chlorpyrifos, trifluralin and fenpropimorph) which are not traditionally considered to be leach-prone. Almost all the deltamethrin and a significant proportion of the other three were probably transported adsorbed to fine mobile soil particles rather than in solution, showing that field drains are no barrier to this form of translocation.

8. Two computerised models of pesticide translocation to the stream were developed and validated during the course of the project. The first, a fugacity model known as SoilFug (Di Guardo *et al.*, 1994a), was designed at the University of Milan as a predictive model of the average pesticide concentration to be expected in the water flowing out of catchments during rainstorms, but it uses a minimum of catchment-specific information. SoilFug had already received extensive validation on two Italian catchments. Of the 74 pesticide translocation events studied at Rosemaund for the purpose of model development, 50 (68%) were modelled successfully by SoilFug, success being defined as a prediction of the flow-weighted mean concentration lying within a factor of ten of the observed value. The least successful predictions were made for the dissociated phenoxy herbicides (dichlorprop, MCPA and mecoprop), for which such models would not be expected to apply. Overall, SoilFug shows promise as a model for predicting worst-case concentrations in water of pesticides that are still at the early stages of risk assessment and have not yet been used on a wide scale in the field.

9. The second model was developed by the Institute of Hydrology (IH) as a much more catchment-specific tool than SoilFug, by combining a detailed hydrological model with a pesticide behaviour model. The intention was to predict mean and peak pesticide levels at the outflow from a catchment under a variety of rainfall regimes, to predict the effects of changing land-use on those levels, and to provide guidance for pesticide sampling strategies in freshwater monitoring programmes. Model runs for 33 pesticide translocation events showed that predictions were more than an order of magnitude different from observed mean concentrations in only two cases (94% success rate), although the peak predicted by the model was always several hours earlier than the observed peak.

Despite these successes, both the SoilFug and IH models would benefit from further validation with data from a wider variety of catchments.

10. Three translocation events (involving the phenoxy herbicide dichlorprop, the carbamate insecticide carbofuran and the organophosphate insecticide chlorpyrifos) were monitored by an *in situ* stream bioassay, which measured the feeding rate and mortality of caged specimens of the amphipod crustacean *Gammarus pulex*. The dichlorprop event was used as a negative control to test the system, as this herbicide is of very low toxicity to crustacea. As expected, the bioassay did not respond to dichlorprop, but in both of the insecticide events the test organisms stopped feeding and almost all died or became moribund. Although one can never be sure about causative factors in field observations of this type, laboratory toxicity data indicated that the insecticides were almost certainly responsible for the observed effects.

11. Stream sediments were also collected after the deltamethrin events and bioassayed in the laboratory with a sensitive sediment-dwelling insect larva, the midge *Chironomus riparius*. The deltamethrin-contaminated sediments did not affect the growth of *C. riparius*, showing that the translocated insecticide was firmly bound to particulates and not bioavailable. Finally, it is worth noting that several of the herbicide translocation events (especially those involving isoproturon, trifluralin, atrazine and simazine) produced peak concentrations in stream water which approached or exceeded proposed Environmental Quality Standards for UK waters. Although herbicide effects on aquatic plants were not studied, a risk to plants could be implied from these exceedances.

12. An ecological survey of the Rosemaund stream benthic invertebrate fauna was conducted by the NRA in 1994 to investigate whether repeated exposure to pesticides had caused damage to the stream community. The survey revealed that the faunal assemblage was very impoverished for this type of habitat, with sensitive species such as *Gammarus pulex* either absent or rare. This environmental degradation could not be unequivocally attributed to pesticides because the supposedly pesticide-free control site, on a similar stream elsewhere in the River Lugg catchment, also had an impoverished fauna. However, no pesticide

analytical data are available for the latter site, so even though its surrounding land-use (woodland and grass) should result in minimal pesticide application, it cannot be assumed that it was not contaminated. In conclusion, it seems likely that at least some of the environmental degradation in the Rosemaund stream has been due to pesticides which have been transported from the fields via the field drains.

13. In summary, this project has shown that field-drained soils prone to by-pass flow will tend to facilitate the appearance of transient pesticide peaks at $\mu g\ l^{-1}$ concentrations in a headwater stream after rainfall. This occurs to a large extent independently of chemical properties, although it has proved possible with computer models, which use basic physicochemical data and broad assumptions about soil properties and rainfall, to predict with reasonable accuracy the mean concentrations of most pesticides in the stream during translocation events. However, it should be noted that the maximum amount of any single pesticide mobilised from the fields to the stream in a given event was only 1.1% of the total applied. Despite these small amounts of briefly mobilised material, the *in situ* bioassays have shown that some insecticides can nevertheless cause biological damage to stream dwellers, and may also be causing actual ecological degradation. Several herbicides are also probably causing damage to aquatic plants.

14. The report concludes with a number of recommendations (Section 6). There is now an urgent need to target headwater streams in agricultural areas for integrated investigations of pesticide concentrations, bioassay responses and ecological impacts. Limited evidence already exists that unexplained ecological degradation is occurring at sites of this type, but more research is required to link this with transported pesticides. Such studies would also provide the opportunity to obtain further field validation data for the various models which have been developed to predict pesticide exposure in surface waters. Despite the remaining uncertainties and the current trends in pesticide usage, however, it seems clear that some headwaters are at risk from transported pesticides. It is now for the pesticide regulatory authorities to consider how the processes uncovered at Rosemaund can usefully be accounted for in their aquatic risk assessments.

1 Introduction

1.1 Pesticides in water

The introduction of effective annual grass weed herbicides and more effective cereal fungicides in the 1970s was largely responsible for a dramatic rise in the use of agricultural pesticides. This trend has recently been reversed, but pesticide usage has led to serious concern about contamination of the environment, and one important medium at risk is the aquatic environment. The effects of pesticides in water, on both aquatic life and potable water supplies, are of particular concern.

Reviews of pesticides in drinking water sources in England and Wales (Lees and McVeigh, 1988; Drinking Water Inspectorate, 1992) have indicated that a number of sources contain individual pesticide levels greater than the Maximum Acceptable Concentrations (MAC) laid down in the European Union Drinking Water Directive (Council of the European Communities Directive, 1980). This directive stipulates a MAC of any single pesticide in potable waters of 0.1 $\mu g\ l^{-1}$. Although this MAC may be over-cautious from the standpoint of human health, the failure of a proportion of samples to comply has caused public concern.

The Water Resources Act 1991, which consolidated the Water Act 1989, allows for the Secretary of State to set water quality objectives (WQOs) for controlled waters. If and when they become statutory, the NRA will be responsible for ensuring compliance with these WQOs, which will include use-related objectives and standards and will incorporate the requirements of relevant EU Directives. It is therefore vital that the movement and fate of pesticides in the aquatic environment is well understood and predictable. Without such information it is difficult to envisage how compliance with such standards could be achieved.

Published data on pesticide concentrations in field drains and streams are available, but such studies generally originate from North America, where agricultural systems are often irrigation-based rather than rain-fed as in the UK (Johnston *et al.*, 1967; Frank *et al.*, 1982; Spencer *et al.*, 1985; Muir and Grift, 1987; Thomas and Nicholson, 1989; Wauchope, 1978). Further, in most cases details of agrochemicals used in the respective catchments can only be estimated (Hennings and Morgan, 1987; Gomme *et al.*, 1992) and consequently the value of these studies is limited. There is therefore a need to study agrochemical mobility under experimental conditions in controlled catchments in the UK, particularly in headwater streams close to treated fields.

In addition to the need for field data on pesticide concentrations in the aquatic environment, there is also a requirement for accurate predictions of transport patterns of currently used products from particular catchments, on the basis of land use and agricultural practice. Such descriptions or models would be invaluable to the agencies responsible for aquatic environmental regulation and control in the UK, i.e. the NRA in England and Wales and the River Purification authorities in Scotland.

1.2 The Rosemaund pesticide transport study

The Rosemaund pesticide transport study was initiated to contribute to the fulfilment of these requirements. The study's main objectives were to assess the movement, distribution and aquatic environmental impact of selected pesticides, applied according to current farming practice, on a whole catchment basis. This allowed the investigation, development and validation of hydrodynamic models of the movement and fate of agricultural pesticides between the place of application and the receiving watercourses. The ADAS Rosemaund farm was chosen principally because the stream catchment is contained almost entirely within its boundaries. This allows good knowledge of pesticide applications to the entire catchment, essential if the data produced are to be used for the development and calibration of models. Further, the use of a research farm allows some influence over the selection of pesticide groups to be studied, provided they are applied within the constraints of good agricultural practice. Finally, the geology and soil structure at ADAS Rosemaund prevent significant loss of rainfall to groundwater, thus maximising chemical transport to the drains and outflowing stream. These hydrological conditions are not an unusual scenario as they represent 45% of agricultural land in the UK (Cannell *et al.*, 1978).

It was for these reasons that, following a desk study, a project was initiated in 1985-86 by IH, funded by the Welsh Water Authority (subsequently the Welsh Region of the NRA) based at, and supported by, personnel of the ADAS Rosemaund Research Centre (formerly ADAS Rosemaund Experimental Husbandry Farm) near Hereford. In 1987 the MAFF (Fisheries Laboratory, Burnham on Crouch), in collaboration with the Building Research Establishment (BRE) and later the Soil Survey and Land Research Centre (SSLRC), began investigations into movement of pesticides and their effects at ADAS Rosemaund, and ADAS Soil and Water Research Centre (SWRC) carried out investigations on the drainage of selected fields on the farm.

To place this study into the perspective of current agricultural practice, the results and conclusions should be viewed in the context of trends in the use of pesticides in agriculture during the period of the study. The increasing trend in pesticide usage from the 1970s has generally been reversed in recent years, and during the period of this study, 1987-1993. The following crops will be used to illustrate the changes:

- Cereals: the predominant arable crop
- Oilseed rape: the most important combinable break crop
- Potatoes: an intensive arable cash crop

All figures for pesticide use quoted in the following sections are for Great Britain.

Cereals

The area of all cereals fell by 11% between 1988 and 1992 (Table 1.1), although wheat increased by 9% over the same period. The area of cereals treated with insecticides increased by 80%, although the weight of active ingredient fell by 38%. The pattern for fungicides is similar, with +26% and -29% equivalent figures. This indicates lower rates of product usage and a trend for new products to be more effective at a low rate of active ingredient.

The area treated with herbicides increased by 9% but the weight of active ingredient was 36% less, indicating a similar trend to the other pesticides. With the advent of the newer herbicides such as fenoxaprop-p-ethyl, metsulfuron-methyl and fluroxypyr, used in spring, there was a move away from the autumn residuals such as chlorotoluron and tri-allate. This trend will have significance for pesticide transport over winter.

Oilseed rape

The area of oilseed rape increased steadily by 21% between 1988 and 1992 and is now at a plateau and may decrease. The area treated with insecticides actually increased by 78%, yet the total weight of active ingredient used decreased by 67%. A fall in the use of triazophos to control pollen beetle was an important factor. Fungicide area and active ingredient increased by 22% and 26% respectively, in line with the increased area. However, this masks a peak in 1990 and the progressive decline since then, as the need for prochloraz or carbendazim treatments has been questioned more critically. The herbicide area increased by 12% while the weight of active ingredient decreased by 47%, reflecting the same trends of reduced rates and more effective products as in cereals.

Potatoes

The area of potatoes remained static between 1988 and 1992 and there was a trend towards increased unit size with a greater concentration on irrigated

***Table 1.1** Changes in Great Britain agricultural pesticide use and crop area 1988-92: cereals, oilseed rape and potatoes*

	Cereals		**Oilseed Rape**		**Potatoes^A**	
	1988	**1992**	**1988**	**1992**	**1988**	**1992**
Crop area '000 ha	3,840	3,433	346	420	168	169
Insecticide						
Area treated '000 ha	1,282	2,305	260	463	143	340
Active ingredient used (t)	311	194	51	17	122	223
Fungicide						
Area treated '000 ha	7,978	10,033	415	506	851	1,123
Active ingredient used (t)	4,462	3,605	352	442	996	1,319
Herbicide						
Area treated '000 ha	7,970	7,276	718	808	256	355
Active ingredient used (t)	10,361	6,618	688	368	249	316

^{A} : Potatoes are not grown at ADAS Rosemaund, but are a locally important cash crop.
Source: MAFF Pesticide Usage Survey Reports

lighter textured soils. Despite the static area, the area and active ingredient of insecticide increased by 137% and 82% respectively. The pattern for fungicides was similar, with increases of 38% and 32% for areas sprayed and active ingredient respectively. Herbicides likewise increased by 38% for area sprayed and 27% for active ingredient. Desiccants, mainly sulphuric acid, increased to a lesser extent by 16% area and 9% weight of active ingredient. It is interesting to note that by weight of active ingredient, sulphuric acid accounts for 83% of total pesticide use in potatoes and 36% of total pesticide use across all arable crops!

This general increase in pesticide use in potatoes, contrary to the trend in combinable crops, is probably explained by the concentration of the crop into the hands of large specialist growers with closer rotations and a higher level of input to achieve the yield and quality necessary for a premium in the market place.

Therefore, these crops illustrate a general decrease in the tonnage of pesticide applied to agricultural land in recent years. However, this will not necessarily result in reduced environmental impact. Whether the lower load of pesticides of greater activity now applied will result in more or less biological damage cannot yet be estimated. The regulatory process for pesticide registration and management (see Section 6) should continue to reduce the environmental impact of available pesticides, but it is also worth noting that a greater area of agricultural land now receives pesticide applications (Table 1.1). Potentially this may mean that a greater proportion of drainage water from agricultural land may be contaminated with pesticides, albeit at a lower concentration.

The prime purpose of this project was therefore to provide reliable field data on the transport of pesticides from a 'worst case' catchment into a headwater stream. The experiments were designed to provide data to validate predictive models of the pesticide transport process. A secondary objective was to use bioassays to assess the potential impacts of such transport on the aquatic environment.

2 Methods

2.1 Study Site

The study catchment lies mainly within the boundaries of ADAS Rosemaund 15 km north-east of Hereford, UK (Figure 2.1). The farm is owned by the Ministry of Agriculture Fisheries and Food (MAFF), operated by ADAS and has been managed as an experimental unit since 1949. The catchment has an area of 1.5 km^2 with an altitude range of 76 m to 115 m and correspondingly gentle slopes. The soils are from three series, the Bromyard, the Middleton and the Compton, and have been mapped and analysed by the Soil Survey and Land Research Centre (SSLRC), (Figure 2.2). The field work for this study was presented in an interim report (Carter and Cope, 1990). The Bromyard series comprises two phases, the normal and the shallow phase, differentiated by the depth to the underlying geology. The Bromyard series predominates and is found on the slope areas of the catchment. The wetter Middleton and Compton series tend to occur on flatter ground and towards the lower end of the slopes. Details of the soil textures of the four main series are given in Table 2.1. Generally, the soil texture is silty clay loam or silty clay. All soils are subject to considerable cracking following periods of low rainfall during the summer months. The organic matter content of the surface 25 cm cultivated layer under long-term arable cropping is within the range 1-3 percent with little organic carbon present below 35 cm. The geology is effectively impermeable siltstones and mudstones from the Devonian era which lie between 1 m and 3 m below the surface, with alluvium in the valley bottom.

The land within Rosemaund Farm is used for a wide mixture of agricultural enterprises. Of the 176 ha, approximately 30% of the area is grassland, another 40% of the farm is in cereals with 20% in oilseed rape, peas and root crops and 10% is in hops. The average annual rainfall is 664 mm. The catchment is drained by a single stream that continues to flow (mean flow 11 l s^{-1}) in all but the driest years. The stream flows into the River Lugg, a major tributary of the River Wye. Most of the fields have been under-drained using plastic pipes at a depth of 1 m, with permeable backfill to within 500 mm of the surface. The average drain spacing is 20 m (Figure 2.3).

2.2 Sampling strategy

The original objective of the study was to monitor the pesticide transport from an agricultural catchment under conditions of normal agricultural practice. A monitoring site was chosen close to the point where the stream left the land farmed by ADAS Rosemaund in order that as much of the

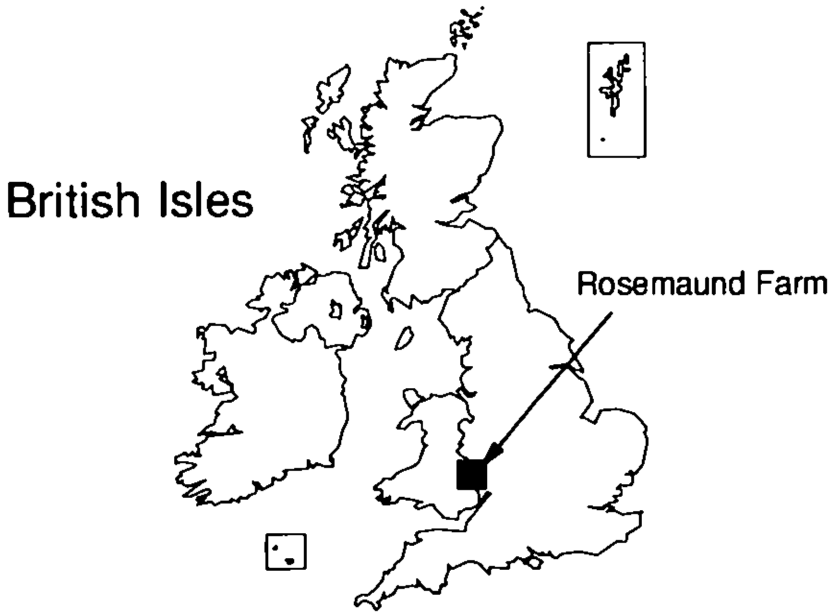
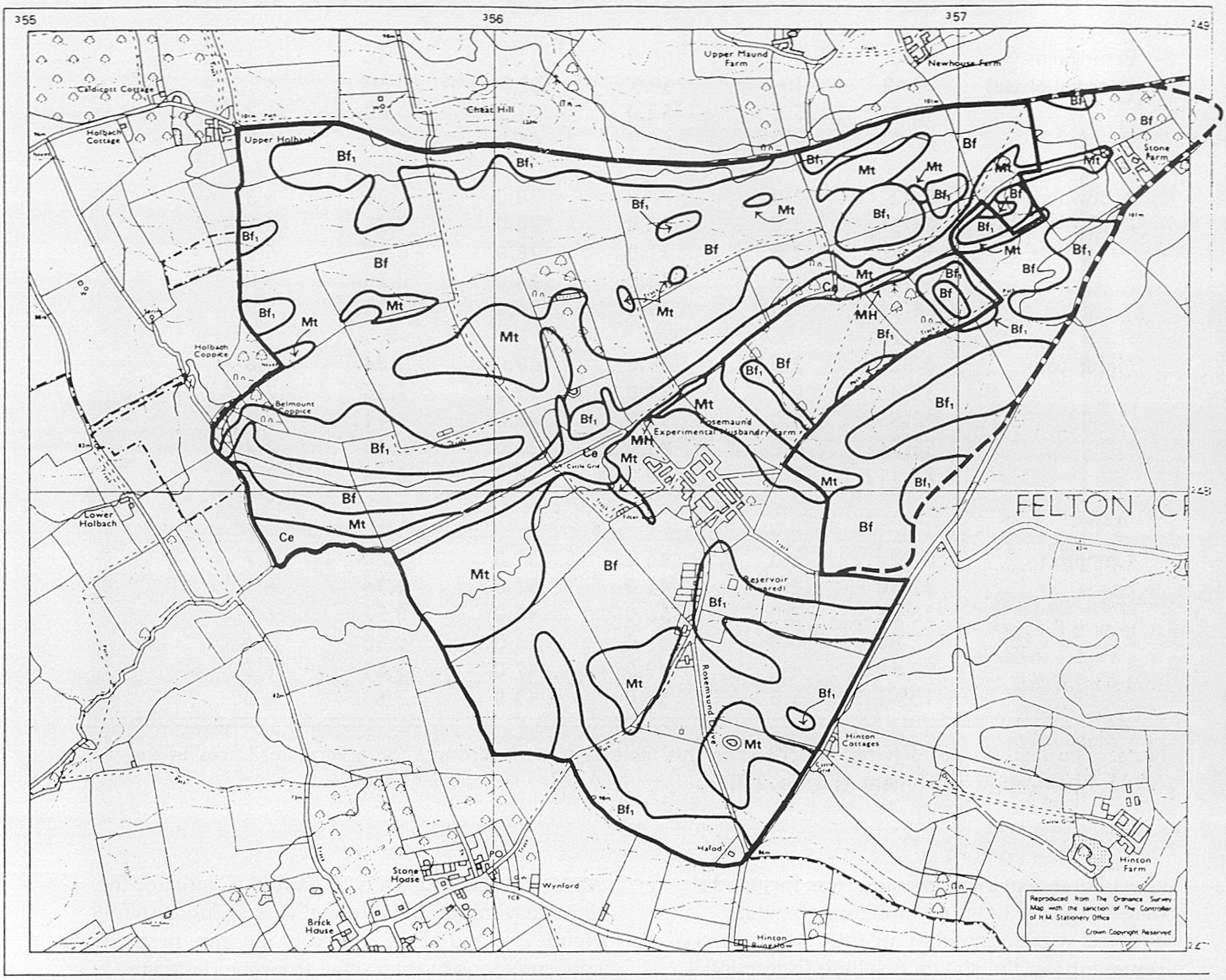


***Figure 2.1** Location of the Rosemaund catchment within the British Isles*

The Soils of Rosemaund Catchment, Worcester and Hereford

Soil map and accompanying report by Soil Survey and Land Research Centre



Head of the Soil Survey and
Land Research Centre: P. Bullock,
Map drawn by the Cartography Dept.,
Soil Survey and Land Research Centre

CONVERSION SCALE

Feet 500 0 500 1000 2000 Feet 1 foot = 0.3048 metre

Metres 100 0 100 500 Metres 1 metre = 3.2808 feet

SSLRC

Symbol	Soil series	Topsoil characteristics	Subsoil characteristics	Soil water regime
Bf	Bromyard	Stoneless silty clay loam	Permeable stoneless reddish silty clay loam passing to soft blocky reddish and greenish grey siltstone and mudstone at about 55 cm depth	Slight seasonal waterlogging. Upper subsoil is wet for short periods during winter and early spring. Possibility of by-pass flow and surface runoff
Bf$_1$	Bromyard (shallow phase)	Stoneless silty clay loam	Permeable stoneless reddish silty clay loam over soft blocky reddish and greenish grey siltstone and mudstone at about 35 cm depth. Locally over harder siltstone or sandstone	
Ce	Compton	Stoneless silty clay loam	Deep moderately permeable prominently mottled stoneless reddish alluvial clay	Waterlogged for most of the winter and spring by fluctuating groundwater
MH	Mathon	Stoneless silty clay loam	Deep moderately permeable slightly mottled stoneless reddish alluvial silty clay loam	Waterlogged for part of the winter and spring by fluctuating groundwater
Mt	Middleton	Stoneless silty clay loam	Moderately permeable slightly mottled stoneless reddish silty clay loam becoming slowly permeable below 70 cm depth	Slight seasonal waterlogging. Subsoil is wet for short periods during winter and early spring. Possibility of by-pass flow but less risk of surface runoff

▬ Rosemaund Experimental Husbandry Farm boundary

- - - Watershed above the farm

Figure 2.2 *Map showing the distribution of the main soil series at ADAS Rosemaund*

***Table 2.1** Physical properties of the soil profiles for the soil series found at ADAS Rosemaund (Carter and Beard, 1992)*

Soil series	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Organic carbon(%)	pH(1:2.5) in water
Bromyard (Normal phase)	0-30	9.0	60.0	31.0	1.66	6.3
	30-48	10.0	58.0	32.0	0.91	6.8
	48-67	5.0	52.0	43.0	0.66	6.7
	67-83	4.0	50.0	46.0	0.37	6.7
Bromyard (Shallow Phase)	0-22	1.0	70.0	28.0	1.80	6.3
	22-31	3.0	66.0	30.0	1.35	6.5
	31-60	3.0	71.0	28.0	0.30	6.2
	60-78	1.0	73.0	26.0	0.28	5.8
	78-112	1.0	79.0	20.0	0.29	5.8
Middleton	0-32	3.0	49.0	48.0	2.84	6.6
	32-40	0.0	51.0	49.0	1.56	7.0
	40-55	0.0	52.0	48.0	1.11	7.3
	55-74	0.0	68.0	32.0	0.62	7.2
	74-112	2.0	60.0	38.0	0.48	7.1
Compton	0-22	3.0	46.0	51.0	3.30	6.7
	22-30	2.0	45.0	53.0	2.34	6.9
	30-65	2.0	56.0	42.0	0.57	6.9
	65-80	0.0	47.0	53.0	0.88	7.1
	85-105	4.0	49.0	47.0	5.51	6.5
	105-115	5.0	52.0	43.0	7.63	6.3

Note: The Mathon series is not described in this table as it only accounts for a very small area in the ADAS Rosemaund catchment (Figure 2.2)

agricultural activity as possible was included (Site 0, Figure 2.4). The monitoring strategy adopted was designed to measure pesticide concentrations in the stream resulting from rainfall events falling on recently treated fields within the catchment. Thus an automatic sampler was used to take a series of water samples at short intervals (usually one hour but intervals of half an hour and four hours were also used) over the duration of rainfall events. In order that these concentrations could be linked to the hydrological response of the catchment, a flow measuring structure was built in the stream at the monitoring site. Stream samples were also taken manually every two weeks to assess the baseflow concentrations before and after rainfall events. At around the same time MAFF established a similar monitoring site and sampling protocol further upstream (Site 1, Figure 2.4).

Later in the study, as the emphasis shifted more towards understanding the processes that control pesticide movement, additional monitoring sites were established. The new sampling sites were chosen to represent the plastic pipe drainage system that existed in the majority of the fields at ADAS Rosemaund. Thus IH started to monitor the drain leaving the field known as Longlands (Site 5, Figure 2.4) and MAFF started to measure pesticide concentrations in the outfall from the drainage system under part of the fields known as Foxbridge, Stoney and Brushes (Site 3, Figure 2.4).

Additionally, SSLRC soil suction samplers were deployed within Longlands field to estimate the pesticide concentration in solution at different depths through the profile. Throughout the study soil samples were taken, by BRE, from Foxbridge, Longlands, Stoney and Brushes following selected applications so that total soil residues could be monitored.

In the final phase of the study, an investigation of the particulate movement of pesticides was undertaken for highly-sorbed chemicals. Four surface transport traps were located in Longlands field to monitor surface movement of pesticide during rainfall events. Additionally, sediment traps were placed in the stream bed at Site 1 and Site 0 to measure the concentration of pesticide in bed sediments mobilised during rainfall.

Plate 1 *The stream at ADAS Rosemund*

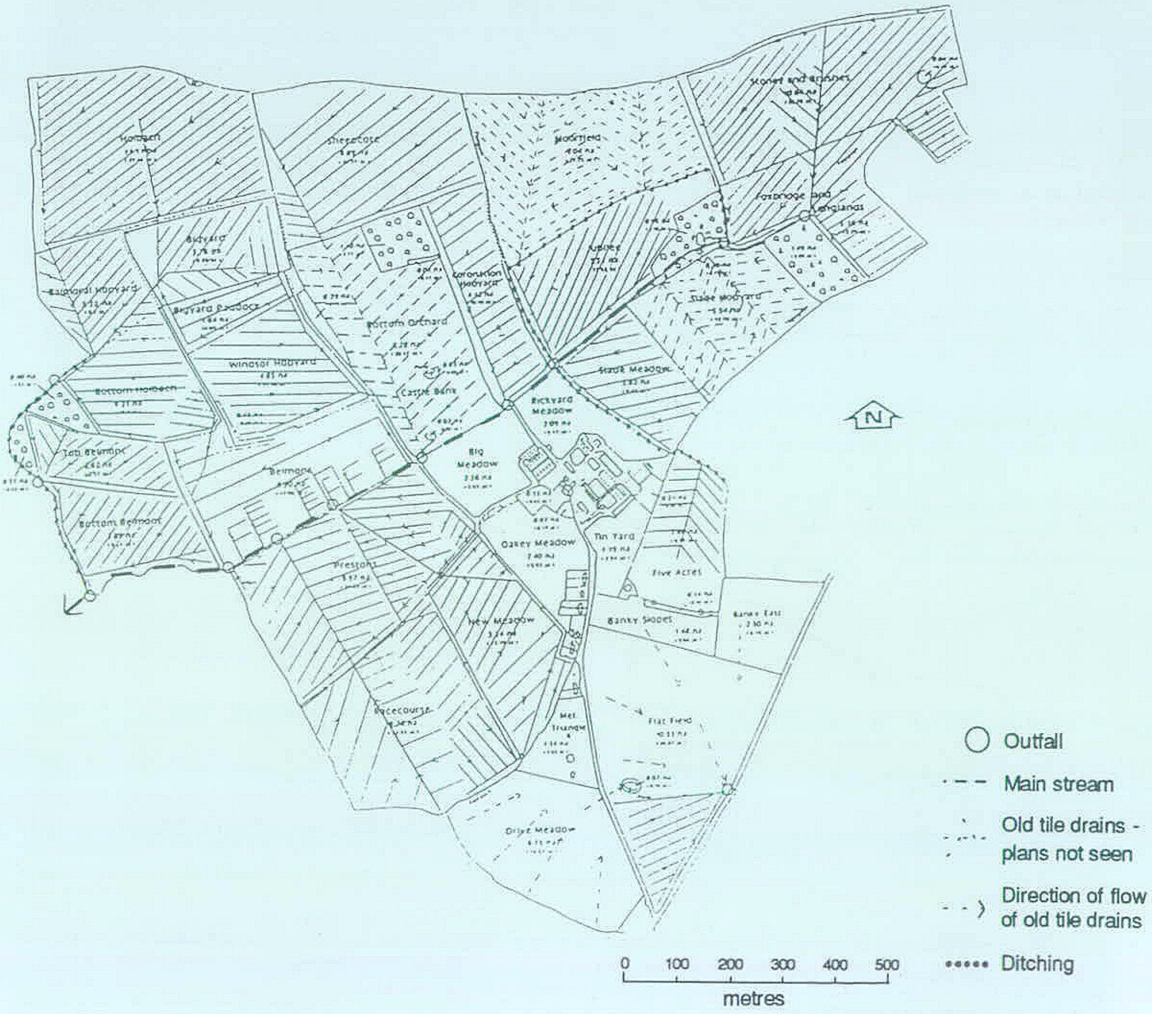


Figure 2.3 *Map showing the extent of the sub-surface drainage system at ADAS Rosemaund*

To summarise, within the catchment four water monitoring sites were instrumented. At each site flow-rate was measured continuously. Water samples for pesticide residue analysis were taken at frequent intervals during rainfall events following pesticide application and less frequently between events. Total soil residues were monitored following application, as was the soil water pesticide concentration at different depths.

2.2.1 Stream flow measurement and meteorological data

Stream flow was calculated from the stream level retained behind standard V-notch and rectangular notch weirs as appropriate, the stream level being recorded at 15 or 30 minute intervals (Matthiessen *et al.*, 1992). Drain flow was measured using drainflow weirs (Plates 2 and 3) designed and installed by ADAS Soil Water Research Centre (formerly Field Drainage Experimental Unit).

The primary source of meteorological information used in the study was an IH Automatic Weather Station (AWS) (Strangeways, 1972; 1976). This instrument takes readings every 5 minutes and averages or sums them to provide hourly values of the following variables:

- Rainfall;
- Wet and dry bulb temperature;
- Solar and net radiation;
- Wind speed and direction;
- Soil temperature.

ADAS Rosemaund staff maintain a full daily Meteorological Office weather station and this provided a backup system for the AWS. The AWS was located within the Meteorological Station site (Figure 2.4).

2.2.2 Pesticide sampling

Water samples

Water samples were taken from Sites 0, 1, 3 and 5 as shown in Figure 2.4. At all locations, water samples were taken during rainfall events and background samples were taken for a limited time before and after the rainfall events. The method of sampling was similar at all sites. Rainfall event samples were collected using two types of automatic water samplers: a suction sampler and a peristaltic pump sampler. Each sampler collected samples into 24 one-litre brown glass bottles. To minimise the risk of contamination and/or loss of active ingredient, the sample tubes were made from PTFE and the internal parts of the samplers were almost entirely constructed from stainless steel or coated with PTFE. Up until June 1988 the samplers were started when a predetermined amount of rain had fallen in a given time. After that date a method was used that started the sampler when the stream rose to a specified level. This proved to be a more reliable method.

Soil samples

Soil samples were taken from the fields onto which the pesticides had been applied. They were taken from randomly chosen points on the intersection of a 25 m grid superimposed on the fields. Samples

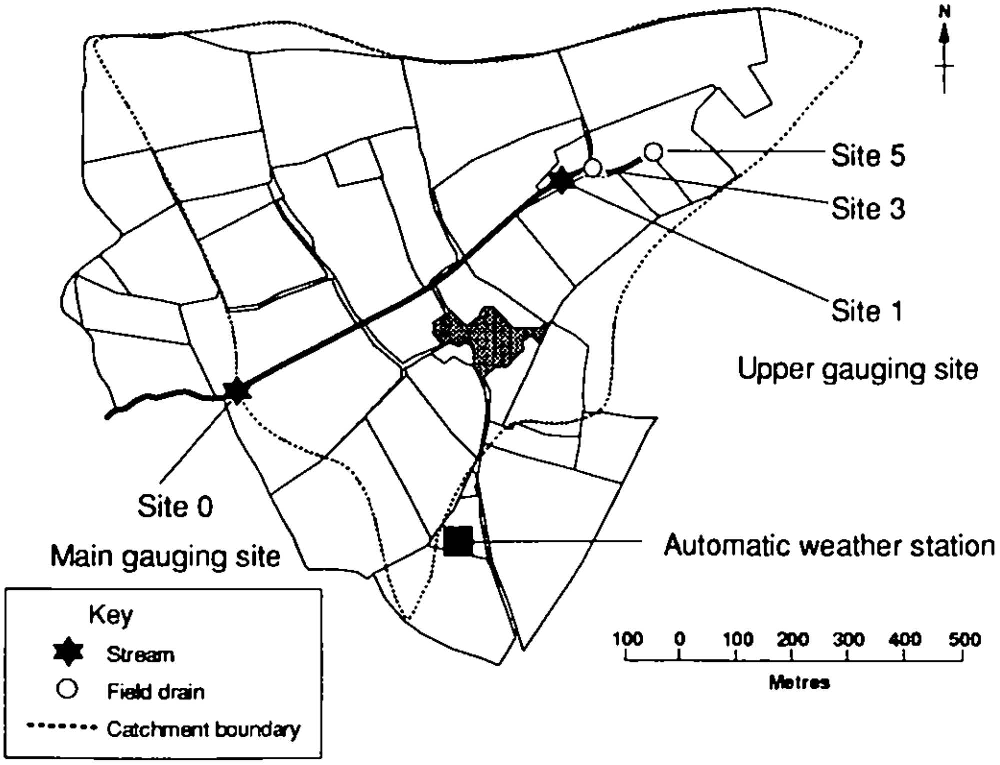


Figure 2.4 *Location of monitoring sites within ADAS Rosemaund*

Plate 2 *A gauging weir at low and high flow, at Site 5, ADAS Rosemaund*

were taken to a depth of 1 m using a steel corer. Cores were placed in plastic bags, sealed, and then stored at -20°C until analysed. The frequency of sampling was based on the expected lifetimes of the chemicals in the soil. In addition, samples were taken as soon as possible following a rainfall event. In all cases samples were taken to give a mean soil pesticide concentration in the top 1 or 0.25 m of the soil.

Soil water samples

Soil water samples were collected by SSLRC using soil suction samplers constructed of inert material designed specifically for pesticide studies. The design of the samplers is shown in Figure 2.5. Samplers were installed at 50, 100 and 150 cm depths at various locations in Longlands (Figure 2.7) throughout the 1989/90, 1990/91 and 1991/92 seasons. Each sampling location had a number of replicate samplers. Each sampler was installed in the following manner. A 10 cm diameter hole was augured to just below the required monitoring depth and the bottom was lined with dry sand. The sampler was placed on the centre of the sand with the mid-point of the cup at the required depth. Further sand was poured in to pack around and cover the ceramic cup. Sand is used to ensure good hydraulic contact and also as a reservoir for percolating water. Excavated soil was firmly repacked horizon by horizon and the most clayey horizon

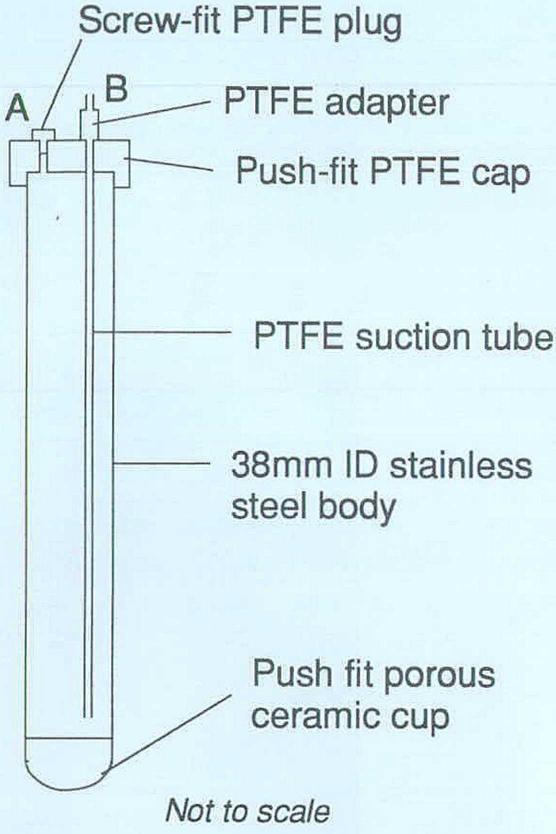


Figure 2.5 *Detail of an SSLRC soil suction sampler used for extracting soil water samples (Carter and Cope, 1990)*

Plate 3 *Soil sampling at ADAS Rosemaund*

was compacted in the hole to prevent preferential vertical water movement to the ceramic cup. In the last two seasons Bentonite clay was also used as an extra guarantee.

The sampling strategy for the suction samplers was to respond to all events of 10 mm or greater falling after application of the target pesticide. A vacuum of 700 mbar was applied to each sampler using a hand-held pump. The suction was left on over night and the water drawn to the sampler was recovered the following day and transferred to amber glass bottles. Any residual suction in the samplers was noted on collection of the sample.

Surface runoff samples

Surface runoff samples were collected using SSLRC surface runoff traps (Figure 2.6). The traps were 1 m wide steel troughs with three short pipes protruding from one side, while the other side was sloped with a 10 cm wide lip. The sampler was placed into a hole in the soil with the sloping side placed facing up-slope and the lip inserted into the soil at a depth of about 1 cm. A lid was placed over the trough to stop direct capture of rainwater. Brown glass bottles were placed on the ends of the pipes to collect the water trapped by the sampler. After a rainfall event the bottles were collected and replaced with new ones. The contents of the three bottles were combined before being analysed for the target pesticide.

Bed sediment samples

The sediment sampler buckets (manufactured from PTFE-coated stainless steel) were located in pits dug in the stream bed. These were of such a depth that approximately 2.5 cm of the bucket wall protruded above the stream bed. This method was used to trap only the mobile bed sediments that settled out during or after events.

After each rainfall event the buckets were removed carefully from the stream-bed with as little disturbance as possible to the collected sediment and moved to a safe site. A new clean bucket was used to replace the old one in the pit, again ensuring the minimum disturbance to the site. If, in the moving of the bucket, there was disturbance of the collected sediment, the sediment was allowed to settle before further processing. With the sediment stable and settled, surplus water was decanted off until the sediment itself started to be disturbed. The sediment was then poured into the sample bottles (0.5 l wide-mouthed jars). Any remaining sediment was 'swept' into the bottle, using a PTFE spatula. The bottles were sealed and labelled.

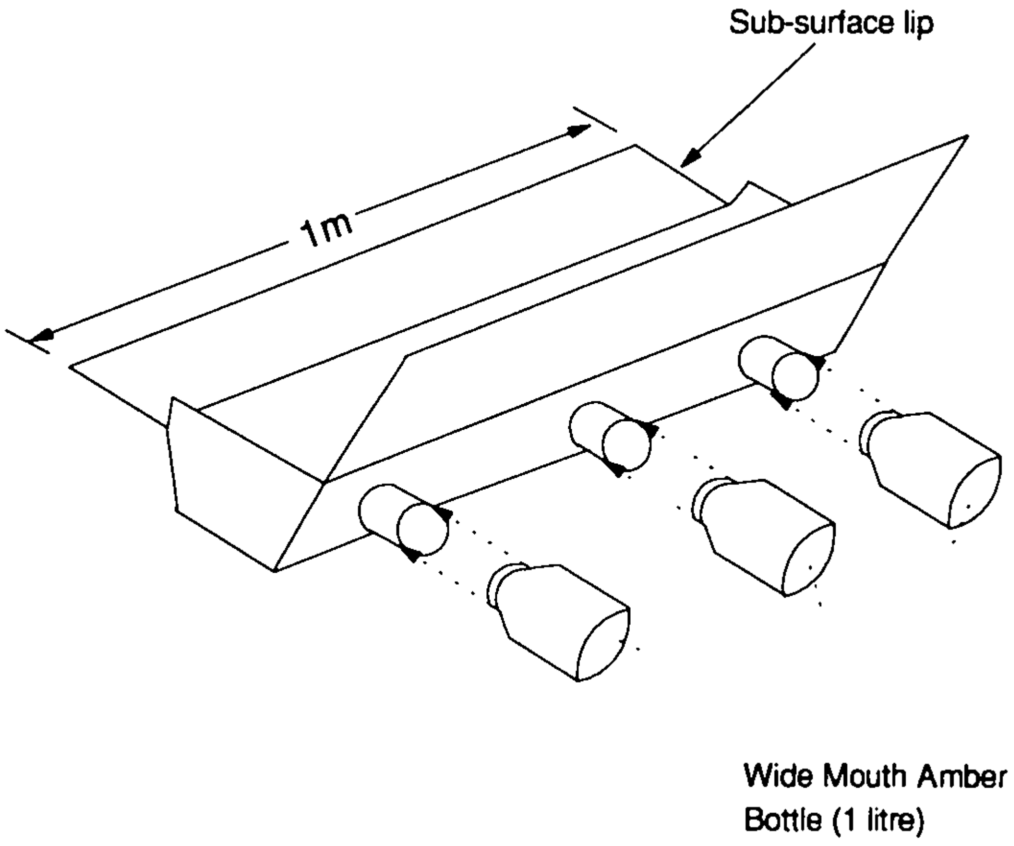


Figure 2.6 *Detail of a surface runoff interception trap*

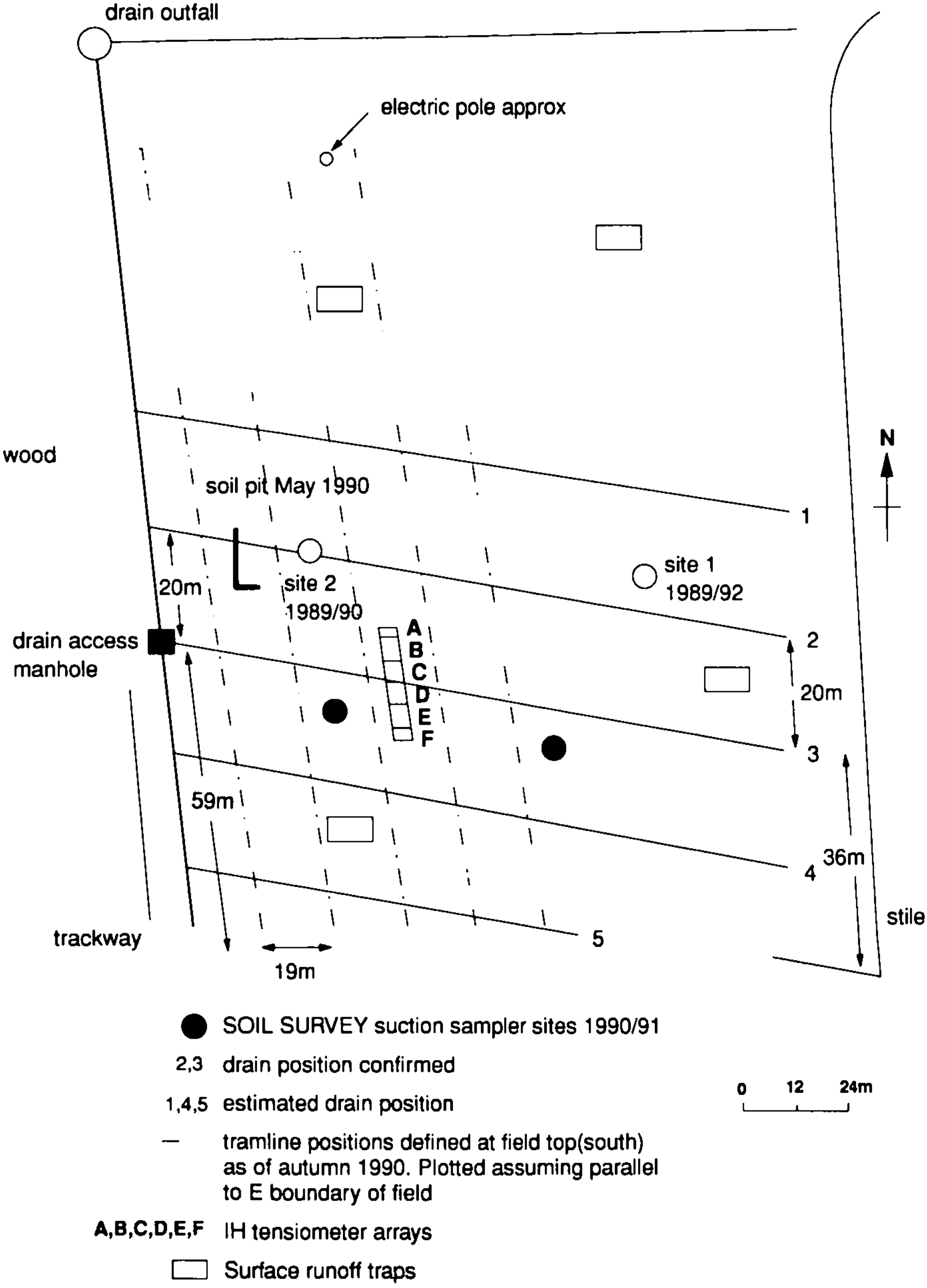


Figure 2.7 *Layout of instrumentation in Longlands field over the duration of the study. The exact location of some equipment will have changed from year to year.*

2.2.3 Soil hydrology

The soil hydrology experiments at Rosemaund started in the autumn of 1989 and continued for three crop years ending in the summer of 1992. The objective of this part of the study was to gain an insight into the soil water pathways through and over the soil profile and how these might influence pesticide movement. Once determined, these pathways would become the foundation for a physically based model of pesticide movement within the Rosemaund catchment.

The soil-physics experiments were carried out in Longlands field. Figure 2.7 shows the location of the experiments over the duration of the study. Although the detail of the experimental design was modified and refined throughout the three years of the study, the basic philosophy remained the same. Arrays of mercury manometer tensiometers were used to determine the soil water potentials, both down the soil profile and across the slope of the field. Soil water contents were also measured using a neutron probe. In the light of the importance of the tile drainage system on water movement, the final experimental design concentrated on the soil water potentials around a representative drainage element. Figure 2.8 shows the layout of tensiometers used in the 1990/91 crop season. Soil water potentials were monitored within a vertical plane extending 10 m on either side of the line of a field drain to the mid-drain position. An array of tensiometers was set out as six profiles, each of six tensiometers, at depths 10, 30, 60, 90, 120 and 150 cm.

Since water moves from high potential to low potential, knowledge of the potential field around a representative drainage element allows the direction of water movement to be determined. If the moisture content of the soil is measured at the same time at the depth of the tensiometers, then soil water release curves can be drawn for each of the soil depths. These curves then give the water storage capacity, and some idea of the pore size distribution of the soil.

2.2.4 *Gammarus pulex* and *Chironomus riparius* bioassays

During a few experiments at Rosemaund (dichlorprop in 1990; carbofuran in 1992; chlorpyrifos in 1993), individually caged specimens of a common amphipod crustacean *Gammarus pulex* were placed in the stream at Site 1 in order to monitor the effects of transient pesticide contamination by measuring mortality and feeding rate during and after rainfall events (Plate 5). The methods used are described in Maltby *et al.* (1990 a and b) and Matthiessen *et al.* (1995), and involved placing approximately 100 *G. pulex* in the stream for periods of several weeks and measuring their rate of consumption of conditioned alder leaf discs.

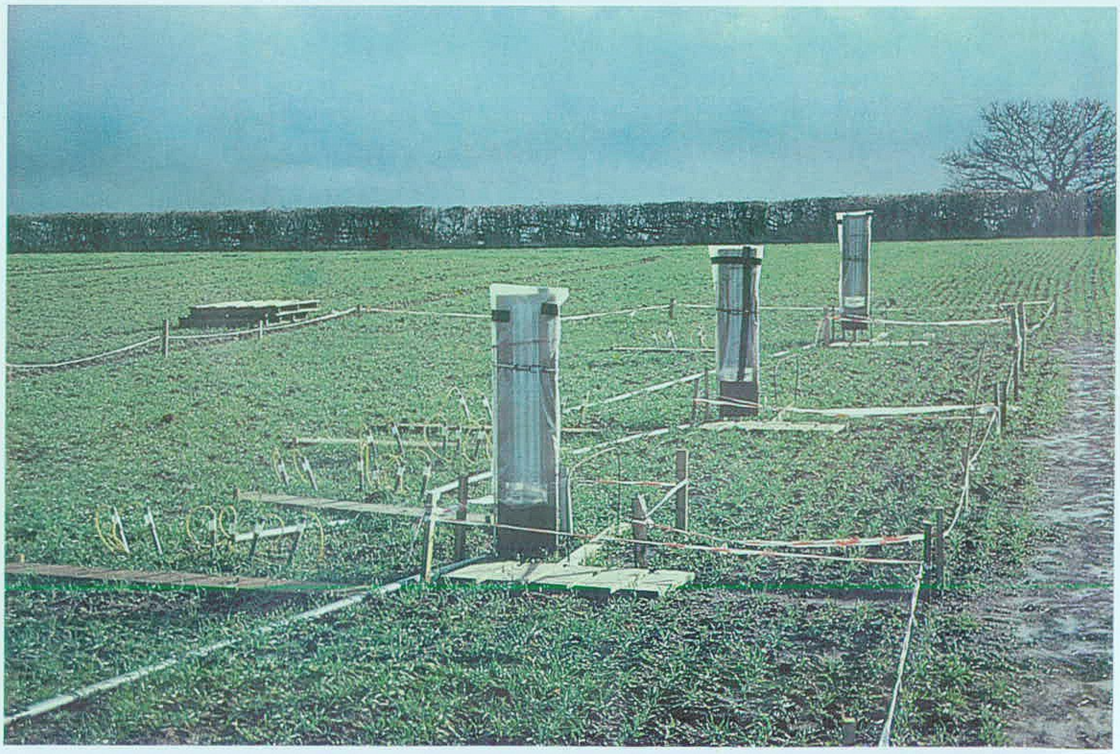


Plate 4 *An array of mercury manometer tensiometers used to investigate the soil hydrology at ADAS Rosemaund*

Each 50 mm diameter PVC cage was oriented parallel to the stream flow with mesh covering the upstream and downstream ends, and contained one 44 mg adult animal and four 1.5 cm diameter leaf discs. The cages were inspected weekly for mortalities, and for replacement of leaf discs; any remaining leaf material was weighed. Water temperature and dissolved oxygen were monitored continuously during the bioassay deployments.

After the deltamethrin application in December 1992, deposited sediments (surface 2 cm) were collected from the stream in the vicinity of Site 1, and from the flow gauging chambers at Sites 3 and 5, and subjected to sediment bioassays using larvae of the midge *Chironomus riparius*. These bioassays measured growth of 20 2nd instar larvae exposed to 150 cm^3 of sediment at 20°C over a 10-day period. The larvae were fed at three-day intervals, and their guts were purged for 24 h prior to weighing. Full methods are described in ASTM (1993).

2.3 Pesticides studied

In a typical agricultural enterprise large numbers of different pesticides are used in the normal run of crop production. This is particularly true of a Research Centre such as ADAS Rosemaund, where a great number of field experiments are undertaken. It was not practicable to consider carrying out analyses for every pesticide applied and a decision was made, in principle, to concentrate on four chemicals each year, two in autumn and two in spring. A likely list of pesticides was drawn up at the start of the study by the collaborators, using the following criteria:

- Include some of the most commonly used pesticides,
- Choose pesticides that represent a range of the chemical groups,
- Pesticides chosen should have a range of physico-chemical properties,
- Analytical methods should be available for low concentration determinations,
- Application rates should be sufficiently high that if transport occurred environmental residues would probably be at detectable levels,
- The chemicals must be appropriate for the normal crop rotation employed at ADAS Rosemaund.

The chemicals chosen for each year of the study, including comments on the reasons for the choices made, are given in Table 2.2. Some chemicals were monitored in more than one crop year, most notably isoproturon and simazine. This was done primarily in order to build up experience with individual chemicals under changing hydrological conditions. Isoproturon was of interest because of its large usage and its increasing occurrence in

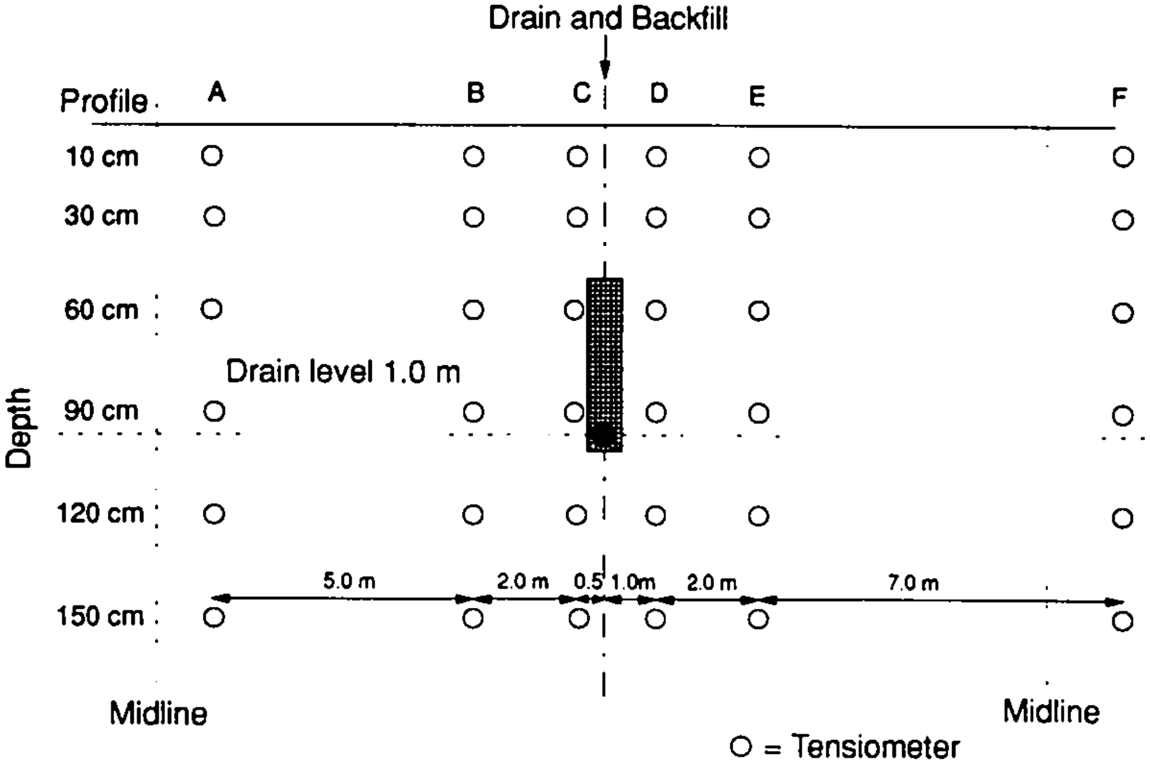


***Figure 2.8** Diagrammatic representation of the tensiometer array (vertical section) placed along a representative drainage element in Longlands Field*

Plate 5 *Gammarus pulex specimen and cage used during the bioassay experiments*

Plate 6 *Application of a pesticide during the ADAS Rosemaund study*

Table 2.2 Chemicals monitored during the Rosemaund Pesticide Transport Study

Cropping year	Season	Pesticide	Comments
1987/88	Autumn	Mecoprop, Dicamba, 2,4-D	Phenoxy acids, low sorption, mecoprop widely used.
	Spring	Simazine[A]	Triazine herbicide, moderately sorbed and persistent
1988/89	Autumn	Simazine, Triclopyr[B], 2,4-D[B]	Triclopyr pyridyloxy herbicide (in the 2,4-D formulation)
	Spring	Simazine[A]	
1989/90	Autumn	Isoproturon[B], Lindane	Isoproturon (urea herbicide) widely used. Lindane (organochlorine insecticide) persistent and sorbed.
	Spring	Mecoprop[B], Dichlorprop[B]	Dichlorprop phenoxy herbicide.
1990/91	Autumn	Isoproturon, Dimethoate, Simazine	Dimethoate, organophosphorus insecticide with short half life and low sorption.
	Spring	MCPA[B], Oxydemeton-Methyl, Simazine	Oxydemeton organophosphorus insecticide
1991/92	Autumn	Atrazine, Carbofuran	Carbofuran and aldicarb, carbamate insecticides.
	Spring	Aldicarb, Simazine[A], Atrazine	
1992/93	Autumn	Trifluralin, Isoproturon, Deltamethrin	Trifluralin (dinitro aniline herbicide) and Deltamethrin (pyrethroid insecticide) both strongly sorbed[C].
	Spring	Fenpropimorph, Chlorpyrifos	Morpholine fungicide and organophosphorus Insecticide both strongly sorbed.

[A] Only analysed by IH/NRA
[B] only analysed by MAFF (University of Birmingham)
[C] Sorption coefficient and half life are given in Table 2.3

surface waters. Simazine, although not a widely used chemical agriculturally, is used annually at Rosemaund on hops and is easily analysed. Some key physico-chemical properties of the chemicals included in Table 2.2 are given in Table 2.3. Finally, it should be noted that not all the chemicals listed in Table 2.2 were analysed by all the bodies involved in the study, usually because of either work load or because no established method was available at a given laboratory.

2.4 Pesticide analytical methods

The samples taken by the research institutes were analysed by different laboratories. These were generally in-house facilities or laboratories closely controlled by the main funding bodies. In the case of the soil samples these were contracted out to commercial laboratories. While each laboratory had its own detailed methods of analysis, these were based on the so called "Blue Book" methods, (Standing Committee of Analysts, 1985), and the principles of Good Laboratory Practice (GLP) were followed throughout. A summary of the methods employed by these laboratories for both soil and water samples is given in Tables 2.4 and 2.5.

Pesticide analysis at the low concentrations experienced in the environment is notoriously difficult and analysis being carried out by a number of laboratories is an added complication. In order to cross check between laboratories and hence to give more confidence in the use of the data as a whole, two inter-laboratory calibration exercises were carried out. The exercises involved only water samples and were organised by the Building

Table 2.3 Physico-chemical properties of the chemicals monitored during the course of the study

Chemical	Half Life (days)	K_{oc}[A] (ml/g)	Water solubility (mg/l)
Mecoprop	21.0	20.0	660000 (pH7)
Dicamba	14.0	2.0	400000
2,4-D	10.0	20.0	890 (as acid)
Simazine	60.0	130.0	6.2
Isoproturon	12.0-29.0[B]	130.0	65[B]
Triclopyr	46.0[B]	126.0[B]	8100 (pH7)[B]
Lindane	400.0	1100	7
Dichlorprop	10.0	1000	50
Dimethoate	7.0	20.0	39800
MCPA	25.0	20.0	866000 (pH7)
Oxydemeton-methyl	10.0	10.0	1000000
Atrazine	60.0	100.0	33
Carbofuran	50.0	22.0	351
Aldicarb	30.0	30.0	6000
Trifluralin	60.0	8000.0	0.3
Deltamethrin	2.0-5.0[B]	110000[C]	$<0.2\times10^{-3}$
Fenpropimorph	15.0-93.0	4715[C]	4.3 (pH7)
Chlorpyrifos	30.0	6070	0.4

[A] K_{oc} describes the distribution of a pesticide between the soil water and soil organic carbon phases. Values from Wauchope *et al.*, 1992 unless indicated

[B] Agrochemicals Handbook, 3rd Edition

[C] Calculated from Karichoff 1981, $K_{oc} = 0.41\ K_{ow}$, where K_{ow} describes the distribution of the pesticide between octan-1-ol and water (determined in the laboratory)

Research Establishment. The laboratories included were: University of Birmingham (MAFF samples); NRA Welsh Region (IH samples); IH and MAFF Pesticide Laboratory, Cambridge (first year only). The MAFF Cambridge laboratory was not involved in any Rosemaund analysis but was included as a well respected outside control.

The results of the exercises were generally satisfactory in that they showed an acceptable level of agreement between laboratories. The first exercise also highlighted an error in a method for mecoprop being used by one laboratory. Although an amended method proved to be satisfactory, it was not possible to reanalyse mecoprop samples taken during the 1990/91 season. Although a great deal of potentially interesting data was lost, at least wrong conclusions on mecoprop mobility were not drawn on faulty data. Details of the methods employed in the inter-calibration exercises and the full results can be obtained elsewhere (Hack, 1994).

2.4.1 Bed sediments

The bed sediments arrived at IFE River Laboratory frozen and were allowed to thaw. Coarse samples were sieved through a 2 mm stainless steel sieve. The samples were then frozen overnight and finally freeze-dried overnight. The samples were lightly crushed and stored under nitrogen gas in the dark at around 5°C prior to analysis. The samples were later extracted and analysed by standard procedures described elsewhere (House *et al.*, 1992; House and Ou, 1992).

2.4.2 Suspended solids

The water samples were stored in the dark at 5°C and separated as soon as possible by a procedure described previously (House and Ou, 1992). The pesticides in the water samples were extracted with dichloromethane (DCM). The suspended solids were collected on GF/F glass microfibre pads, nominally 0.7 µm pore size: the filters had been pre-treated to remove organic carbon by heating to 520°C overnight. The filters were placed in soxhlet extraction thimbles, frozen overnight and then freeze dried overnight prior to soxhlet extraction in DCM. The extracts were then concentrated by solvent exchange using the same methods employed for preparation of the bed sediments. All weights were noted to enable the calculation of the suspended solids concentration in µg l^{-1} in the aqueous phase and µg kg^{-1} (dry weight) for solids.

Table 2.4 Analytical methods used for soil samples during the study

Chemical	Extraction	Clean Up/Derivatisation	Quantitation method (final solvent)
Mecoprop	acidified, dichloromethane	reaction with BrPFT, extraction into *i*-octane	GC, EC detector (*i*-octane)
Simazine	water/methanol	acidified, hexane wash, extracted into dichloromethane	GC, NP detector (ethyl acetate)
2,4-D	methanolic sodium hydroxide	dichloromethane wash, acidified, extraction into dichloromethane, butylation, hexane extraction, silica gel column	GC, EC detector (trimethylpentane)
Isoproturon	acetone/water	hexane wash, extraction into dichloromethane	HPLC, UV detector (methanol/water)
Lindane	ethyl acetate/ hexane		GC, EC detector (hexane)
Dimethoate	chloroform		GC, flame photometric detector (toluene/trimethyl pentane)
MCPA	acidified, dichloromethane	reaction with BrPFT, extraction into *i*-octane	GC, EC detector (*i*-octane)
Atrazine	alkaline, ethyl acetate	dichloromethane extraction from sodium hydroxide solution	GC, NP detector (ethyl acetate)
Carbofuran	acetone/water		GC, NP detector (toluene)
Aldicarb	acetone/water with oxidising agent	partition into chloroform, Florisil column using ethyl acetate/hexane	GC, EC detector (toluene)
Trifluralin	methanol/water	diluted with sodium chloride solution, extraction into dichloromethane	GC, EC detector (toluene)
Deltamethrin	acetone/water	partition into dichloromethane, Florisil column using ethyl acetate/ hexane	GC, EC detector (toluene)
Chlorpyrifos	acetone/water	partition into dichloromethane	GC, flame photometric detector (toluene/trimethyl pentane)

Notes: GC = gas-liquid chromatography
EC = electron capture
NP = nitrogen-phosphorus
HPLC = high pressure liquid chromatography
BrPFT = α-bromo-2,3,4,5,6-pentafluorotoluene

Table 2.5 Analytical methods used for water samples during the study

Chemical	Laboratory	Extraction	Quantification method (final solvent)
Mecoprop 1987	NRA Welsh Region^	acidification then dichloromethane	GC, EC detector
	MAFF Burnham	acidification then dichloromethane	GC-MS
Mecoprop 1990	Birmingham Univ.	SPEC$_{18}$ cartridge	GC, UV detector (methanol/water)
Dicamba	NRA Welsh Region^	as mecoprop 1987	
	MAFF Burnham	acidification then hexane	GC, EC detector
2,4-D	MAFF Burnham	acidification then hexane	GC, EC detector
	NRA Welsh Region^	as mecoprop 1987	
Isoproturon	Birmingham Univ.	ammonia/ dichloromethane	HPLC, UV detector (acetonitrile/water)
	NRA Welsh Region	ammonia/ dichloromethane	HPLC, Diode Array detector (acetonitrile/water)
	IH	dichloromethane	HPLC, UV detector (acetonitrile/water)
Lindane	NRA Welsh Region	dichloromethane	GC-MS SIM (dichloromethane)
	Birmingham Univ.	hexane	GC, EC detector (hexane)
Dimethoate	Birmingham Univ.	HCl/dichloromethane	GC, NP detector (hexane)
	NRA Welsh Region	dichloromethane	GC-MS SIM (dichloromethane)
Simazine	NRA Welsh Region	ammonia/ dichloromethane	GC-MS SIM (dichloromethane)
	MAFF Burnham	dichloromethane	GC, N detector (methanol)
	IH	dichloromethane	HPLC or GC, UV detector (acetonitrile/water)
Triclopyr	MAFF Burnham	acidification then hexane	GC, EC detector
MCPA	Birmingham Univ.	SPEC$_{18}$ cartridge	HPLC, UV detector (methanol/water)
Atrazine	Birmingham Univ.	SPEC$_{18}$ cartridge	GC-MS SIM (ethyl acetate)
	NRA Welsh Region	ammonia/ dichloromethane	GC-MS SIM (dichloromethane)
	IH	dichloromethane	HPLC or GC, UV detector (acetonitrile/water)
Carbofuran	Birmingham Univ.	SPEC$_{18}$ cartridge	GC-MS SIM (ethyl acetate)
	NRA Welsh Region	dichloromethane	HPLC, Diode Array detector (acetonitrile/water)
Aldicarb	Birmingham Univ.	dichloromethane	HPLC, post-column derivitization, fluorescence detection. (methanol/water)
	IH	dichloromethane	HPLC, post-column derivitization, fluorescence detection. (methanol/water)
Trifluralin	Birmingham Univ.	hexane	GC, EC detector
	IH	dichloromethane	HPLC, UV detector (acetonitrile/water)
Deltamethrin	Birmingham Univ.	hexane	GC, EC detector
Chlorpyrifos	Birmingham Univ.	hexane	GC, EC detector
	IH	dichloromethane	GC, EC detector
Fenpropimorph	Birmingham Univ.	hexane	GC-MS SIM

Notes: GC = gas liquid chromatography
EC = electron capture
NP = nitrogen-phosphorus
HPLC = high performance liquid chromatography
MS = mass spectrometry
SIM = selective ion monitoring mode
SPE = solid phase extraction
^ = At the time the Welsh Water Authority

3 Results

3.1 Soil hydrology

The study of the soil hydrology of the Rosemaund catchment was a major piece of work carried out by the Agrohydrology Section of IH. Two unpublished reports have been written (Bell *et al.*, 1991; 1992) that give detailed information on the season by season changes in the soil water pathways as observed over the first two years of the study in Longlands field. A summary of the findings is given here as a help in explaining the results of the pesticide monitoring study (Section 3.2) and forming the basis of one of the pesticide models (Section 4.2).

3.1.1 Macropores

The hydrological role of macropores in these soils is crucial. Because the conductivity of the soil matrix is so low, it is the macropores that form the dominant flow pathways within the soil. A macropore may be defined loosely as a planar or tubular pore which traverses the soil and which is created by a secondary influence (e.g. earthworms). It may be 'blind', i.e. not joined to another macropore, or it may be part of an interconnected plexus; both have important roles in these soils. Being larger than most of the pores of the soil matrix (eg. anything from about 0.1 mm to 10 cm) these openings have the potential to conduct water freely but are only able to do so if the soil water potentials are very high (close to, or at, saturation) or if water, ponded elsewhere, is able to pour down them at a rate exceeding the ability of the adjoining matrix to absorb it.

A distinction needs to be made between two types of macropore. One type is created by the shrink/swell process, and varies in size and depth of penetration according to the soil water content. These largely (but perhaps not totally) close during winter with swelling of the soil. They form a pathway for rapid bypass flow at times where they are open, but only to saturated or quasi-saturated flow. Ponding of water somewhere in or on the soil profile is necessary before they conduct, but once such conditions are established, large amounts of flow can be accommodated, albeit for short periods. This flow may be downwards to feed the groundwater system where shrinkage cracks have penetrated to join the geological strata, or lateral 'interflow' down-slope to the valley bottom. These cracks form a considerable proportion of the volume of the dry soil, and they also act as a quick-fill reservoir to hold water and thus facilitate the re-wetting of the lower soil surface. The fate of pesticides in these two types of circumstance would differ considerably.

The second type of macropore is created by biological activity, mainly that of worms, but some are due to dead root holes. These seem to remain active throughout the winter period and provide the poorly conductive soil with an enhanced saturated conductivity, which it otherwise would not have. Worm activity is largely concentrated in the upper soil during winter and is probably responsible for such lateral flow as there is from the mid-drain zone towards the drains. It seems likely that the presence of the drains encourages worm activity in that zone, because of lower water tables and better aeration, and this may explain the differences in behaviour of the mid-drain zone and the drain zone.

3.1.2 Summary of the annual cycle

For simplicity the annual cycle has been divided into four stages: stage 1 will be referred to as 'the summer phase', stage 2 as 'the soil re-wetting phase', stage 3 as 'the drainage phase' and stage 4 as the 'crop abstraction phase'.

The summer phase

The summer phase is characterised by progressive downward drying of the soil as the rooting zone of the crop advances and demand for water increases. This is accompanied by development of an intricate network of shrinkage cracks, dividing the soil into irregular 'peds', 50-75 cm across.

The summer of 1990 was exceptionally dry and the cracks penetrated to at least 1 m, where they almost certainly became linked to the joint system in the underlying geological formation — soft, compact, blocky, silty mudstone. However, in wetter summers, this may not necessarily be so. When the soil re-wets, such cracks obviously re-swell and close, although not necessarily completely. The data taken as a whole suggest that residual cracks may persist throughout the entire winter, unless disturbed by ploughing, albeit at a much lower conductivity.

The soil re-wetting phase

In general, autumn re-wetting will be controlled by the timing and characteristics of autumn rainfall and by the timing of cultivation in relation to these. The re-wetting process will probably take one of two distinctly different forms:

(i) If there is little prolonged heavy autumn rain prior to cultivation, or if the preceding summer was so wet that shrinkage crack development was minimal, events will follow those of 1990/91, with the creation of a persistent wet layer overlying very dry soil. Autumn-applied pesticides will be introduced into the finer soil pores of this layer and subsequently would be expected to be less mobile, moving slowly by piston flows because of the poor conductivity of the actual soil. The duration of this stage will depend on the amount of rain.

(ii) If however, heavy rain occurs before cultivation early in autumn and is of sufficient intensity and amount for the dry soil to be unable to accept the influx, the resulting surface saturation will run down the cracks and wet up the entire soil profile within a few days. Water movement through the fissures will predominate. This water will go primarily to recharge the shallow aquifer of the underlying geological formation, but if the input rate is high enough, the water table will rise temporarily above drain level in the zone close to the drains, and may be sufficient to produce intermittent pulses of drain flow. It is possible that this is what was observed in the autumn of 1989, but the data set for that period is too limited to compare directly with the autumn of 1990.

The drainage phase

Once water tables have generally risen above drain level, normal drainage starts. Water percolates vertically down through the unsaturated zone until it meets the water table, after which it moves laterally as saturated flow, mainly via the macropores along the hydraulic gradient to the drain.

During this phase the vertical gradients of total potential below the water table are as close to zero as can be measured, so unless the saturated conductivity is very high indeed (unlikely) there is no further deep drainage at this stage. The only water movement is lateral, and that is entirely in the saturated zone, mainly via the various fissures and joints.

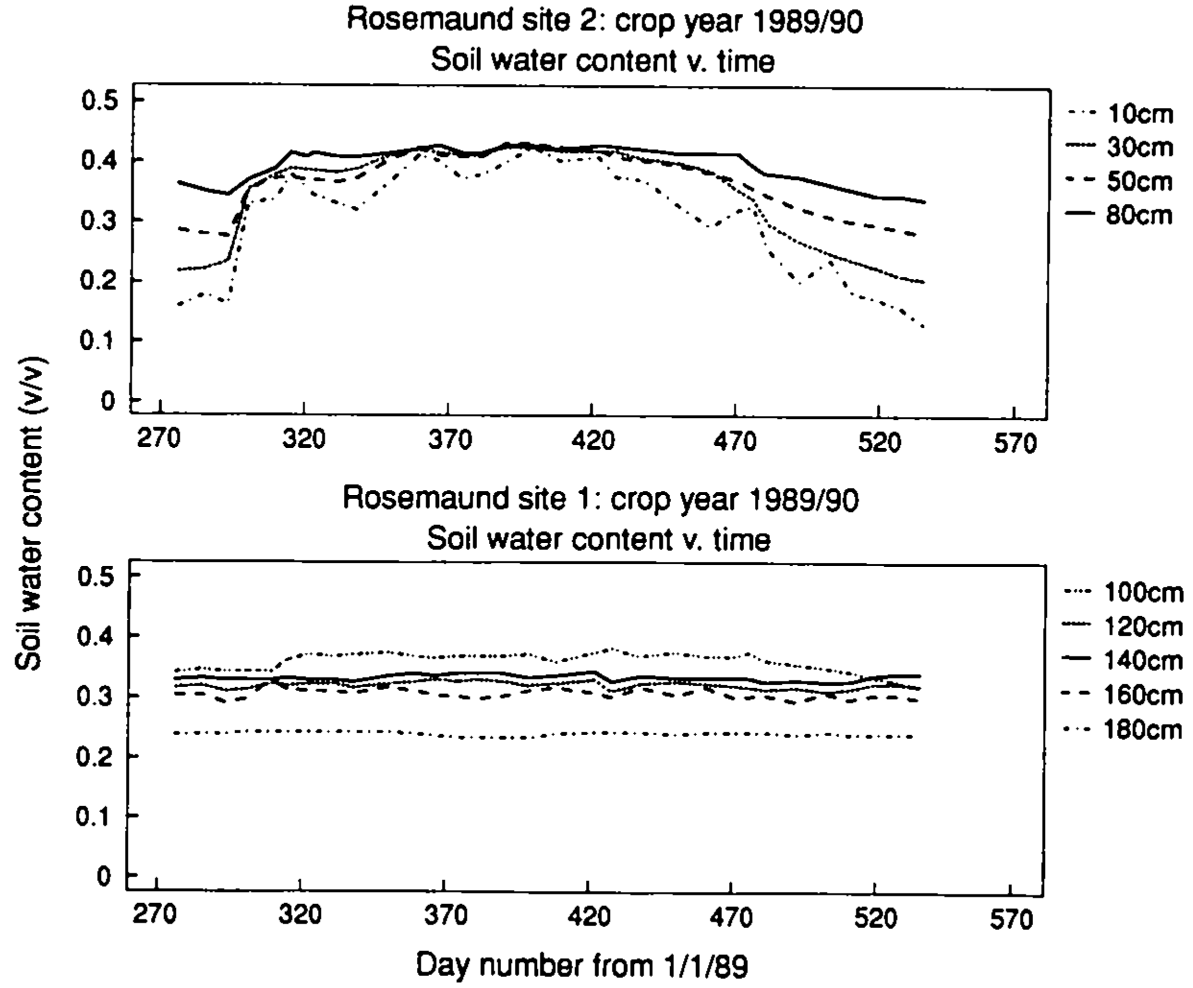


Figure 3.1 *Soil water content variation, 1989/90, for soil layer (0 to 80 cm) and geological material below (100 to 180 cm)*

The crop abstraction phase

In most years, by early April, the water demand of the crop starts to exceed the average rain input rate, so that the root zone starts to become drier and a zero flux plane develops beneath it. This zone of upward fluxing water encroaches downwards into the zone beneath as the roots advance and deplete the water reserves of the upper layers. This 'soil moisture deficit' acts as a barrier to further inputs of rain to the lower profiles, with the result that the water table recedes to below the drains level into the geological formation. Drainflow is impossible under these conditions and will not start again until the next winter. The cycle is completed with the return to the summer phase.

3.1.3 Down-slope saturated flow through the aquifer

Much of the saturated flow beneath the water table converges on the drain and soon exits at the outfall. However, it must be remembered that there is a topographic effect which has not yet been discussed. The Longlands field has an average slope of about 6%, and the water table overall can be expected to conform to this gradient, subject to localised troughs corresponding to the lines of the field drains. This implies that there will be an un-quantified but fairly constant lateral flow below drain level within the geological formation, presumably to exit as 'base flow' at the valley bottom.

While it seems that most of the conductivity of these soils and the underlying geology is derived from the cracks and joints, it must be noted that the water-holding capacity of these pathways is very small, probably much less than 1% of the soil volume. This is clear from the soil water content data of 1989/90, which show a marked difference between the soil of the upper metre and the geological material below 1 m (Figure 3.1). Thus, the velocity of the water passing through these pathways must be relatively high.

3.1.4 Summary of soil water pathways

Almost all the fields in ADAS Rosemaund are underdrained and therefore it is possible to generalise the observations made from the soil water in Longlands to the entire catchment. This is best done by considering a representative drainage element. This is the part of a field that extends from one mid-drain position to the next, a distance of 20 m. The component parts of this drainage

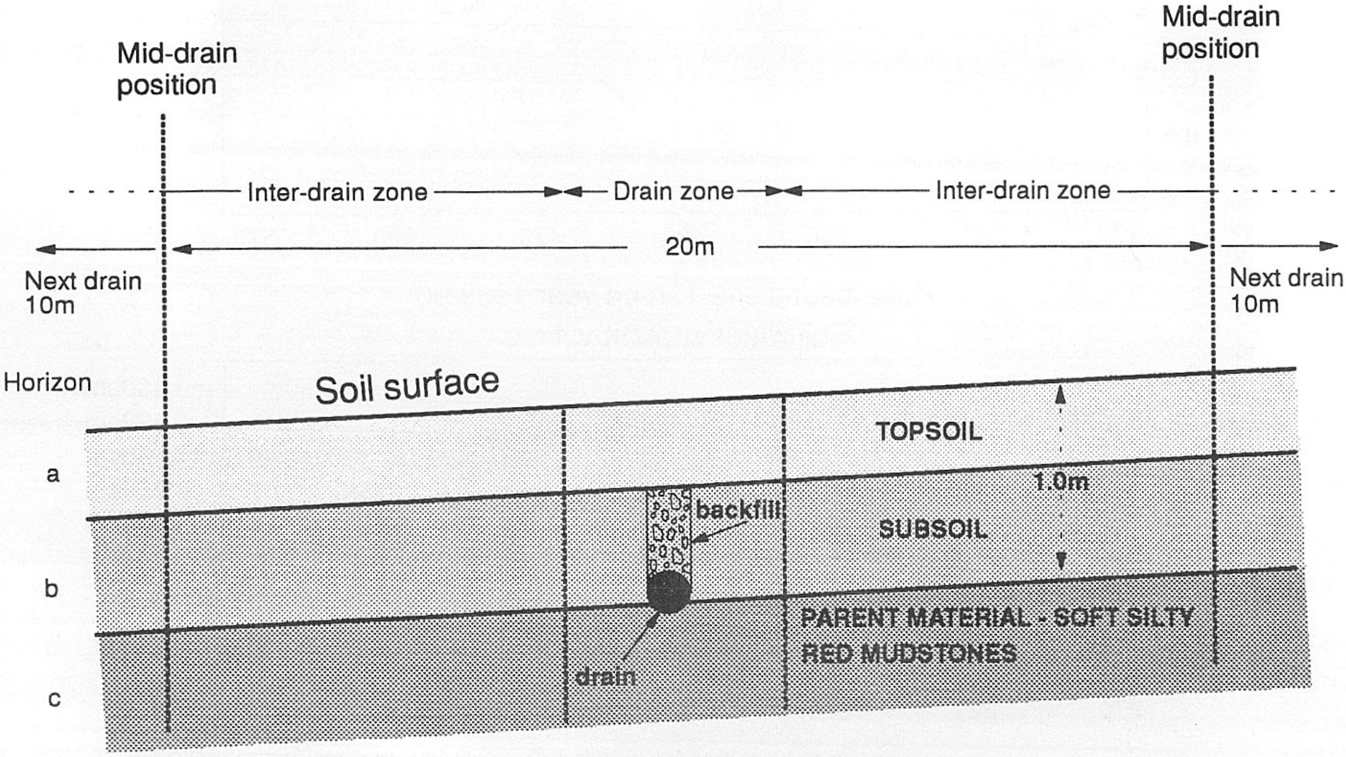


Figure 3.2 *The main features of a vertical cross-section through the main hydrological unit affecting soil water movement at ADAS Rosemaund*

element are shown in Figure 3.2. The soil profile can be divided into three horizons: (a) a moderately conductive topsoil with many macropores, (b) an almost non-conducting subsoil with fewer macropores, and (c) a blocky structured parent material (geology) in which any water movement is confined to macropore flow. Superimposed on this vertical structure is a horizontal division between the area around the drain (drain zone) and the inter-drain zone. The drain zone is characterized by high conductivities and high macropore density. The inter-drain area has a very low, near zero, permeability with some, but far fewer, macropores.

In the autumn, before the water table rises above drain level, heavy rainfall may exceed the acceptance potential of the soil surface and flood down the large shrinkage cracks remaining from the summer. Such rain falling on the drain zone enters the drain through the backfill due to ponding at the base of the macropore zone. Some of this water may pass through the drain to recharge the groundwater. Water falling on the inter-drain zone is absorbed into the soil peds and probably little of this goes anywhere else. The foregoing process depends on the rainfall being heavy, because prolonged light rain causes shrinkage cracks to close.

Cultivation of the topsoil, while destroying the crack structure, will allow lateral movement of water over the impermeable topsoil to the drain zone and hence into the drain. Once a water table is established and has risen above the subsoil, rapid lateral movement to the drains will also occur through macropores and more slowly through the soil matrix. Thus for some modelling purposes the drain and inter-drain zones require separate treatment, which also has to take account of seasonal changes in water table and in soil macropore conductivity.

3.2 Pesticides in water

The objective of this section is to summarise all the pesticide transport data that have been collected during the monitoring exercise carried out at ADAS Rosemaund. Data presented from sites 0 and 5 were collected by IH, and from sites 1 and 3 by MAFF. The discussion will, as far as possible, take the data set as a whole and identify patterns in the pesticide transport and illustrate this by detailed descriptions of representative plots of pesticide concentrations during rainfall events. This approach has been adopted because it would be impossible to present all the data for all the individual events monitored. Details of all these events have been archived in a series of unpublished reports by the Rosemaund Management Steering Group (Bird *et al.*, 1991; Hack, 1991; Hack, 1994; Mitchell, 1995) and most of the data have been published in the open literature (Brooke and Matthiessen, 1991; Williams *et al.*, 1991a; Williams *et al.* 1991b; Carter and Beard, 1992; Matthiessen *et al.*, 1992; Di Guardo *et al.*, 1994b; Matthiessen *et al.* 1994; Matthiessen *et al.*, 1995; Turnbull *et al.* 1995a; Turnbull *et al.*, 1995b; Williams *et al.*, 1995).

3.2.1 Pesticide concentrations and losses

The pesticide transport events monitored over the period of the study are summarised, by chemical, in Table 3.1. Details are given of applications to the catchment areas above each sampling location, which were made prior to, or between, monitored events. On occasions the monitoring of a particular event did not coincide with the hydrograph. This was mainly due to failure of the automatic trigger mechanism and subsequent manual initiation of sampling.

Defining an event as the concentration profile of a single pesticide through a hydrograph at a given location, then 123 such events were monitored in the course of the study. Of these 123 events, in only eleven cases was the maximum concentration of pesticide either absent or below the detection limit. In 99 of the events the maximum concentration was greater than the MAC level for drinking water of 0.1 $\mu g\ l^{-1}$ laid down by the EC. This number falls to 90 if the flow-weighted mean concentration is used as the criterion.

In general, when pesticide was applied to a field draining to both a drainage system and the stream, the higher concentrations were found in the drain. This is because usually all the catchment area of the drainage system was treated, while the stream concentration could be diluted with water from untreated areas. The maximum concentration of any pesticide measured during the study was 264.0 $\mu g\ l^{-1}$ of carbofuran on 8 January 1992 in the drain at Site 3. This was in response to a very large rainfall event of 72.5 mm in 25 hours; such an event occurs approximately once every 50 years at Rosemaund. Atrazine concentrations were also measured in the same event at drain Sites 3 and 5. These were again high with maximum concentrations of 51.3 $\mu g\ l^{-1}$ and 81.4 $\mu g\ l^{-1}$ respectively.

Maximum concentrations over 10 $\mu g\ l^{-1}$ occurred quite often during the study, with 25 events exceeding this value. Peak values in the range 1-10 $\mu g\ l^{-1}$ occurred in 48 events, while 50 events had peak values of less than 1 $\mu g\ l^{-1}$. A more detailed study of those events which gave rise to the lower pesticide peak concentrations reveals several factors which seem to control this behaviour (ignoring those events that missed the hydrograph peak as they may have given unrepresentatively low concentrations, see Section 3.2.2).

Table 3.1 *Summary of pesticide applications and subsequent transport data collected as a result of rainfall events during the Rosemaund Study*

	Application				Rainfall							
Compound	**Date**	**Rate^A (kg/ha)**	**Area^B (ha)**	**Amount (kg)**	**Date**	**Amount (mm)**	**Lag^C (days)**	**Site^F**	**Maximum conc. (µg/l)**	**Mean^D conc. (µg/l)**	**Mass out (g)**	**I_m^E**
2,4-D	20/11/87	1.000	5.18	5.18	20/11/87	9.0	0	0	0.15	0.06	-	0.034
			5.18	5.18	16/12/87	9.0	26	0	5.12	2.57	3.2	0.006
			5.18	5.18	16/12/87	9.0	26	1	1.00	0.71	0.09	0.024
	08/12/88	0.600	5.12	3.07	24/02/89	13.5	78	1	<0.01	<0.01	-	0.000
Aldicarb	27/02/92	0.55	2.00	1.10	14/04/92	17.5	47	5	3.15	1.02	0.002	0.186
			4.20	2.31	28/05/92	28.0	91	0	0.21	0.46	0.34	0.002
			4.20	2.31			101					
	05/06/92	1.30	2.00	2.60	07/06/92	8.0	2	0	2.84	0.90	0.44	0.017
Atrazine	27/11/91	2.800	5.20	14.56	18/12/91	5.0	21	0	1.76	0.60	0.02	0.080
			2.00	5.60	05/01/92	4.0	39	5	56.50	35.70	0.085	1.785
			5.20	14.56	08/01/92	72.5	42	1	5.70	2.00	9.9	0.251
			2.14	5.99	08/01/92	72.5	42	3	51.30	10.60	13.5	0.708
			2.00	5.60	08/01/92	72.5	42	5	81.40	15.90	4.79	1.724
			5.20	14.56	08/01/92	72.5	42	0	0.37	0.23	0.39	0.063
			5.20	14.56	25/01/92	9.0	59	1	49.40	1.90	0.15	0.206
			2.14	5.99	25/01/92	9.0	59	3	58.40	5.70	0.013	0.582
			5.20	14.56	14/04/92	17.5	139	1	2.40	0.11	0.009	0.082
			2.14	5.99	14/04/92	17.5	139	3	9.90	0.45	0.005	0.231
			2.00	5.60	14/04/92	17.5	139	5	16.20	11.20	0.022	0.562
			5.20	14.56	28/05/92	14.5	183	1	0.02	0.06	0.004	0.049
			2.14	5.99	28/05/92	14.5	183	3	0.18	1.60	0.001	0.139
			5.20	14.56	28/05/92	14.5	183	0				
	02/05/92	1.00	8.00	8.00	28/05/92	14.5	26	0	1.76	0.90	0.83	0.054
			5.20	14.56	07/06/92	14.5	193	0				
			8.00	8.00	07/06/92	8.0	36	0	3.00	1.07	0.53	0.048
Carbofuran	03/12/91	3.00	3.00	9.00	18/12/91	5.5	15	0	35.50	3.77	0.15	0.051
			3.00	9.00	08/01/92	72.5	36	0	<1.00	<1.00	-	0.038
			3.00	9.00	08/01/92	72.5	36	1	26.80	10.40	52.6	0.153
			1.00	3.00	08/01/92	72.5	36	3	264.00	25.70	32.8	0.350
			3.00	9.00	25/01/92	9.0	53	1	49.40	6.20	0.49	0.121

Table 3.1 Continued

		Application			Rainfall							
Compound	Date	Rate^{A} (kg/ha)	Area^{B} (ha)	Amount (kg)	Date	Amount (mm)	Lag^{C} (days)	Site^{F}	Maximum conc. (µg/l)	Mean^{D} conc. (µg/l)	Mass out (g)	I_m^{E}
Carbofuran			1.00	3.00	25/01/92	9.0	53	3	58.40	37.20	0.09	0.276
			3.00	9.00	14/04/92	17.5	133	1	2.40	0.46	0.038	0.040
			1.00	3.00	14/04/92	17.5	133	3	9.90	1.00	0.011	0.091
			3.00	9.00	28/05/92	28.0	177	1	0.02	0.01	0.0004	0.022
			1.00	3.00	28/05/92	28.0	177	3	0.18	0.09	0.00007	0.050
Chlorpyrifos	19/03/93	0.72	1.96	1.41	06/04/93	11.0	18	5	2.90	1.91	0.0012	0.466
			2.14	1.54	06/04/93	11.0	18	3	2.78	1.68	0.008	0.195
			1.96	1.41	08/04/93	12.0	20	5	< 0.05	<0.05	-	0.445
			2.14	1.54	08/04/93	12.0	20	3	4.29	1.36	0.056	0.186
			4.58	3.30	26/04/93	4.5	38	0	<0.05	<0.05	-	0.010
Deltamethrin	15/12/92	0.005	4.58	0.023	16/12/92	9.0	1	1	0.008	0.001	0.00027	0.001
			2.14	0.011	18/12/92	20.0	3	3	0.02	0.005	0.001	0.001
			4.58	0.023	18/12/92	20.0	3	1	1.87	0.07	0.16	0.000
			2.14	0.011	05/01/92	6.0	21	3	0.001	<0.001	-	0.000
			4.58	0.011	05/01/93	6.0	21	1	0.011	0.002	0.0003	0.000
			2.14	0.011	06/04/93	11.0	112	3	0.012	0.005	0.00002	0.000
			2.14	0.011	08/04/93	12.0	114	3	0.010	0.001	0.00005	0.000
Dicamba	20/11/87	0.425	5.20	2.21	^{H}16/12/87	9.0	26	1	0.60	0.45	0.053	0.017
			5.20	2.21	^{H}16/12/87	9.0	26	0	2.24	1.176	-	0.004
	08/12/88	0.255	5.20	1.33	24/02/88	13.5	78	1	<0.01	<0.01		0.001
Dichlorprop	20/03/90	2.600	5.20	13.52	19/05/90	12.0	60		1.00	0.35	0.021	0.053
Dimethoate	28/11/90	0.300	16.00	4.80	25/12/90	10.5	27	1	3.05	1.20	0.1	0.009
			16.00	4.80	08/01/91	15.0	41	1	0.22	0.03	0.031	0.002
			5.20	1.56	08/01/91	15.0	41	3	0.58	^{G}0.22	-	0.005
			2.00	0.60	08/01/91	15.0	41	5	<0.02	<0.02		0.005
			2.00	0.60	21/02/91	11.5	85	5	<0.02	<0.02		0.000
			2.00	0.60	04/03/91	12.0	96	5	<0.02	<0.02	-	0.000

Table 3.1 Continued

		Application			Rainfall							
Compound	Date	Rate[A] (kg/ha)	Area[B] (ha)	Amount (kg)	Date	Amount (mm)	Lag[C] (days)	Site[F]	Maximum conc. (µg/l)	Mean[D] conc. (µg/l)	Mass out (g)	I_m[E]
Fenpropimorph	19/03/93	0.75	2.14	1.61	06/04/93	11.0	18	3	1.25	0.90	0.004	0.246
			2.14	1.61	08/04/93	12.0	20	3	1.58	0.66	0.027	0.240
Isoproturon	01/11/89	1.000	2.14	2.14	18/11/89	28.5	7	3	8.40	4.30	0.12	0.358
			2.14	2.14	09/11/89	10.5	8	3	13.70	6.70	0.15	0.351
	17/11/89	0.375	3.06	1.15			26	3				
			2.14	2.14	13/12/89	52.5	42	3	8.80	3.20	0.76	0.309
			5.20	5.20			42	1				
			10.80	4.05	13/12/89	52.5	26	1	5.00	3.30	3.8	0.131
	11/10/90	1.000	10.80	10.80			75	1				
	28/11/90	1.900	5.20	9.88	25/12/90	10.5	27	1	17.20	10.60	0.9	0.230
			10.80	10.80			89	1				
			5.20	9.88	08/01/91	15.0	41	1	2.62	0.96	0.52	0.174
			3.06	3.06			89	3				
			2.14	4.07	08/01/91	15.0	41	3	12.10	[G]3.54		0.444
			0.00	0.00			89	5				
			2.00	3.80	08/01/91	15.0	41	5	0.38	0.14	0.001	0.837
			10.80	10.80			133	1				
			5.20	9.88	21/02/91	11.5	85	1	2.10	0.92	0.4	0.072
			0.00	0.00			133	5				
			2.00	3.80	21/02/91	11.5	85	5	2.70	1.40	0.21	0.347
			0.00	0.00			144	5				
			2.00	3.80	04/03/91	12.0	96	5	2.50	[G]1.70		0.279
			10.80	10.80			75	0				
			5.20	9.88			27	0				
	13/10/90	1.000	5.00	5.00			73	0				
	06/11/90	0.500	23.40	11.70	25/12/90	10.5	49	0	1.76	0.49	0.51	0.091
			10.80	10.80			86	0				
			5.20	9.88			38	0				
			5.00	5.00			84	0				
			23.40	11.70	05/01/91	9.5	60	0	5.20	0.36	0.65	0.073
			10.80	10.80			89	0				

Table 3.1 Continued

	Application				Rainfall							
Compound	Date	Rate^A (kg/ha)	Area^B (ha)	Amount (kg)	Date	Amount (mm)	Lag^C (days)	Site^F	Maximum conc. (μg/l)	Mean^D conc. (μg/l)	Mass out (g)	I_m^E
Isoproturon			5.20	9.88			41	0				
			5.00	5.00			87	0				
			23.40	11.70	08/01/91	15.0	63	0	6.70	^{G}0.60		0.069
			10.80	10.80			133	0				
			5.20	9.88			85	0				
			5.00	5.00			131	0				
			23.40	11.70	21/02/91	11.5	107	0	<0.02	<0.02		0.028
			10.80	10.80			156	0				
			5.20	9.88			108	0				
			5.00	5.00			154	0				
			23.40	11.70	16/03/91	10.0	130	0	16.20	4.95	0.76	0.018
	30/10/91	0.500	5.50	2.75			49					
	30/11/91	0.500	4.00	2.00			18					
	04/12/91	0.500	12.20	6.10			14					
	05/12/91	0.500	5.00	2.50	18/12/91	5.5	13	0	15.10	6.12	0.24	0.063
			5.50	2.75			211					
			4.00	2.00			180					
			12.20	6.10			176					
			5.00	2.50			175					
	27/12/91	0.500	18.00	9.00	28/05/92	5.5	153	0	7.80	4.82	3.6	0.005
			5.50	2.75			221					
			4.00	2.00			190					
			12.20	6.10			186					
			5.00	2.50			185					
			18.00	9.00			163					
	03/06/92	1.500	2.00	3.00	07/06/92	5.5	4	0	10.00	4.39	2.1	0.024
Lindane	01/11/89	0.560	2.14	1.20	08/11/89	28.5	7	3	4.50	1.20	0.007	0.228
			2.00	1.12	08/11/89	28.5	7	5	1.90	^{G}0.85	-	0.553
			2.14	1.20	09/11/89	10.5	8	3	4.10	1.20	0.027	0.227
			2.14	1.20	13/12/89	24.0	42	3	0.45	0.14	0.034	0.214
			5.20	2.91	14/12/89	18.0	43	1	0.29	0.12	0.16	0.076
			2.00	1.12	15/12/89	40.0	44	5	2.55	^{G}0.57	-	0.519

Table 3.1 Continued

Compound	Date	Application Rate[A] (kg/ha)	Application Area[B] (ha)	Amount (kg)	Rainfall Date	Rainfall Amount (mm)	Lag[C] (days)	Site[F]	Maximum conc. (µg/l)	Mean[D] conc. (µg/l)	Mass out (g)	I_m^E
Lindane			5.20	2.91	[I]15/12/89	40.0	44	0	0.75	[G]0.16	-	0.076
			2.14	1.20	19/03/90	9.0	138	3	0.03	0.01	0.00008	0.181
			5.20	2.91	19/03/90	9.0	138	1	0.02	0.01	0.0007	0.064
MCPA	28/02/91	1.68	16.00	26.88	04/03/91	15.5	4	1	12.44	1.92	0.096	0.674
			5.21	8.75	04/03/91	15.5	4	3	18.80	5.40	0.33	1.504
			16.00	26.88	03/07/91	26.5	7	1	1.98	1.20	0.29	0.620
			16.00	26.88	16/03/91	10.0	16	1	6.00	1.90	0.72	0.483
			5.21	8.75	[H]19/03/91	11.0	19	3	46.80	14.60	0.70	0.992
Mecoprop	17/11/87	2.000	5.50	11.00	19/11/87	25.0	2	1	11.70	4.20	7.5	0.288
			5.50	11.00	[H]20/11/87	25.0	3	0	0.12	0.04	0.04	0.066
			5.50	11.00	[H]16/12/87	11.5	29	0	1.57	0.84	1	0.028
			5.50	11.00	[H]16/12/87	11.5	29	1	<0.01	<0.01	-	0.811
	22/03/90	0.650	10.80	7.02	15/05/90	12.0	54	1	1.40	0.30	0.019	0.033
Simazine	02/03/88	1.700	4.12	7.00			91	0				
	05/03/88	1.700	3.76	6.39	01/06/88	16.5	88	0	1.83	0.93	0.25	0.031
	08/12/88	1.150	6.00	6.90	24/02/89	13.5	78	1	1.80	0.50	0.3	0.078
			6.00	6.90			78	0				
	16/02/89	1.700	4.12	7.00			8	0				
	17/02/89	1.700	3.76	6.39	24/02/89	13.5	7	0	68.00	22.40	60.6	0.100
			6.00	6.90			84	0				
			4.12	7.00			14	0				
			3.76	6.39	02/03/89	10.5	13	0	15.70	8.20	9.2	0.093
	23/11/90	1.200	3.76	4.51	25/12/90	10.5	32	0	4.12	1.70	1.77	0.021
			3.76	4.51	05/01/91	9.5	43	0	1.50	0.90	1.6	0.018
			3.76	4.51	08/01/91	20.5	46	0	0.84	[G]0.49	-	0.019
			3.76	4.51	21/02/91	11.5	90	0	0.36	0.26	1.25	0.011
			3.76	4.51			113	0				
	02/03/91	1.700	4.85	8.25	16/03/91	9.5	14	0	15.30	3.30	11.8	0.054

Table 3.1 Continued

Compound	Application				Rainfall							
	Date	Rate[A] (kg/ha)	Area[B] (ha)	Amount (kg)	Date	Amount (mm)	Lag[C] (days)	Site[F]	Maximum conc. (µg/l)	Mean[D] conc. (µg/l)	Mass out (g)	I_m[E]
Triclopyr	08/12/88	0.195	5.18	1.01	24/02/89	13.5	78	1	<0.01	<0.01		0.009
Trifluralin	08/11/92	1.10	2.00	2.20	11/11/92	10.5	3	5	14.12	3.49	0.032	1.063
			2.14	2.35	11/11/92	10.5	3	3	3.01	0.56	0.0054	0.437
			4.58	5.04	11/11/92	10.5	3	1	0.94	0.58	0.069	0.136
			4.58	5.04	11/11/92	10.5	3	0	0.37	0.12	0.23	0.034
			2.00	2.20	14/11/92	5.0	6	5	2.20	0.39	0.01	1.026
			2.14	2.35	14/11/92	5.0	6	3	0.64	0.19	0.003	0.422
			4.58	5.04	14/11/92	5.0	6	1	0.38	0.22	0.024	0.132
			4.58	5.04	15/11/92	5.0	6	0	0.08	<0.08	-	0.033
			2.00	2.20	[H]25/11/92	17.5	17	5	1.00	0.72	0.011	0.904
			2.14	2.35	[H]25/11/92	17.5	17	3	0.11	[G]0.67	-	0.371
			4.58	5.04	[H]25/11/92	17.5	17	1	0.13	0.79	0.015	0.116
			2.00	2.20	16/12/92	9.0	38	5	0.32	0.14	0.002	0.709
			4.58	5.04	16/12/92	9.0	38	1	0.08	0.03	0.006	0.091
			2.14	2.35	18/12/92	20.0	40	3	0.39	0.08	0.029	0.285
			4.58	5.04	18/12/92	20.0	40	1	1.04	0.13	0.28	0.089
			2.14	2.35	05/01/93	6.0	58	3	0.18	0.070	0.00009	0.231
			4.58	5.04	05/01/93	6.0	58	1	0.01	0.05	0.009	0.072
			2.14	2.35	06/04/93	11.0	149	3	0.11	0.07	0.0003	0.081
			2.14	2.35	08/04/93	12.0	151	3	0.11	0.06	0.0025	0.079

Notes:
A. Application rate of active ingredient.
B. Area treated draining to the sampling point.
C. Time in days between application date and rainfall event.
D. Flow weighted mean concentration (unless otherwise indicated).
E. I_m = Index of mass available for transport, see Section 4.2.4
F. See Figure 3.2 for locations.
G. Simple mean, no flow data available.
H. Chemical sampling missed main hydrograph.
I. Multiple events captured with longer sampling interval.

The main factors seem to be the number of half-lives that pass between the application date and the rainfall event, and the fraction of the catchment that is treated. In the dicamba event of 8 December 1988 for example, there was a delay of almost 8 half-lives between application and rainfall event. The atrazine and carbofuran events of 28 May 1992 also occurred several half lives after application. The simazine events of 8 January 1991 and 21 February 1991 followed pesticide applications to only 3.76 ha of a catchment whose total area is some 151 ha. The triclopyr data demonstrated the effect of combining a low application rate to a small area of a large catchment, with three half-lives between application and rainfall event. The lindane events occurring after November 1989 nearly all show low peak concentrations. While the latter two events occurred many days after application, it was not a long time compared to lindane's quoted half-life of about 400 days. However, measurement of soil residues (Williams *et al.*, 1991a) shows that the real half-life in the field was closer to 40 days.

It seems therefore that consideration of the degradation rate of the chemical combined with knowledge of the amount and area of treatment can indicate expected peak concentrations in surface waters as they are influenced by the timing of rainfall events. Based on this evidence an attempt has been made to develop an index of pesticide transport, I_m, based on the data in Table 3.1. However, I_m and pesticide transport were not consistently related. The calculation of the index and a discussion of its success is given in Section 3.2.4.

While the maximum concentration of a pesticide is the standard by which the quality of an agricultural non-point source is judged, the actual amount of pesticide translocation to water is also of considerable interest. Table 3.1 includes the results of calculating the mass of pesticide passing each sampling point in each event. In the majority of cases the amounts were very small, with most below 1 g. The highest recorded loss was 60.6 g of simazine recorded at Site 0 in spring 1989, which represented 0.3 % of the total applied to the catchment. The highest cumulative translocation of pesticide recorded was 1.1 % of the total applied and was measured in the water leaving the drain at Site 3, following an application of carbofuran. When compared to the application rates these small mass losses of pesticide may seem trivial. However, they give rise to very high concentrations of potential biological significance, albeit for short lengths of time. It would seem almost impossible to prevent chemicals deliberately introduced into the environment, as is the case with pesticides, from reaching surface waters in such small amounts, whatever the method of application and agricultural practice used. The implication, therefore, is that the ecotoxicity of pesticides should be made sufficiently low so as to avoid environmental damage being caused by this inevitable contamination of streams and rivers.

3.2.2 Patterns of pesticide translocation

This section examines in more detail the way in which pesticide concentrations relate to rainfall and flowrate for individual events. The shapes of the pesticide concentration curves can be divided into three main types:

- Those which showed no obvious pattern at all;
- Those when the peak value occurred at the start of monitoring;
- Those which showed a dilution in concentration through the hydrograph and subsequent return to base levels.

The majority of events fall into group 2, while there are a significant number in group 1. The pesticide concentrations showing least pattern generally occur at the main gauging site and reflect the greater variety and lengths of pesticide pathway that operate at the catchment scale compared to those operating at the field scale. The following discussion will deal with each of these three groups. For ease of reference they will be identified as type 1, type 2 and type 3 events respectively.

Type 1 events

This type of pesticide response to rainfall events accounts for only about 10% of the events observed. As was stated above, the majority of these were monitored at the outlet from the farm catchment at Site 0. Two examples should be sufficient to illustrate this type. Figure 3.3 shows isoproturon concentrations at Site 0 following 10.0 mm of rainfall, the applications having been made over the period 16 October 1990 to 28 November 1990 (Table 3.1). The flow response to the rainfall is as expected, however the two distinct isoproturon peaks show no correlation to either rainfall or flow. Figure 3.4 shows a similar lack of correlation between, in this case, atrazine, rainfall and flow. Here a single application of atrazine was made some 21 days before a small rainfall event which occurred on 17 December 1991 (Table 3.1). Although the atrazine concentration did seem to reach a peak during the recession limb in the hydrograph, there is no apparent reason why it should lag behind the peak flow by approximately 12 hours.

Type 2 events

In this type of event rainfall produces a corresponding peak in pesticide concentration in the stream or drainage water. The pesticide peak may either occur shortly before the peak in the hydrograph or coincide with it. This type of event

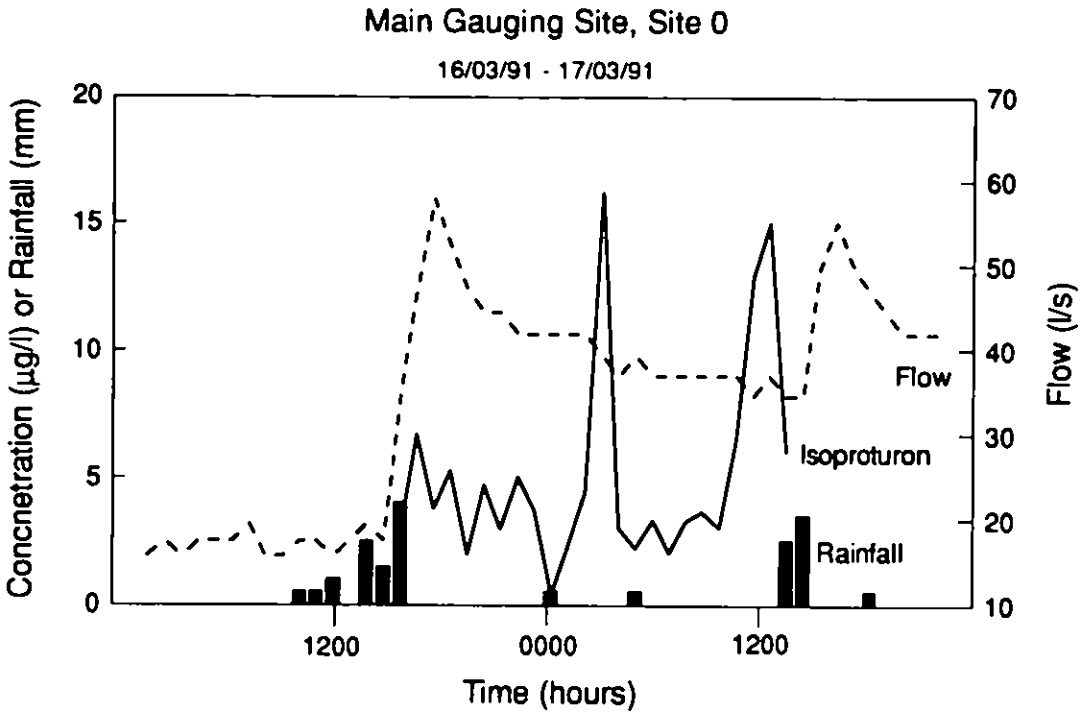


Figure 3.3 Isoproturon concentrations in the stream draining ADAS Rosemaund following a rainfall event

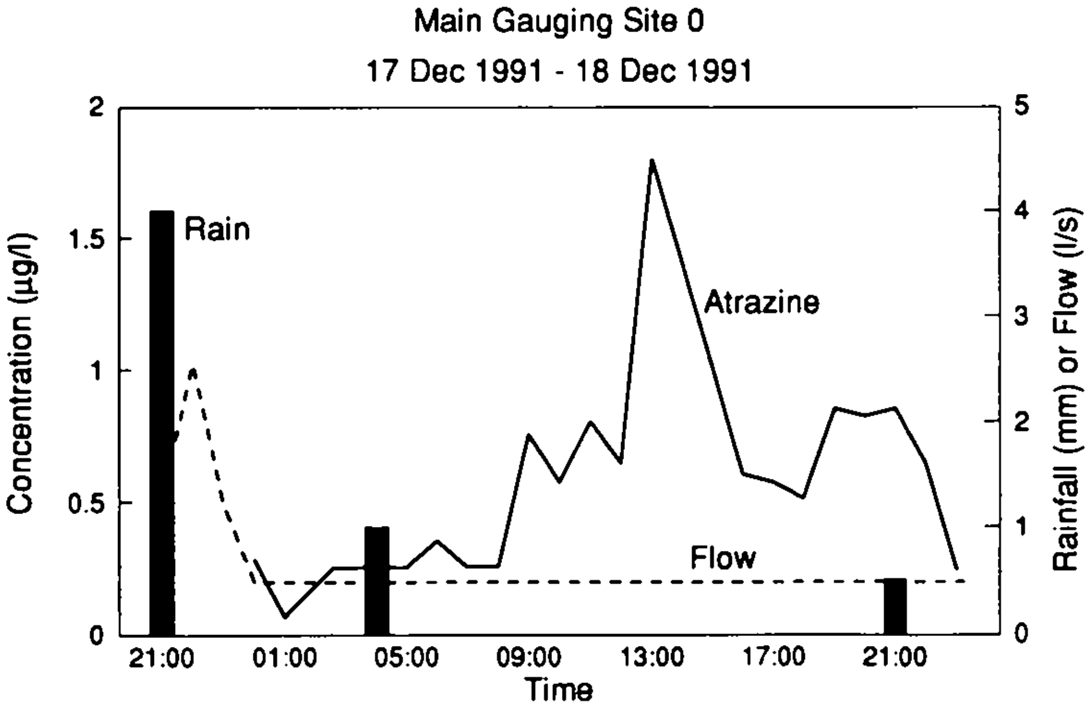


Figure 3.4 Atrazine concentrations in the stream draining ADAS Rosemaund following a rainfall event

formed the majority (approximately 80%) of those monitored at Rosemaund. Figures 3.5 and 3.6 are excellent examples of this type of event. Both graphs show the change in simazine concentrations at Site 0 resulting from a rainfall event which occurred shortly after pesticide application (see Table 3.1 for details). In both cases the peak simazine concentration occurred before the hydrograph peak, the concentrations then fell off rapidly through the peak and recession of the hydrograph. It is interesting to note that this is the same event as shown in Figure 3.3 that produced a Type 1 response for isoproturon. A slightly different response is shown in Figure 3.7, also for simazine concentrations following a recent application. Here the rain fell over two close but separate periods, the first rainfall causing a simazine peak slightly after the first hydrograph peak, and the second rainfall giving rise to a coincidence of the pesticide and hydrograph maximum.

This type of response was not confined to simazine. Figure 3.8 shows the change in the concentration of the breakdown products of aldicarb in the drainage water from Longlands field. In this case, due to a build up in the soil moisture deficit, the rainfall event produced only a small change in drain flow. However, the coincidence of pesticide and hydrograph peak is clearly illustrated. A similar response can be seen for trifluralin for the same location and under conditions that gave rise to a very similar hydrological response (Figure 3.9 and 3.10). This chemical is interesting because it has a high sorption coefficient, yet it behaves similarly to other less sorbed chemicals (see Section 3.2.3).

There are two possible hypotheses that can be put forward to explain type 2 responses. The first is based on the likelihood that pesticide concentrations do not equilibrate between the dissolved and solid phases instantaneously. When a pesticide is applied to soil, some will adsorb to the soil while some will dissolve into the soil water, the relative concentrations depending on the sorption coefficient for the particular molecule/soil combination. In the initial stages of a rainfall event, the rain displaces the original soil water, which is of high pesticide concentration, and forces it to move down the profile. If there are by-pass routes available this water will reach the drainage system, and hence the stream, in a short space of time, thus causing an initial peak pesticide concentration. During the remainder of the event there is insufficient time for full equilibrium to be established between the displacing water and the soil matrix, and thus the remaining water moving to the drains is of a lower concentration. Between rainfall events, equilibrium is re-established and so each event starts with a pesticide flush, albeit of slightly lesser magnitude each time.

The second explanation assumes an instantaneous equilibrium is reached between dissolved and solid phases, and that the shape of this type of event is a consequence of having a by-pass flow system present in the soil. In this model, soil water from near the surface, which has a high pesticide concentration, is transported rapidly by the incoming rainfall to the drains via macropores. Since an instantaneous equilibrium is assumed, this occurs throughout the rainfall event. Water is, however, moving via the larger pores in the soil

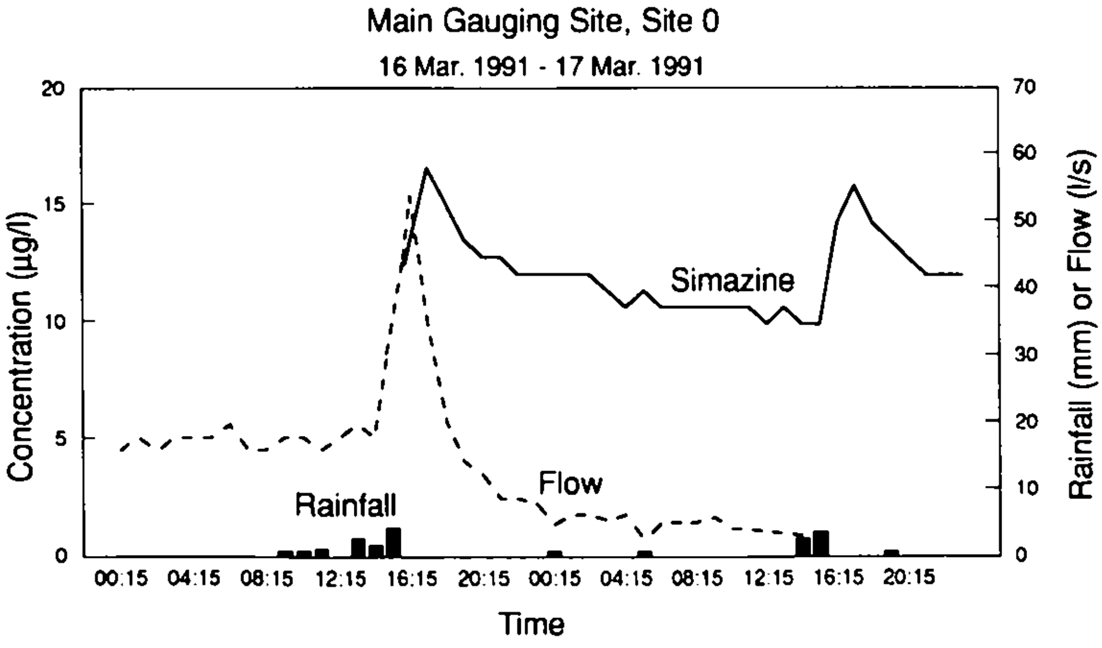


Figure 3.5 *Simazine concentrations leaving the ADAS Rosemaund catchment following a rainfall event after an application*

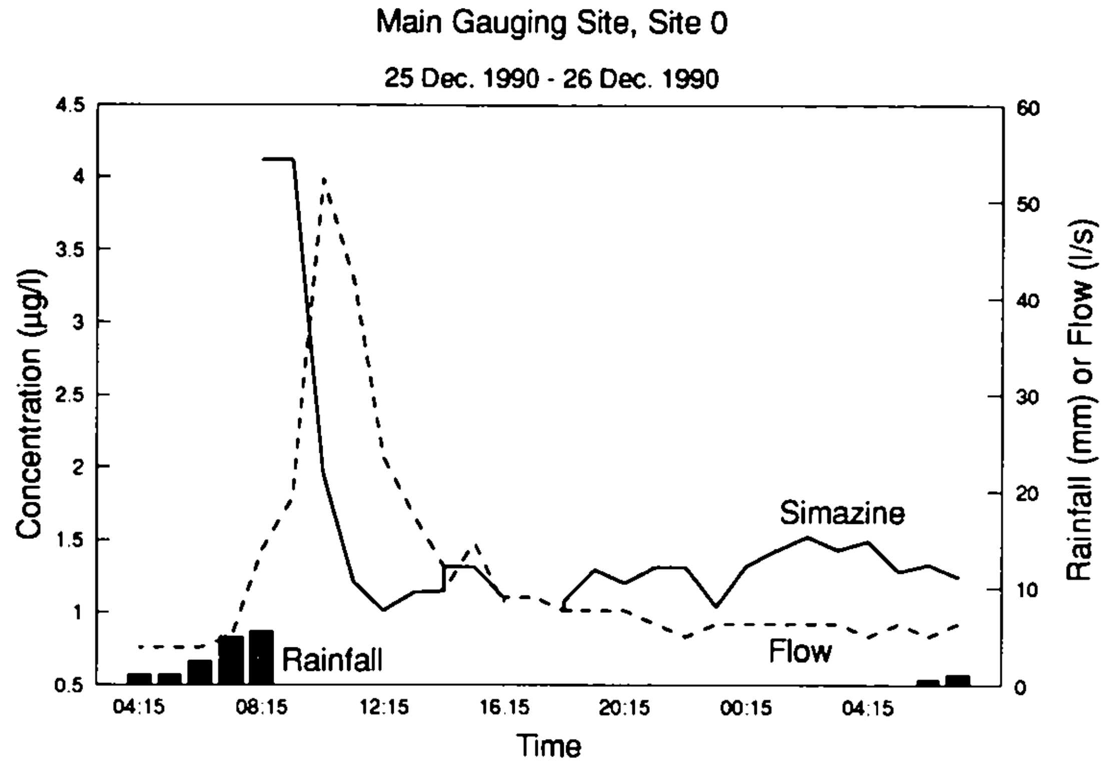


Figure 3.6 *Simazine concentrations leaving the ADAS Rosemaund catchment following a rainfall event after application*

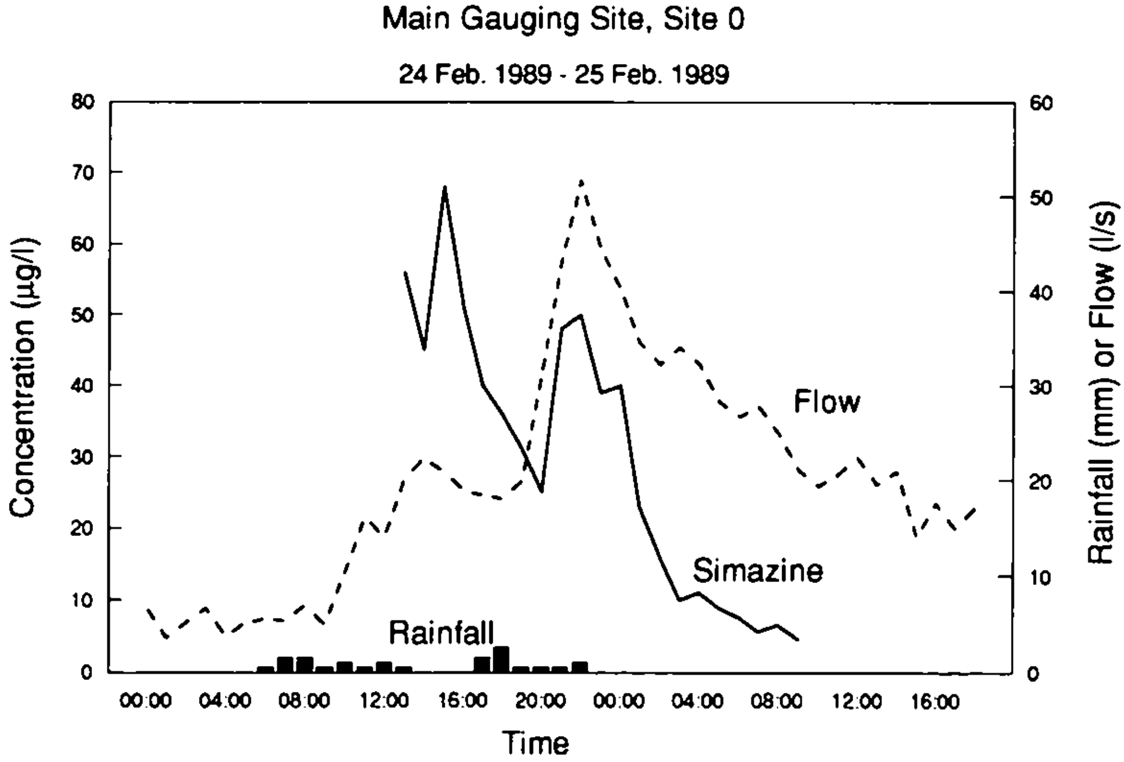


Figure 3.7 *Simazine concentrations in the stream leaving the Rosemaund catchment following rainfall after an application*

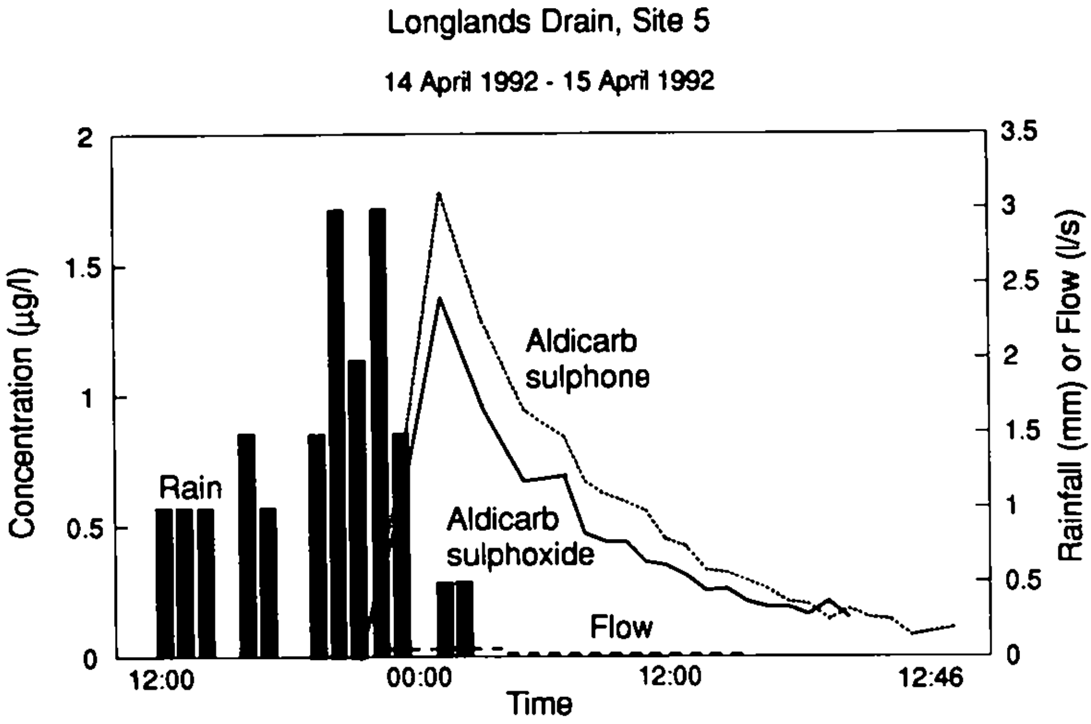


Figure 3.8 *Concentrations of the breakdown products of aldicarb in the drains under Longlands field following rainfall after an application*

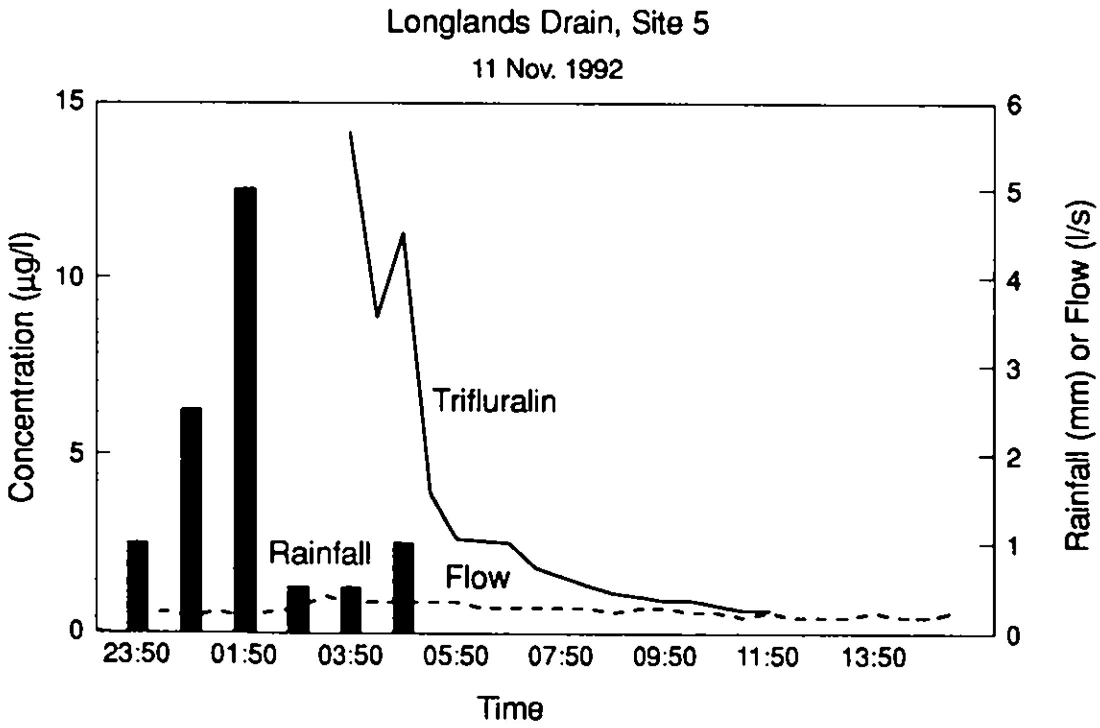


Figure 3.9 *Concentrations of trifluralin in the drains under Longlands field following rainfall after an application*

matrix, especially in the highly conductive zone around the drains and is much larger in volume than the macropore flow. The pressure exerted by this water will after some hours cause the water in the deeper layers (and of low pesticide concentration) to flow toward the drains and thus dilute the water from the macropores.

In reality, the explanation may be a combination of both of these hypotheses. They have in common the need to move water rapidly from the surface to the drainage system, which requires the presence of macropores. The generation of drain and stream flow is certainly not controlled soley by the movement of water from the surface and some contribution is made from the deeper soil water. Although there is some evidence that equilibrium may not be instantaneous under field conditions, such a combination leads to a very complicated conceptualisation of the system and therefore, for the purposes of modelling what happens at Rosemaund, the second of the two hypotheses stated above has been adopted (see Section 3.2).

Type 3 Events

In this type of event, instead of rainfall causing a peak in pesticide concentration, a reduction in concentration is observed. This type of event has only been observed on two occasions in late spring 1992 and is illustrated well in Figure 3.11. Isoproturon concentrations are shown for Site 0 following a very intense rainfall event. The initial concentration was high (around 8 $\mu g\ l^{-1}$) but fell rapidly through the hydrograph to 1 $\mu g\ l^{-1}$. Levels then recovered to close to their original values by the end of the event. A similar response was observed at the same site during a smaller event which occurred some 10 days later (Figure 3.12).

This type of response is typical of a contaminant that is being supplied to the stream by the base flow which is then diluted by clean water from incoming rainfall. Thus during the event the base flow concentration is first diluted by clean rain water moving rapidly from the top soil to the drains, but then rises again as the proportion of deeper soil water increases on the recession limb of the hydrograph.

3.2.3 Particulate pesticide transport

The significance of particulate transport for the movement of pesticides to streams and drains was investigated in the final phase of the Rosemaund study through use of the highly sorbed chemicals trifluralin (K_{oc} = 8000), deltamethrin (K_{oc} = 110,000), chlorpyrifos (K_{oc} = approx. 6000) and fenpropimorph (K_{oc} = approx. 4715). The following summary largely uses the trifluralin data, but many of the conclusions apply to the other three substances. Samples were taken from Longlands drain for three rainfall events following trifluralin application using the normal methods described in Section 2.2. Three samples containing the highest sediment loads (by visual inspection this was the first three samples in each case) were selected and sent to the Institute of Freshwater Ecology (IFE) River Laboratory, Wareham, for separate analysis of the particulate and dissolved pesticide concentrations. The concentrations of pesticide in mobile bed sediment were also measured during and after a large event.

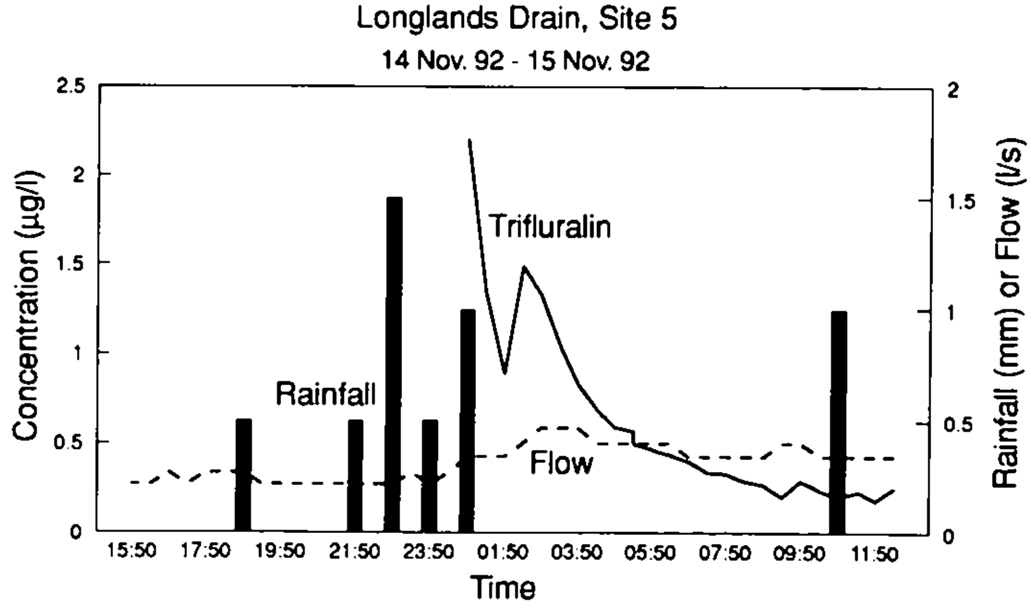


Figure 3.10 *Concentrations of trifluralin in the drains under Longlands field following the second rainfall event after application*

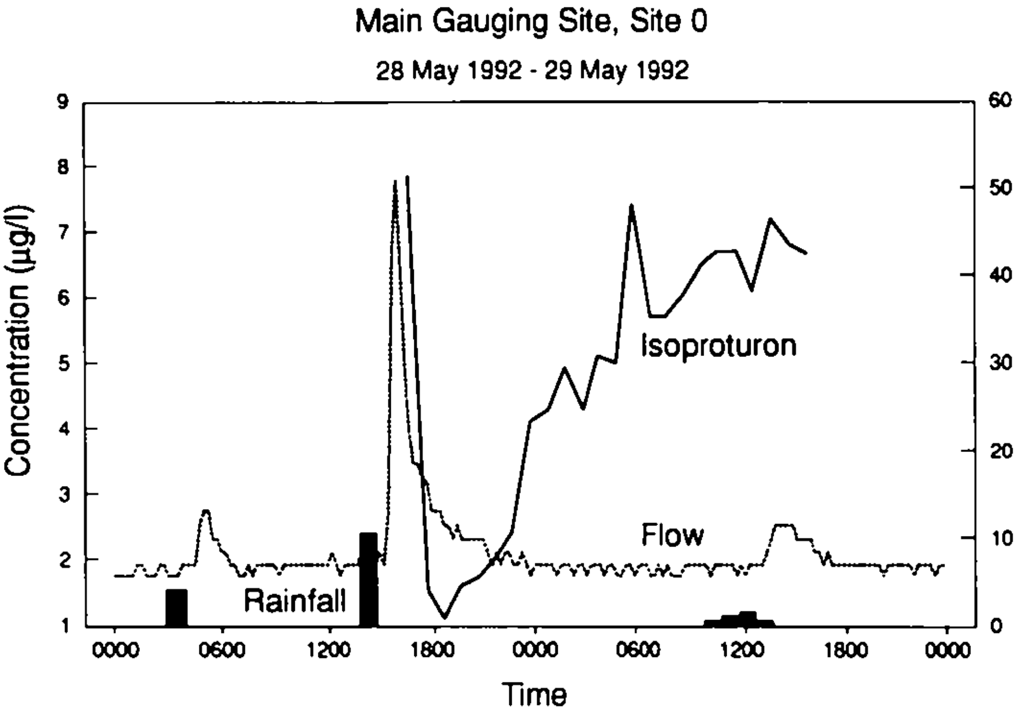


Figure 3.11 *Isoproturon concentration in the stream leaving the Rosemaund catchment following a rainfall event following an autumn application*

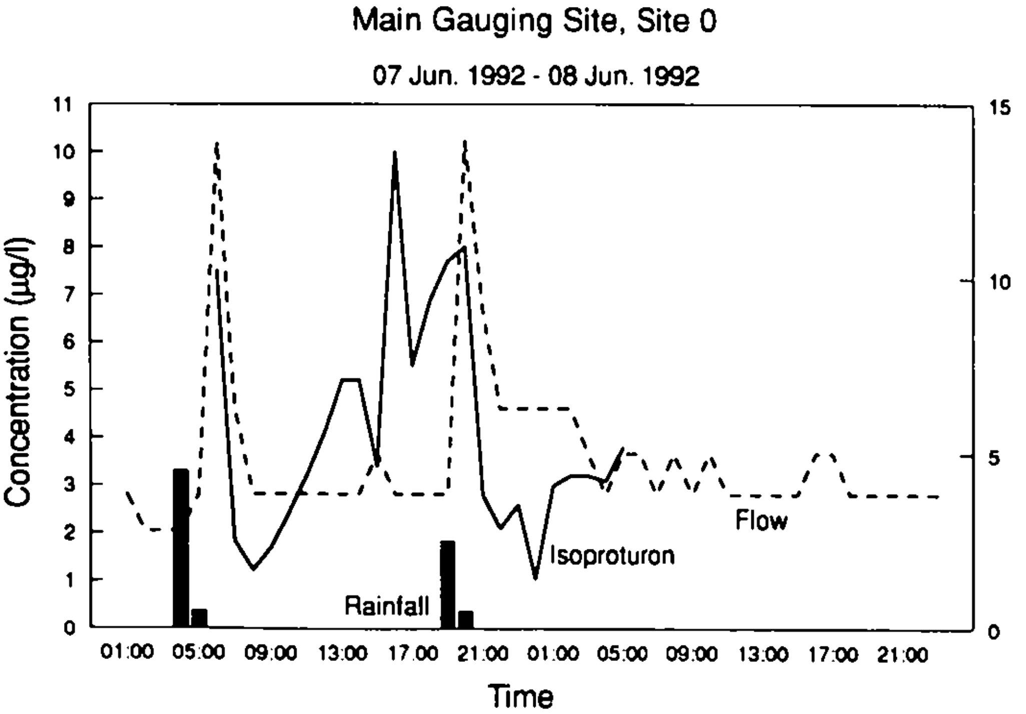


Figure 3.12 *Isoproturon concentrations in the stream leaving the Rosemaund catchment after rainfall following an autumn application*

***Table 3.2** Details of trifluralin concentrations and suspended sediment masses in three rainfall events collected from Longlands Drain, Site 5*

Date	Mass of sediment (g)	Volume of water (litres)	Trifluralin Concentrations			
			Suspended Sediment		Filtered Water	
			Concentration (µg/g)	Load (µg)	Concentration (µg/l)	Load (µg)
11 Nov 92	1.092	0.970	1.044	1.14	12.9	12.51
11 Nov 92	1.866	0.970	1.554	2.90	5.9	5.72
11 Nov 92	2.991	0.960	1.618	4.84	6.2	5.95
15 Nov 92	0.353	0.955	2.215	0.78	1.4	1.34
15 Nov 92	0.567	0.960	1.834	1.04	0.32	0.31
15 Nov 92	0.492	0.960	1.110	0.55	0.32	0.31
26 Nov 92	0.033	1.043	0.848	0.03	0.32	0.33
26 Nov 92	0.027	0.980	1.185	0.03	0.27	0.26
26 Nov 92	0.003	0.980	0.867	0.06	0.37	0.36

Table 3.2 gives details of the trifluralin concentrations and sediment masses carried in the water samples taken from Longlands drain. The highest concentrations of both trifluralin and sediment were found in the first event of 11 November 1992. However, the highest of the three pesticide values for this event was from the first sample, in which the vast majority of the pesticide (92% by weight) was transported in the dissolved phase. In the third sample in this first event the pesticide transported was divided equally between the particulate and dissolved phases. On only two occasions, both within the same event, did the particulate load of pesticide exceed that in the water phase. The third event was only sampled at the tail of the hydrograph and consequently sediment loads were low, as were the loads of associated pesticide.

As was noted in Section 3.2.2 above, the highly sorbed nature of this pesticide does not seem to alter the way in which it responds to rainfall, i.e. it fits well into the set of Type 2 events described above. Since this highly sorbed chemical seems to have behaved in the same manner as the less sorbed pesticides discussed earlier, then it may be reasonable to treat it in the same way. Certainly the significance of particulate transport of the less sorbed chemicals that are commonly found in surface water can be considered negligible. This conclusion is based on a small data set for one chemical, as sufficient resources were not available for a more extensive study of pesticides of this type. However, it should be noted that even a very highly sorbed pesticide such as deltamethrin was found at up to 1.9 $\mu g\ l^{-1}$ in the stream at Site 1 (Table 3.1), probably all adsorbed to suspended particulates. This shows that a combination of bypass flow and the presence of field drains can lead to significant translocation of pesticides traditionally considered to be immobile.

Mobile sediments

The concentrations of trifluralin in mobile surface sediments in the stream during rainfall events are given in Table 3.3. The concentrations were quite similar in all the samples collected and in all cases were much lower than the concentrations measured on the suspended particles. These limited data suggest that the fine particles are responsible for the bulk of the pesticide transport and these are not deposited on the stream bed during or after events. It would be of interest to know whether these concentrations in the sediment are of any environmental concern.

***Table 3.3** Trifluralin concentrations measured in the mobile stream bed sediments during rainfall events*

Date	Site	Concentration (µg/g)
24 Nov 92	0	0.020
25 Nov 92	1	0.140
25 Nov 92	1	0.079
30 Nov 92	1	0.053
30 Nov 92	1	0.074

Overland flow

Trifluralin concentrations were also measured in water samples collected by the overland flow traps following a number of rainfall events, and the results are given in Table 3.4. It should be noted that the design of the traps removed large particles before the water sample was collected; fine particles could remain in the collected water. The highest concentrations were measured following the first rainfall event after application. Thereafter runoff concentrations were about an order of

Table 3.4 Trifluralin concentrations measured in surface runoff traps in Longlands field following rainfall events

Date	Trifluralin concentrations (µg/l)			
	Trap 1	Trap 2	Trap 3	Trap 4
12 Nov 92	20.0	86.0	15.5	-
09 Dec 92	2.5	0.43	1.74	0.15
27 Dec 92	0.99	2.0	0.61	0.91
20 Jan 93	0.80	-	-	1.55

the first rainfall event after application. Thereafter runoff concentrations were about an order of magnitude lower for all traps. The concentrations measured in the traps were quite similar and imply an even application of pesticide to the field. It is clear that rainfall events occurring soon after application have the maximum likelihood of producing high pesticide concentrations in overland flowing water.

3.2.4 Pesticide translocation to water, and degradation rate

It was suggested in Section 3.2.1 that there might be a relationship between the physico-chemical characteristics of a pesticide and its detection during monitoring at Rosemaund. This section proposes an index of pesticide translocation, I_m, which is based on the relationship between three factors that might logically influence peak concentrations. These three factors are:

- The half life of the pesticide assuming a first-order decay reaction;
- The length of time between the pesticide application and the rainfall event;
- The area of the catchment above the sampling site.

The factors are combined thus:

$$I_m = (M e^{-kT})/A$$

where M is the mass of pesticide applied (kg), k is the decay rate of the pesticide (day^{-1}), T is the time between application and rainfall event (days), and A is the area of the catchment above the sampling site. If there has been more than one application, then the effective I_m is the sum of the individual indexes for each application. The logic behind this choice of index is that the time between application and rainfall event combined with the pesticide half life gives an estimate of the amount of pesticide left in the catchment. The catchment area is used as a surrogate for flowrate, i.e. larger catchments generate larger flows. If the area treated is small compared to the catchment area then the value of I_m will be small.

Values of I_m have been calculated for all the events monitored at Rosemaund and the values are presented in Table 3.1. Figure 3.13 presents the same data graphically by plotting the peak pesticide concentration against the index, I_m. The plot identifies each sampling site by representing each point by the site number to which it refers. A cluster of values can be seen close to the origin showing that many events had a low peak concentration and a low value of I_m. In general the expected trend of increasing value of the index and increasing peak concentration is followed. However, the correlation is too poor to formulate a usable mathematical relationship. There is a clear grouping of the points into sites, with Site 0 having the lowest values of I_m and Site 5 the highest. This is due to the inclusion of the catchment area in the formulation of the index and the fact that higher proportions of individual fields get treated than the catchment as a whole.

An alternative plot of flow-weighted mean concentration against I_m is shown in Figure 3.14. As would be expected a similar pattern is observed, with the separation by site still apparent.

Although the value of I_m cannot be used to estimate the peak pesticide value directly, it is possible to define a threshold value that can be used to predict when a given maximum concentration will not be exceeded. For example, using the data in Table 3.1, a value of I_m of less than 0.005 kg/ha will give a maximum pesticide concentration of less than 0.22 $\mu g\ l^{-1}$ and less than 0.1 $\mu g\ l^{-1}$ in the vast majority of cases.

Any relationship developed between an index such as I_m and observed data is clearly only empirical, even if it is based on common-sense relationships. Empirical relationships are only valid within the bounds of the data from which they have been derived and cannot be used safely on more general problems. The lack of a good correlation between I_m and either peak or mean pesticide concentrations indicates that the problem of pesticide transport is more complicated than considered in this treatment. There is therefore a need for a more sophisticated approach, such as that outlined in Section 4 below.

3.3 Bioassays of stream water and sediment

The main purpose of the work at Rosemaund was to monitor the translocation of pesticide residues into the stream, but bioassays which could be used to assess the potential biological effects of the

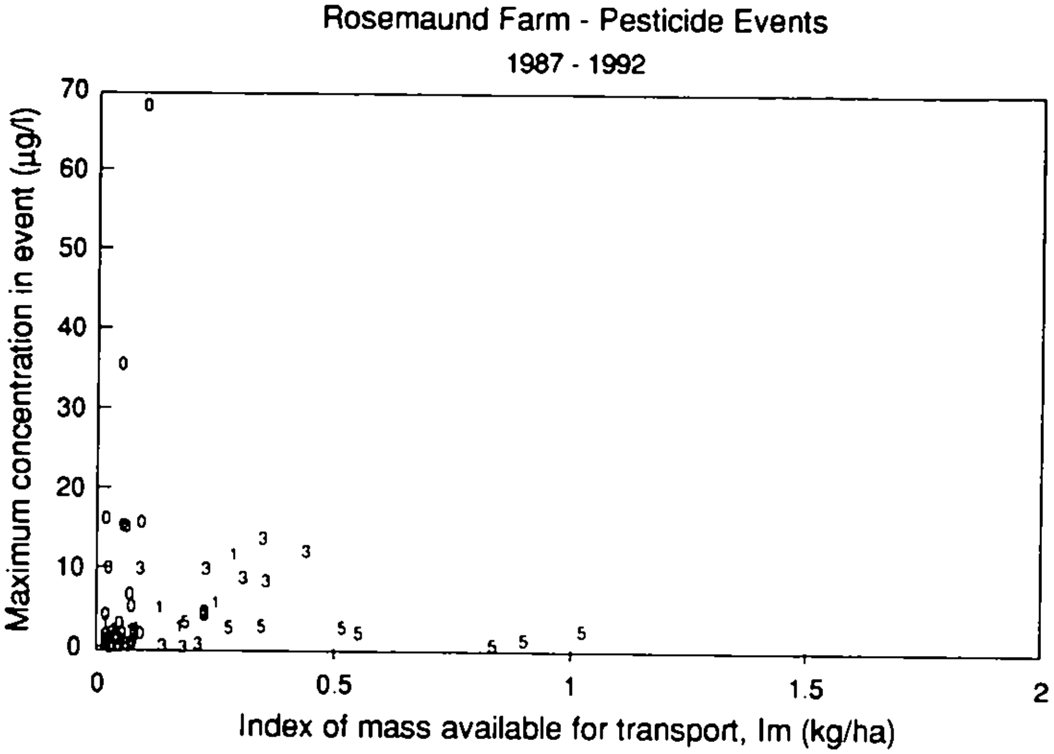


Figure 3.13 *Index of available mass against maximum pesticide concentration. Numbers indicate the monitoring site where the data were collected. Peak value of 264 µg/l not shown to aid clarity of the graph.*

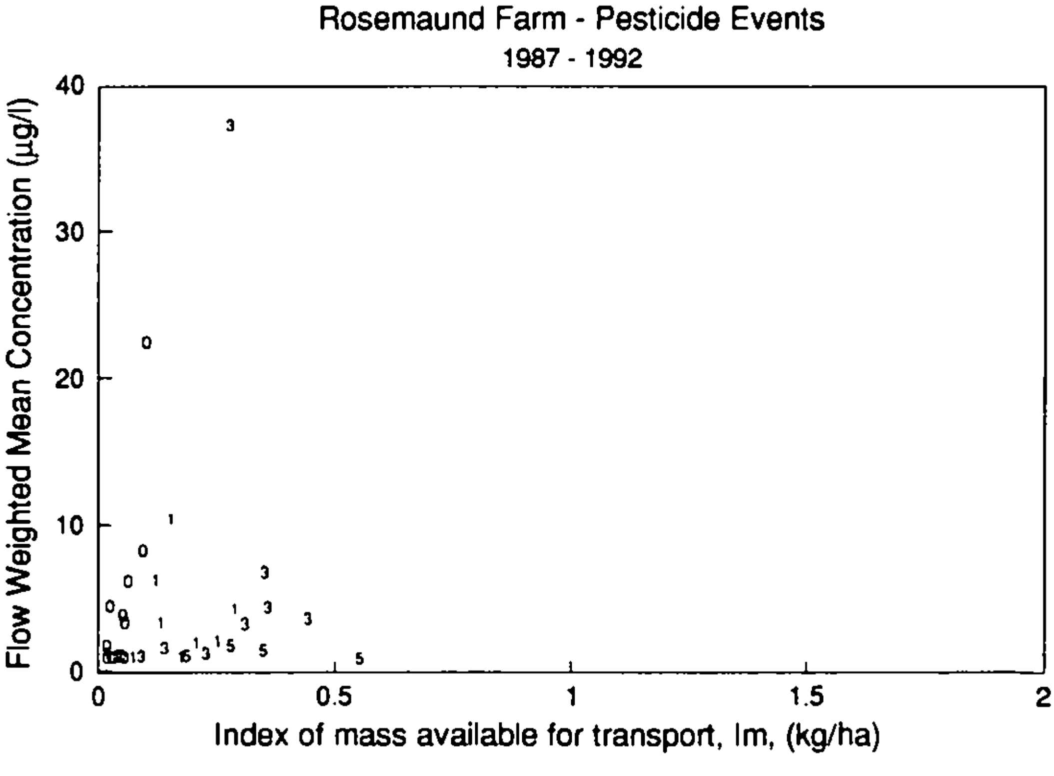


Figure 3.14 *Index of available mass against flow-weighted mean concentration. Numbers indicate sampling site from where data were collected.*

used was the *Gammarus pulex* feeding rate bioassay, in which amphipod crustacea sensitive to certain insecticides were deployed in individual cages *in situ* in the stream at Site 1 for periods of several weeks. Full details of this bioassay are given in Matthiessen *et al.* (1995).

A trial run of the technique was conducted during the dichlorprop event monitored on 20 March 1990 (Table 3.1). Dichlorprop, a phenoxy acid herbicide, is not significantly toxic to *G. pulex*, so any effects on the bioassay caused by non-pesticide factors such as high water flow rate or suspended sediment would have been expected to show up during the trial. In fact, there was no significant mortality or reduction in feeding rate during and after the dichlorprop event, thus providing confidence that the bioassay would only respond to toxic materials in the stream water.

The first operational deployment of the bioassay took place during the carbofuran experiment started on 3 December 1991 when carbofuran (a carbamate insecticide) was applied in a granular formulation on an experimental basis to 3 ha of oilseed rape in the upper catchment at a rate of 3 kg a.i. ha^{-1} (Matthiessen *et al.*, 1995). Rainfall was sporadic until 8-9 January 1992 when 71.5 mm fell, mainly in a 24 hr period. The return rate at Rosemaund for events of this magnitude is about 50 years. Figure 3.15 shows that carbofuran concentrations in the stream during the event reached peaks of 24 and 27 µg l^{-1}, respectively. Although dissolved oxygen levels (48-59% saturation) and pH (7.4-7.9) remained within acceptable limits for *G. pulex*, the carbofuran concentrations exceeded the 24-hour LC50 for this species, causing a cessation of feeding and 100% mortality of the test animals (Figure 3.16). Subsequent laboratory experiments confirmed that carbofuran is very toxic to *G. pulex*, as little as 4 µg l^{-1} causing a significant reduction in feeding rate over a 7-day exposure period. None of the other pesticides that had been used in the catchment in the preceding months (atrazine, benazolin, clopyralid and cycloxydim) was sufficiently toxic to *G. pulex* to have caused the observed effects. It is noteworthy that the subsequent carbofuran event on 25 January 1992, although triggered by a much smaller rainstorm (9 mm), would also have been expected to cause mass mortality of *G. pulex*. However, the bioassay was not deployed at that time.

Subsequently, the *G. pulex* bioassay was again deployed at Site 1, this time after application of the insecticide chlorpyrifos at 0.72 kg a.i. ha^{-1} to 4 ha of the upper catchment on 19 March 1993. Published data show that chlorpyrifos is also highly toxic to *Gammarus* spp. (24 hour LC50 = 0.7-5.6 µg l^{-1}). 36% of the bioassay animals died after the 12 mm rainfall event on 9 April, and a further 47% were scored as moribund and would have died later. Feeding rate declined to almost zero. Unfortunately, no water samples were obtained from the stream during this event, but the chlorpyrifos concentration in the Site 3 field drain about 100 metres upstream from the bioassay cages reached 4.3 µg l^{-1}, so it is almost certain that chlorpyrifos was responsible for the mortalities. The only other pesticide present at this time was fenpropimorph which is of low toxicity to crustacea.

Finally, sediments collected from the stream after the deltamethrin application on 15 December 1992 (and subsequent to the main deltamethrin run-off events summarised in Table 3.1) were subjected to a sediment bioassay which measured the growth of a sediment-dwelling insect larva, *Chironomus riparius*. Deltamethrin is a pyrethroid insecticide with high acute toxicity to insects and crustacea but it is strongly adsorbed to sediments. No significant responses were seen in this bioassay, indicating that any deltamethrin present was not bioavailable to *C. riparius*. No data on the concentrations of deltamethrin in the stream sediments are available for the period in question.

The bioassay results, although not comprehensive, show clearly that transient insecticide peaks seen in the Rosemaund stream have the potential to cause biological effects, provided that their toxicity is sufficiently high and the residues are not bound too firmly to particulates. It is worth noting that peak concentrations in the stream of several of the monitored herbicides (especially isoproturon, trifluralin and atrazine) approached or exceeded environmental quality standards proposed by the Department of the Environment and the National Rivers Authority (NRA), but the potential of these peaks to damage aquatic algae and plants was not confirmed by means of bioassays.

A biological survey of Rosemaund stream was conducted by the NRA in November 1994 in order to assess whether the many pesticide translocation events monitored during the period of this project had caused real environmental damage (Clabburn, 1995). Due to the absence of a suitable upstream control site at Rosemaund, a control sample was taken from Newbridge Brook at Shoal's Bank (NGR SO 394494). This catchment consisted of mainly agricultural grassland and woodland and was thought to be relatively uncontaminated by pesticides. The survey used the standard BMWP scoring system for benthic fauna and showed that the Rosemaund stream was very impoverished in fauna, with BMWP scores in the range 34-42. Interestingly, *Gammarus pulex* was either absent or sparse. However, the cause of this poor biological quality cannot be unequivocally attributed to pesticides because the control site also had poor species diversity (BMWP score = 39). It

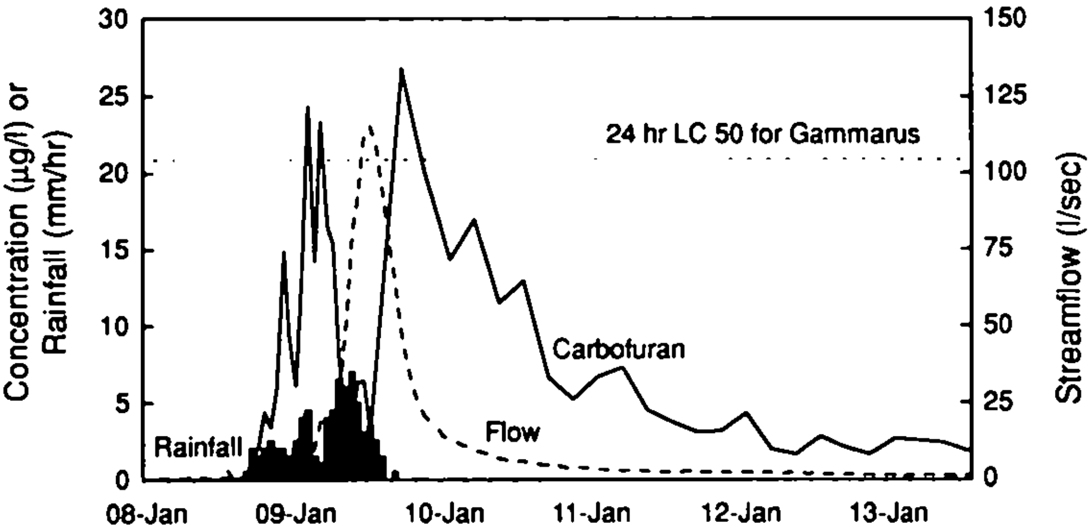


Figure 3.15 *Carbofuran event in the stream at site Rosemaund farm*

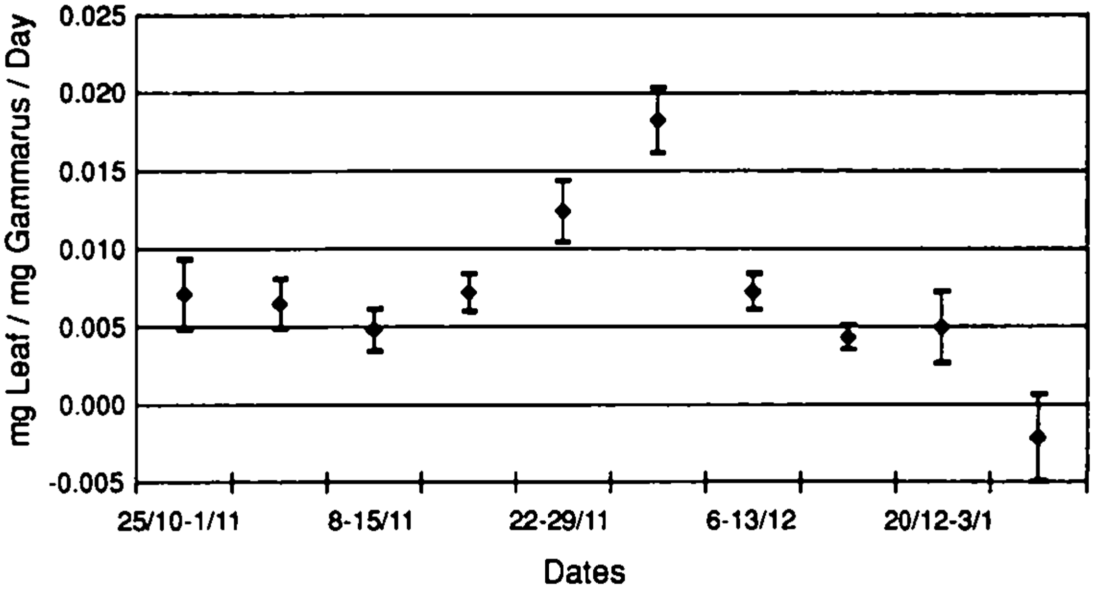


Figure 3.16 *Gammarus pulex feeding rates, October 1991 to January 1992*

Table 3.5 Summary of pesticide concentrations in soil in Rosemaund field experiments

Chemical	First sample[A]		Last sample[B]		Half life[C]
	Conc. (mg/kg)	Time (days)	Conc. (mg/kg)	Time (days)	(days)
Mecoprop	0.091	1	<0.001	31	4
2,4-D	0.027	1	<0.004	48	4
Simazine	0.175	2	0.081	84	84
Lindane	0.040	5	<0.002	90	28
Isoproturon	0.10	5	<0.01	91	14
Isoproturon	0.03	5	<0.01	75	
Mecoprop	0.058	1	0.002	62	11
Isoproturon	0.200	3	0.056	46	21
Dimethoate	0.031	2	<0.005	41	10
Dimethoate	0.022	2	<0.005	14	
MCPA	0.188	1	<0.001	40	8
Carbofuran	0.350	7	0.087	91	38
Atrazine	0.097	1	0.017	124	45
Aldicarb	0.030	7	0.020	69	25-50
Trifluralin	0.063	3	0.049	83	
Chlorpyrifos	0.077	5	0.060	33	80

Notes for table: [A]: First samples are mean concentration on first sampling visit after spraying, with time elapsed since spraying.

[B]: Last samples are mean concentration on last sampling visit, with time since spraying, or detection limit and time of first samples to be below limit.

[C]: Half lives are estimates from field data assuming first order degradation. No value indicates data too variable to allow calculation.

cannot be ruled out that the Newbridge Brook was significantly contaminated with pesticides, but there are no data available on this point. On balance, however, it seems likely that pesticides were at least partly responsible for the observed impoverishment in the Rosemaund stream because the conditions would have been expected to support more crustacean and insect species than was in fact the case.

3.4 Pesticides in soil and soil water

Soil

Data on the levels of pesticides in soil samples are summarised in Table 3.5. The mean levels in the first samples taken after application are shown, together with the time since the application. Also included are either the mean level in the last samples taken, or the detection limit where this was reached before the last sampling visit, together with the time elapsed since application.

In general, the individual samples from a sampling visit showed considerable variability, with the standard deviation often similar in magnitude to the mean level. This reflects the heterogeneous nature of the material being sampled and the difficulty in obtaining an even application over the whole field. The initial concentrations measured were of the order expected from the known application rates. Although one or two were lower than calculated — as one might expect from the effects of drift and other losses — most were in fact higher than calculated. This may reflect the difficulty in avoiding contamination of samples by extra surface soil which has very high initial concentrations.

Two examples of the disappearance of chemical with time are shown in Figures 3.17 and 3.18. The soil data were mainly used to give rough estimates of the half-life for degradation, assuming a first order removal process. In two cases, with lindane and the first mecoprop application, they showed a removal rate greater than that expected from values found in the literature. The lack of chemical found in the stream demonstrates that removal in water did not contribute significantly to the increased removal rate. For the mecoprop application it appears that recent previous applications to the same field had led to an acclimated microbial population which was able to degrade the chemical more rapidly in the subsequent application. The second mecoprop application studied here was not affected by this as it took place in a different field.

For many of the sampling visits, one of the samples was taken over depth intervals, usually 25 cm increments, which were analysed separately. The variability in one-off samples meant that it was

Table 3.6 Pesticide concentrations with depth in soil samples

Chemical	Time after application (days)	Concentration (mg/kg) 0-25cm	25-50cm	50-75cm	75-100cm
Isoproturon	3	0.369	0.041	0.071	0.166
	12	0.205	0.026	0.029	0.037
Atrazine	1	0.214	0.065	0.035	0.009
	45	0.078	0.013	0.008	0.004

Table 3.7 Summary of data on pesticides in soil water at 1.0-1.5 m depth

Pesticide and date	Delay after spraying (days)	Concentration range (μg/l)
Isoproturon (Nov. 89)	15	0.1-53.80
	29	0.3-54.20
Dichlorprop (Mar. 90)	1	<0.2-0.72
	27	<0.2-1.10
Mecoprop (Mar. 90)	1	<0.2-0.22
	27	<0.2-0.24
Isoproturon (Jan. 91)	42	<0.01-6.00
	53	0.03-18.20
Dimethoate (Jan. 91)	37	0.15-0.25
	48	0.02-0.16
Atrazine (Jan. 92)	42	0.01-1.24
	48	0.05-10.69
Carbofuran (Jan. 92)	36	<0.01-0.05
	42	<0.01-1.89
Aldicarb (sulphoxide + sulphone) (Apr. 92)	39	<0.6
	48	<0.6-8.4

difficult to draw firm conclusions from the measurements. In some cases they did appear to show the chemical at depth soon after application (isoproturon in Table 3.6), whilst others showed a more expected profile (atrazine in Table 3.6).

For one application (trifluralin, 1992) samples were taken from sites chosen to represent the different soil types within the field. As only a small number of samples could be taken for each type the results were variable. They did show different behaviour of the soils lying in the valley bottom near the stream (the Middleton and Compton series) which showed an apparent increase in concentration (over 1 m depth) after an initial decrease. This could be related more to their position than to differences in the soil composition. The other soils showed a more expected general decrease. Due to the variability in the data it was not possible to estimate half lives for this application.

Soil water

Pesticide concentrations in soil water obtained by porous pot suction samplers at 1.0-1.5 m depth are summarised in Table 3.7. For each pesticide trial, the range of concentrations found is given for two dates, the first generally being the first occasion after spraying when significant residues were observed, and the second being the subsequent sampling date. It will be apparent that substantial residue concentrations of almost all the pesticides investigated can reach field drain depth (approx. 1 m) within 2-6 weeks of spraying. There was generally little sampling during the first two weeks because the soil water content tended to be too

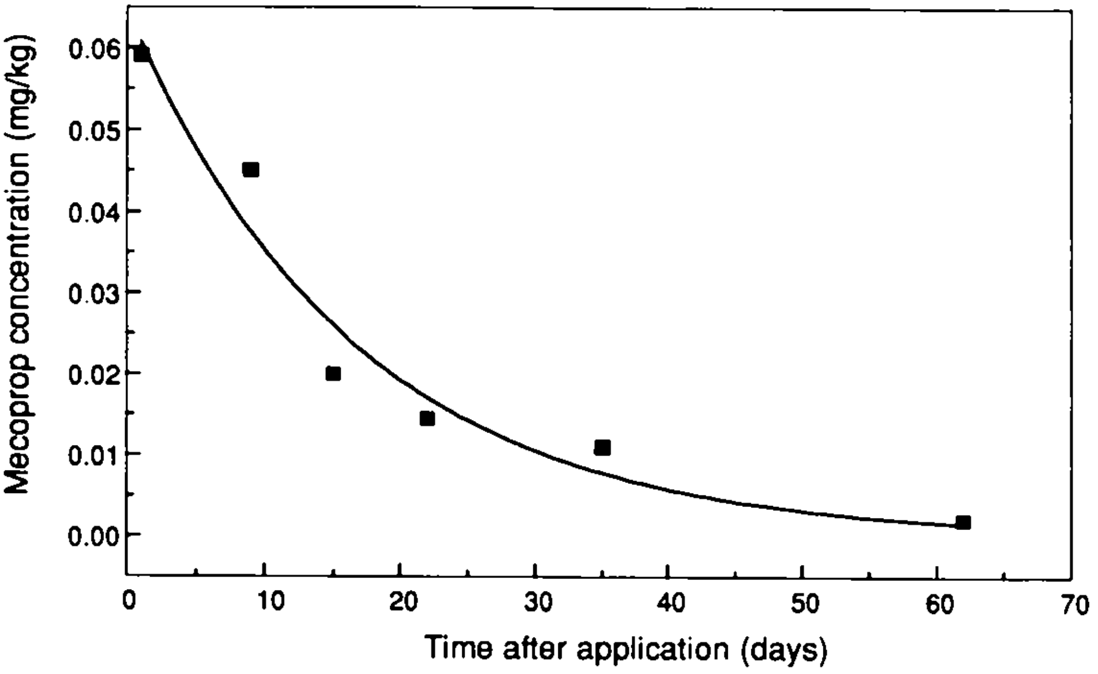


***Figure 3.17** Levels of Mecoprop in Foxbridge and Longlands following Spring 1990 application. Exponential curve fitted.*

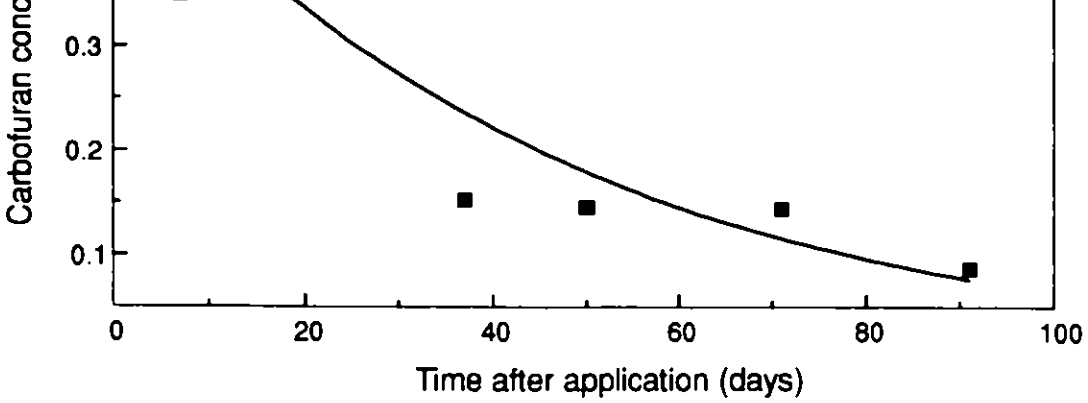


***Figure 3.18** Levels of Carbofuran in Stoney and Brushes following Winter 1991 application. Exponential curve fitted.*

low to permit collection of enough sample, so it is possible that residues were able to translocate to field drain depth in less than 2 weeks. Indeed, the mecoprop and dichlorprop data suggest that measurable residues can even reach 1.0-1.5 m after as little as one day, and this is supported by some of the drain and stream monitoring data (Table 3.1) which show that significant residues are able to be transported to the stream within a few days of spraying. Investigations of the soil hydrology at Rosemaund have confirmed that abundant macropores are available in the early winter to provide the necessary paths for this by-pass flow.

In summary, the soil data confirm the mass-balance calculations which show that almost all of the applied pesticide stayed in the soil and degraded there. There is evidence, however, to suggest that a small proportion of the pesticide residues at Rosemaund can be translocated very rapidly to field drain depth and below, and it is these which make up the bulk of the residues which appear in the field drains and stream after rainfall.

4 Modelling

4.1 Purpose of modelling

The overall objectives of the Rosemaund project were described in the introduction to this report, but the specific aims of the work on modelling will be restated here. A common aim of the modelling approaches is the prediction of levels of pesticide in water arising from agricultural applications; there are differences however in what types of prediction are needed and why. For the NRA and IH the objective was to produce and validate a simple model to estimate pesticide transport from a catchment. This was then to be developed to allow the effects of management options for the use of pesticides to be studied, and to guide sampling strategies for pesticides in surface waters. For MAFF and the BRE the objective was to use the data generated to test the ability of existing models to predict 'reasonable worst case' stream concentrations, with a view to predicting such concentrations for new substances as part of the assessment process before they appear in the environment. Another aim was to gain insight into the ability of simple models to describe the behaviour of chemicals in the environment and to assess how much reliance could be placed on quantitative estimates from such models.

4.2 Modelling approaches

Three modelling approaches have been applied to the Rosemaund data. Two of these are closely related, in that they are both based on the fugacity models developed by Mackay. The third is a model developed from observations of the behaviour of water at the site. The ideas behind the three models are described below. Detailed technical descriptions of the models are not included in this report but can be found in a number of publications referred to in the text.

4.2.1 Fugacity models

This section provides a brief description of the principles behind the fugacity models. A more detailed discussion on this modelling approach can be found in Mackay (1991).

Fugacity is a thermodynamic function. It can be thought of as the escaping tendency of a chemical, which will move from one phase to another in attempting to establish an equal fugacity in both phases. The advantages of fugacity over other measures of equilibrium are that it is linearly related to concentration (at low concentrations) and that absolute values can be established. Mackay introduced fugacity to environmental models in order to simplify the calculations. For each part of the environment a fugacity capacity can be defined, which measures how much fugacity a phase can hold (an analogy would be heat capacity). This fugacity capacity depends on the properties of the chemical as well as on the properties of the environment. The ratio of two values for different phases gives the partition coefficient between those two phases; this simplifies the calculations as only one value per phase is needed rather than partition coefficients between all pairs of phases.

In the fugacity models Mackay combined the use of fugacity with the concept of the unit world. In this the environment is made up of a number of boxes, each of which represents an environmental phase. These phases are also referred to as compartments. It is assumed that each compartment is homogeneous, that is the properties of the compartment (and the concentration of a chemical) are the same at all points within the compartment. The dimensions and properties of the compartments can be varied to produce a range of model environments.

The models can be applied with different levels of complexity depending on the processes included. At the simplest level a fixed amount of chemical is partitioned between the compartments of the model at equilibrium. No removal processes are included. This is usually referred to as Level I.

For the second level a number of loss mechanisms are introduced. Degradation processes can be included in any of the compartments; these are usually represented by first order kinetics. In addition there can be physical removal or advective processes, where the chemical is carried in flowing air or water or perhaps carried on suspended sediment. Such processes can of course also bring in chemicals into the model environment as well as remove it. In the Level II model the removal processes balance a constant input rate of chemical, with either direct release to the model or advective input (or both). The result is still an equilibrium distribution.

The third level model adds resistance to movement between compartments to the Level II model. The input is still continuous. This leads to a steady-state solution where the concentrations in the compartments are no longer at equilibrium.

The second and third level models have a constant rate of input of chemical to the model. This is obviously not the case with pesticides; here a one-off application is followed by the dissipation of the chemical over a period of time through the effects of degradation, water movement and volatilisation. Thus modification of this modelling approach to apply to the Rosemaund situation involved the inclusion of time dependence of the chemical concentration.

4.2.2 BRE approach

In this approach the environment to be modelled is split into two sub-models, one representing the field itself and the other the stream. Figure 4.1 shows the structure of the model.

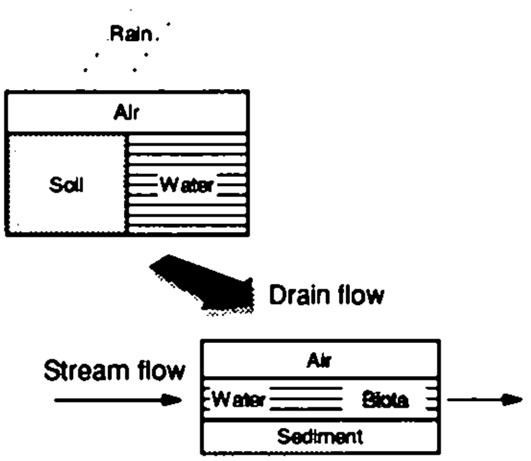


Figure 4.1 *Structure of BRE model*

The field model is made up of three compartments: solid soil, soil water and soil air. The depth of the model is considered to be 1 metre as this is the depth of the under drainage in the fields studied. The actual volumes of the compartments were calculated from this depth, the area treated with the chemical and measurements on soil density and water content (the average water content over the monitoring period was used to give a fixed water volume in the model).

The amount of chemical applied is partitioned between the three phases in the model immediately after application. This is equivalent to a Level I model. In the next step removal processes are allowed to act on the chemical in the appropriate compartment. This is done for a time period which is short in relation to the half-life or lifetime of the relevant process. At the end of this period the remaining chemical is repartitioned between the compartments and the process continues into the next time period.

The removal processes included are degradation and water flow. Degradation operates all the time on the water compartment. Rainfall is used to derive the water flow and to determine when it occurs. The results from the model are a series of concentrations in the three soil compartments with time, and corresponding amounts of chemical removed by water flow.

The second part of the model, the stream, is similar in construction but has four compartments: air above the stream, water, sediment and biota. Chemical input to this model is that removed from the field model by water flow, with a time delay dependent on the time between rain falling and the stream rising. Water flow rates came from actual stream monitoring data. Removal processes included in this model were again degradation and water flow. The results are in the form of a series of concentrations with time.

4.2.3 SoilFug

This model was developed by Antonio di Guardo and co-workers at the Universities of Milan and Toronto (Di Guardo *et al.*, 1994a). It was applied to the data from Rosemaund as part of a project sponsored by the European Science Foundation.

This model considers the field to be made up of four compartments: soil air, soil water, organic matter and mineral matter. The depth of the soil is set to 50 cm; this is considered to be the average length which water has to travel before it reaches the drainage system. Rainfall events are treated differently from the periods between them. In the "before rain event" periods (which include those between events) only degradation and volatilisation are included; transport is added in the "during rain event" periods. For "before rain event" periods the water content of the soil is considered to be equal to field capacity, a fixed value in order to simplify the calculations. For a rain event the volume of water in the soil is increased by the incoming rain and a new volume calculated with a maximum possible value equal to the total porosity of the soil (so that the soil air volume is reduced to zero).

After application the chemical is partitioned between the phases. For the period up to the first rain event degradation and volatilisation are allowed to act; degradation acts on the total soil volume, volatilisation is accounted for by diffusion through the soil air and water and the air boundary layer above the soil. The amount remaining at the end of this period is redistributed through the model world.

For a rainfall period the compartment volumes are recalculated as described above. In this case the three processes are allowed to act: degradation, volatilisation and transport. The volume of transport is taken as the measured outflow from the field over the period. The amount of chemical remaining at the end of the period is repartitioned and the cycle then begins again. The amount transported leads to a concentration in the drainage water and hence to a concentration in the stream which is an average for the rainfall period.

4.3.3 IH Model

The model structure presented here is derived from detailed measurements of the soil water movement and distribution in Longlands field over successive winters by members of the Agrohydrology section of the Institute of Hydrology (see Bell *et al.*, 1991 and 1992). Broadly, an underdrained field at ADAS Rosemaund consists of two types of soil profile which are characterised by the rate at which they allow downward water movement. The bulk of the soil in the inter-drain position has a very low hydraulic conductivity which approaches zero when the soil is saturated; downward water movement through the soil matrix is therefore very slow. The soil above the drains seems to have a much higher hydraulic conductivity and thus water movement through the soil matrix in this part of a field is much quicker. Thus, once the soil below the drains is saturated and the drains begin to flow the hydrological response of the drain is controlled by the soil immediately above and adjacent to the drains.

A diagrammatic representation of the model is shown in figure 4.2. The model considers the top 2 m of the soil profile which is divided into three layers above the level of the drains and one below. Above the drain the layers are subdivided vertically into two to represent the fast and slow parts of the soil profile described above. The fields are generally sloping and in this conceptualization the drain zone is considered to be down slope of the inter-drain zone. The consequent possible directions of water movement are shown by the arrows in Figure 4.2, where dotted arrows indicate the possibility of water moving directly to lower layers (via macropores and/or cracks) without interacting with intervening layers. The transport of pesticide in the system is assumed to be associated with the water movement, the pesticide being partitioned between the soil and water phases at the end of each time-step. The model keeps account of the amounts of water and the dissolved and adsorbed pesticide in each box and calculates changes to these depending on a mass balance of inputs, outputs and internal sources and sinks.

The model keeps a water balance for each box; there is a minimum water content before water can leave a box, and each box has a maximum

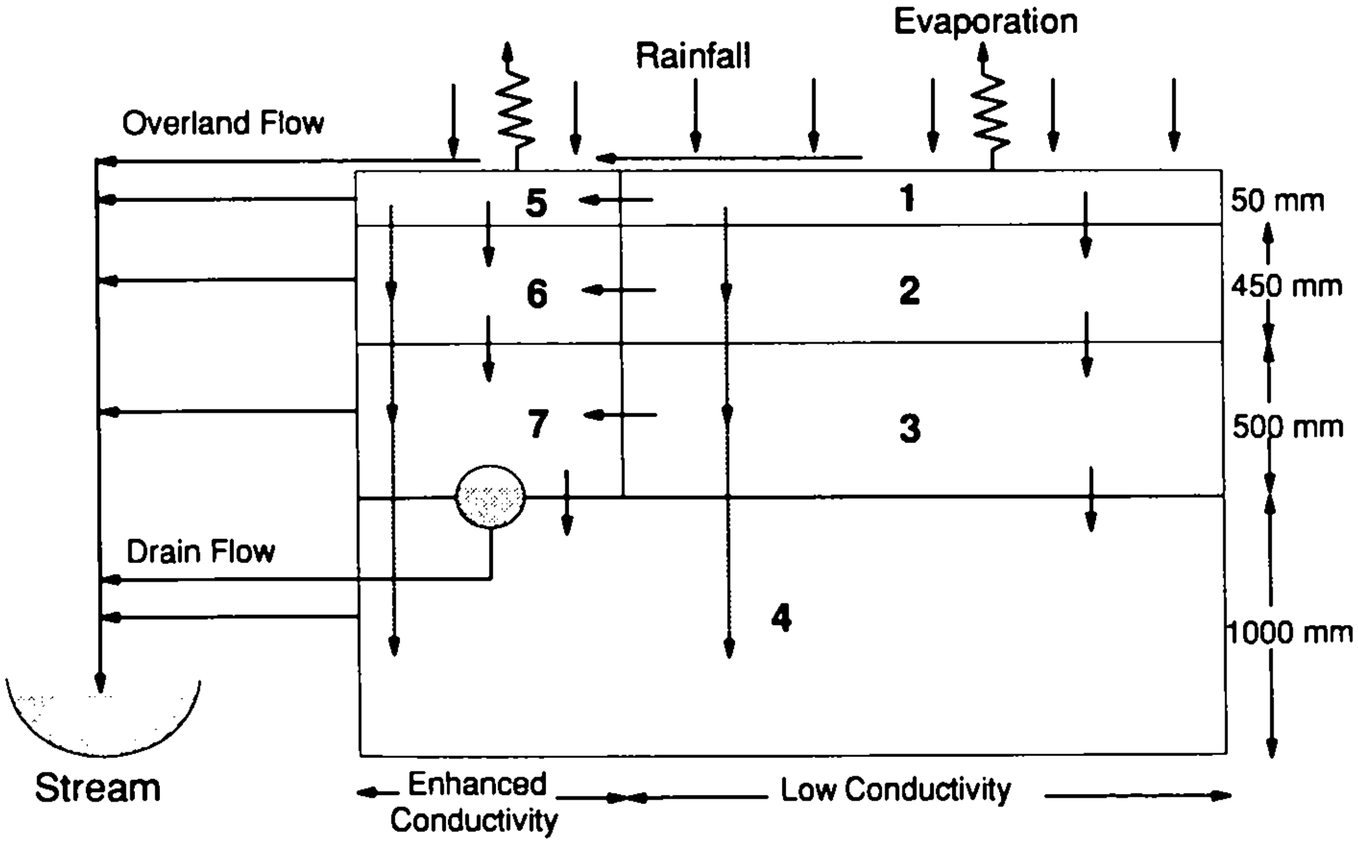


Figure 4.2 Structure of IH model showing division into compartments and water pathways

water content beyond which it will not accept any more. The chemical applied is initially considered to be well mixed into the surface layer. The movement of water carries the chemical through the model and eventually to the drain or the stream.

The model only allows drainflow when the deep soil box, (box 4, Figure 4.2) is at saturation. When this occurs, drainflow is the sum of the vertically draining water from boxes 3 and 7 plus any water from rainfall and boxes 5 and 6 moving via by-pass routes. Water moving from boxes 3 and 7 is assumed to produce drainflow by displacement of water from box 4, while water in bypass routes is directly intercepted by the drain. The concentration of pesticide in the drainflow is thus a mass balance of the contributions from the various flow paths.

Stream flow is the sum of the lateral drainage from each of the boxes, and drain flow. Again the concentration of pesticide is a mass balance of the contributions from all the flow paths. Overland flow is generated when rainfall less evaporation and drainage exceeds the capacity of box 1 to contain water. Water flowing overland from box 1 will infiltrate into box 5 if this box is not saturated. The concentration of pesticide in the overland flow is assumed to be equal to the concentration of the box from which it was generated.

4.3 Results of model applications

This section describes the application of the various modelling approaches to the data generated at ADAS Rosemaund.

4.3.1 BRE model

This model has been applied to five of the pesticide applications. These were mecoprop (1987/88), isoproturon and lindane (1989/90), mecoprop (spring 1990) and MCPA (spring 1991). Initial tests of the model used a water flow rate through the field model equivalent to the total rainfall. This gave very large amounts of chemical removed in the water and hence very high concentrations in the stream model. For the model runs discussed here the water flows in the soil model were calculated as 20% of the actual rainfall.

The results of the modelling exercise on isoproturon and lindane, and the two mecoprop applications were presented in Williams *et al.* (1991a). There was good agreement between the measured levels in the soil and those predicted by the model. For some of the applications the initial calculated concentrations were lower than those actually measured. It is not clear why this should be so; however, as the aim of the project was to develop a predictive model then the amount of each chemical added to the field model was not adjusted. For lindane and mecoprop the rate of disappearance in the field was greater than that predicted from the literature data. A new value for the half life was derived from the measurements and used to recalculate the field model levels. Half lives for other chemicals and all sorption coefficient values were taken from the literature.

In the experiments with isoproturon and lindane the concentration of chemical in water as it emerged from the drains was determined on a number of occasions. As the water in the field model carries chemical out into the stream it is analogous to the drains and so these measurements were compared with the levels calculated for the soil water in the model. For isoproturon the measured values ranged from 1.1 to 8.8 $\mu g\ l^{-1}$ compared to model levels of 4.4 to 4.7 $\mu g\ l^{-1}$; for lindane the measured levels were 0.02 to 0.45 $\mu g\ l^{-1}$ and the calculated levels were around 0.4 $\mu g\ l^{-1}$.

Levels predicted in the stream model were much closer to those measured than in the initial tests for three of the five applications. Example plots showing the output from the model and the measured concentrations in the stream are shown in Figures 4.3-4.5. Although a time series of concentrations is obtained from both the measurements and the model, it is the peak levels which are of most interest. Comparing the peak levels from the model and the stream gave ratios of 1.6 for lindane, 3.0 for isoproturon and 5.8 for the 1987 mecoprop application. The agreement for the second mecoprop application is much worse, giving a ratio of 20.4. This application took place in the spring rather than the autumn as with the first mecoprop application. Studies of the hydrology at Rosemaund have noted the different behaviour of the water regime for different seasons and this may be a contributory factor to the difference between the two mecoprop results. A later test of the model on data for MCPA, another phenoxy alkanoic acid herbicide, gave a ratio of 58 between calculated and measured peaks levels for a spring application.

4.3.2 SoilFug model (Di Guardo *et al.*, 1994b)

The SoilFug model has been applied to a range of areas on the farm site, not just those studied in more detail at the top of the catchment. This allowed the use of data from the main stream monitoring station as well as that from the upper site and the drains. All rain events following applications were modelled and compared to the measured levels where these were available. The model predicts an average concentration over the course of an event so one value is obtained for each event. This resulted in a total of 74 predicted

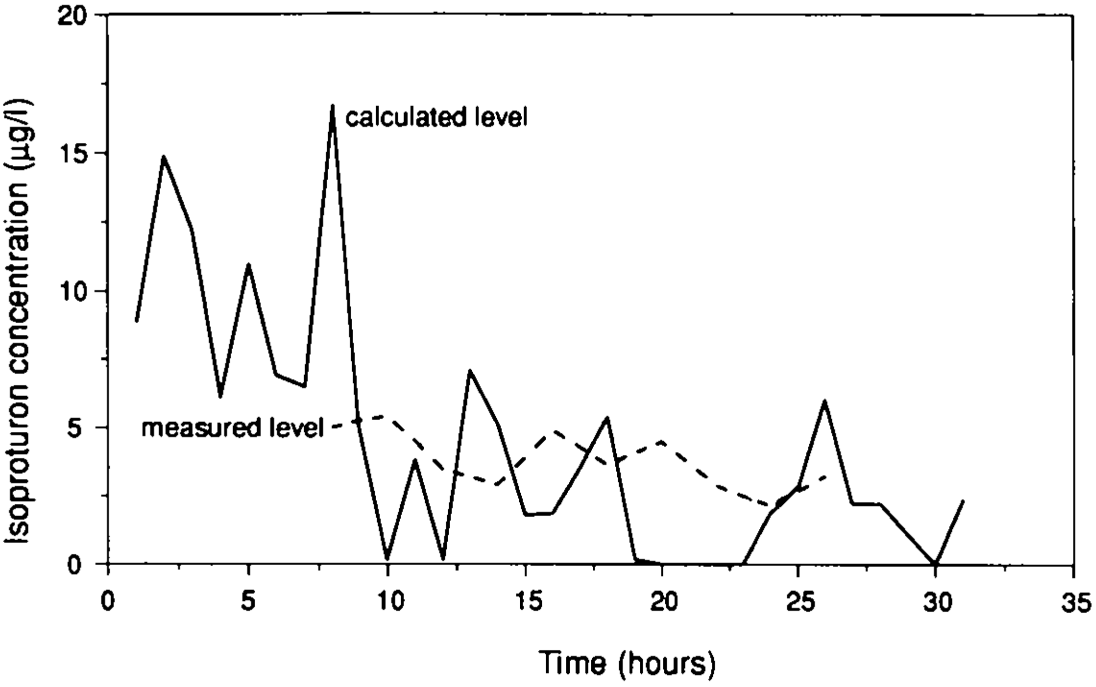


Figure 4.3 *Measured and calculated isoproturon concentrations for BRE model in ADAS Rosemaund stream (site 1) following rainfall event of 13/12/89*

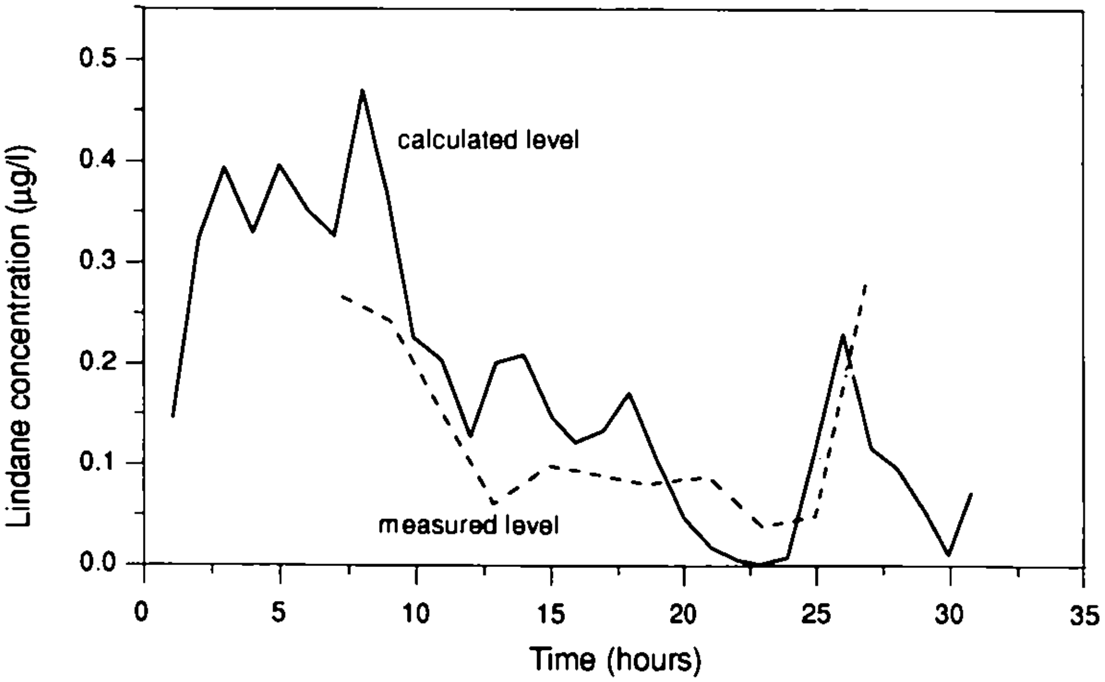


Figure 4.4 *Measured and calculated lindane concentrations for BRE model in ADAS Rosemaund stream (site 1) following rainfall event of 13/12/89*

concentrations with corresponding measured levels. For comparison, a flow weighted mean concentration was calculated for each set of measured values. The chemicals were divided into two types: neutral or undissociated pesticides and phenoxy acid herbicides. Summaries of the results for these two groups of chemicals are shown in Tables 4.1 and 4.2.

For the 67 rainfall events monitored following the application of neutral or undissociated pesticides, 49 (73%) of the predicted average concentrations came within a factor of 10 of the measured average levels. Of the remaining 18 cases only 4 differed by more than a factor of 100. The overall tendency is to overpredict the measured average concentration, with the predictions in general being within a factor of 3 of the maximum measured concentrations. Exceptions to this are the two events involving deltamethrin, where the predicted values are much lower than those measured. The most likely explanation for this is that the deltamethrin is carried in the adsorbed phase and the model does not account for the movement of solid material.

For the phenoxy acid herbicides the situation is somewhat different. In all cases except one the predicted concentrations are between one and two orders of magnitude higher than the measured values. This is perhaps not what one would expect given that the chemicals are expected to be ionised in solution at environmental pH values and hence would be expected to move more easily into water than the neutral compounds. A Koc value of 20 was chosen as suggested by Wauchope *et al.* (1992) as being appropriate for chemicals present in dissociated anionic form at environmental pHs. It may be that this value is not appropriate for these particular chemicals in the specific soils at Rosemaund. It should also be pointed out that there are difficulties in modelling this type of chemical by fugacity; they do not have an appreciable vapour pressure and hence it is difficult to estimate a value for the Henry's law constant which plays an important role in the calculation of the fugacity capacities.

Levels of chemicals in soil tend to be overpredicted, usually by a factor of two or three. In this case a direct comparison with the measured data is not possible as the model considers only the top 50 cm of the soil whereas the measurements are averages over 1 metre.

4.3.3 IH model

The model has been used to simulate the pesticides isoproturon, lindane, simazine, mecoprop, trifluralin and dichlorprop in both field drains and at two locations in the stream. The model is driven by hourly rainfall taken from the automatic weather station (AWS). The AWS also provides estimates of potential (Penman) evaporation which have been taken as actual evaporations where the water content of the surface boxes is sufficient to meet the demand.

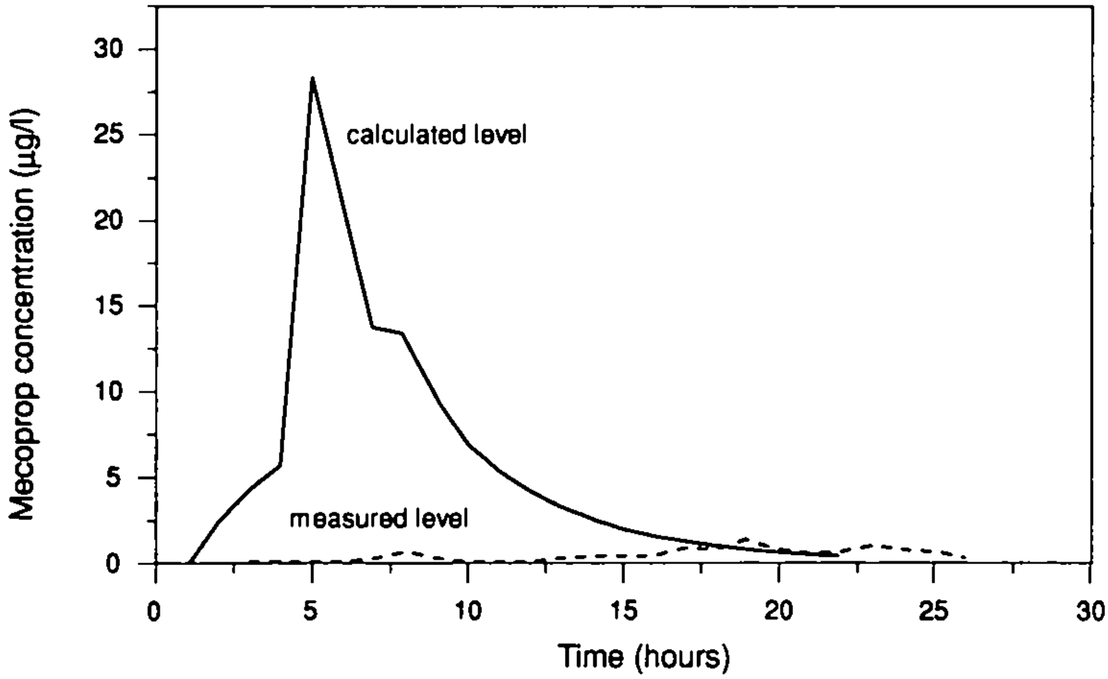


Figure 4.5 *Measured and calculated mecoprop concentrations for BRE model in ADAS Rosemaund stream (site 1) following rainfall event of 15/5/90*

***Table 4.1** Measured and predicted concentrations from the SoilFug model for neutral or undissociated pesticides in the ADAS Rosemaund drains and stream*

Chemical	Year	Site[D]	Measured concentration (µg/l)[A] minimum	maximum	Measured concentration concentration average[B] (µg/l)	Model concentration[C] (µg/l)
Atrazine	91/92	0	0.06	1.79	0.6	6.09
			0.47	1.76	0.9	3.88
			0.01	5.67	2	17.8
			<0.01	13.3	1.9	15.6
			0.02	0.23	0.11	6.18
			<0.01	0.13	0.06	3.79
			0.38	51.3	10.6	50.8
			1.02	7.07	5.7	44.5
			0.09	0.65	0.45	17.7
			0.03	1.73	1.6	10.8
			20.25	56.5	35.7	142
			3.2	81.4	15.9	129
			8.7	16.2	11.2	46.7
Carbofuran	91/92		0.07	26.78	10.4	7.99
			0.04	37.45	6.2	7.11
			0.01	2.35	0.46	2.31
			0.02	<0.01	0.006	1.29
			12.24	264	25.7	53.1
			6.13	58.39	37.2	47.1
			<0.01	9.87	1.0	15.4
			<0.01	0.18	0.09	8.61
Deltamethrin	92/93		<0.001	0.008	0.001	8.2×10^{-5}
			0.024	1.87	0.075	7.9×10^{-5}
Dimethoate	90/91	0		<0.02	<0.02	0.42
				<0.02	<0.02	0.143
				<0.02	<0.02	0.103
			0.28	3.05	1.2	2.86
			<0.05	0.16	0.03	0.69
Isoproturon	89/90	1	2.1	5.4	3.3	5.78
		3	1.2	8.4	4.3	22.9
			1.8	13.7	6.7	21.6
Isoproturon	89/90	3	1.1	8.8	3.2	12.9
	90/91	0	0.05	1.76	0.49	3.33
			0.05	1.76	0.36	2.28
			<0.02	6.7	6.0	2.04
			1.92	17.2	10.6	9.46
			0.1	2.62	0.96	5.76
			0.26	2.07	0.92	1.17
			0.09	0.38	0.14	31.2
			0.02	2.7	1.4	6.81
			1.41	2.46	1.7	3.03
Lindane	89/90	0	<0.001	0.75	0.16	0.20
		1	0.04	0.29	0.012	0.864
			0.004	0.03	0.011	0.668
		3	0.04	4.46	1.2	2.28
			0.06	4.14	1.2	2.27
			0.016	0.45	0.14	2.06
			0.001	0.027	0.013	1.6

Table 4.1 Continued

Chemical	Year	Site[D]	Measured concentration (µg/l)[A] minimum	maximum	Measured concentration concentration average[B] (µg/l)	Model concentration[C] (µg/l)
Lindane		5	0.03	1.74	0.85	5.61
			<0.01	2.55	0.57	5.03
Simazine	88/89	0	4.4	68	22.4	3.57
			4.5	13.9	8.2	3.33
		1	<0.1	1.8	0.5	4.87
	90/91	0	1.01	4.12	1.67	2.10
			0.46	1.49	0.9	1.85
			0.32	0.84	0.5	1.77
			0.1	0.36	0.26	0.88
			0.65	15.3	3.30	1.58
Trifluralin	92/93	1	0.02	0.94	0.58	0.25
			0.10	0.38	0.22	0.24
			0.05	0.13	0.08	0.21
			0.01	0.08	0.03	0.17
			0.06	1.04	0.13	0.16
			0.01	0.10	0.05	0.13
			0.38	14.12	3.1	1.49
			0.18	2.2	0.63	1.43
			0.15	1.0	0.36	1.26

Table 4.2 Measured and predicted concentrations from the SoilFug model for phenoxy acid herbicides in the ADAS Rosemaund drains and stream

Chemical	Year	Site[D]	Measured concentration (µg/l)[A] minimum	maximum	Measured concentration concentration average[B] (µg/l)	Model concentration[C] (µg/l)
Dichlorprop	89/89	1	<0.2	1	0.35	6.93
MCPA	90/91		0.28	12.44	1.9	131
			0.34	2.23	1.2	104
			0.27	12.68	1.9	42.1
		3	0.38	18.8	5.4	291
Mecoprop	87/88	1	<0.2	11.7	4.2	60.5
	89/90	1	<0.2	1.4	0.3	0.343

Notes for Tables 4.1 and 4.2

[A]: Measured concentration: measured maximum and minimum concentrations for the rain event
[B]: Measured concentration average: flow weighted mean concentration during the rain event
[C]: Model concentration: calculated mean concentration during the rain event
[D]: Sites: 0 = main stream;
1 = stream at top of catchment;
3,5 = drains

The properties of the various boxes in the model, e.g. maximum and minimum water contents, organic carbon content etc, were derived from actual measurements or were estimated from experience at the site. The model required calibration to select the values for the parameters controlling the movement of water between the boxes. Initial values were chosen based on observations of the relative magnitude of the water flows at the site. These values were then adjusted based on a comparison of the measured flowrates for the period January to March 1991 with those predicted from the model. The values derived were then used in all later simulations including those for other years and covering additional monitoring sites.

The model requires values for three pesticide related parameters: the application rate, the organic carbon-water partition coefficient and the degradation rate. The application rates came from ADAS Rosemaund, the other values were taken from the literature. No changes in degradation rate are currently made as a result of temperature, soil moisture content or depth.

The results of the model simulations are summarized in Table 4.3 for each event and pesticide combination. Comparisons are made between observed and modelled data in terms of the peak and flow weighted mean pesticide concentrations. The error in the prediction of the timing of the peak is also reported.

The model produced good estimations of the values of both the peak and flow weighted mean pesticide concentrations, generally to better than one order of magnitude. There are only two cases, both for isoproturon, where the measured levels exceed the calculated values by more than a factor of ten; one of these is a rain event where the chemical was not detected whereas the model gave values higher than the detection limit. However the time for the peak concentration was not predicted well, the model always anticipating the observed peak by several hours. The identification of the peak value in the time series of concentrations representing an individual event can present difficulties given the different pesticide transport patterns that have been observed. In Figure 4.6 the observed and modelled data show a similar pattern but the curves are shifted in time; here it is easy to compare peak values and estimate a time error. In Figure 4.7, on the other hand, the comparison is more difficult, the observed data having two peaks, the second being higher than the first. Thus comparison of the peak modelled and observed concentrations in such situations gives a large error in timing. A third pattern of behaviour is shown in Figure 4.8, where good correspondence was achieved between observed and modelled simazine concentrations for the event. However, the model suggests that if sampling had started earlier, higher concentrations of simazine would have been found.

Of particular interest is the fact that the model predicted concentrations of trifluralin as effectively as for any of the other chemicals that were simulated. This confirms the assumption made by the model that even fairly highly sorbed chemicals can be treated in a similar fashion to more soluble chemicals (Figure 4.9).

4.4 Conclusions

The three different modelling approaches described here have been applied to the ADAS Rosemaund data with varying degrees of success. In attempting to draw any conclusions from these exercises it is important to keep in mind a number of factors. The purpose for which a model is required is obviously of importance; so too are ease of use and availability of data. Models for use in a risk assessment process may be required to work with limited data and be relatively easy to use in order to allow a large number of chemicals to be dealt with. If a model is being used to look at management options at a specific site then more detailed information will be available and hence a more complex model may be used.

Looking at the two fugacity based models together, they require similar input data for the most part. SoilFug needs less data on the individual rain events, only overall rainfall and outflow. This model produces estimates of the average concentration which tend to be overpredictions of the measured average levels but are close to the maximum measured levels. Hence this model would be useful at an early stage in a risk assessment in identifying those chemicals which are most likely to cause problems through this route of release. The BRE model produces a time series of concentrations which can be used to generate peak and average levels. However production of a time series requires more data input in the form of time series values for rainfall and stream flowrate; the calculations are also more complex and take more time. The results produced are not very different from those produced by SoilFug and so the extra effort involved to obtain them does not add a great deal to the output. It should also be pointed out that the current BRE software is much less user friendly than the SoilFug program.

The IH model is much more detailed in its description of the field and therefore needs more data. Estimates are needed for the minimum, maximum and field capacity water contents of the boxes in the model and for the parameters controlling

Table 4.3 Summary of the results of the simulation of pesticide concentrations using the IH model at ADAS Rosemaund during a number of rainfall events

Pesticide	Date of event	Site no.	Observed mean[1] (µg/l)	Predicted mean[1] (µg/l)	Error[4]	Observed maximum (µg/l)	Predicted maximum (µg/l)	Error[4]	Time error (hours)
Isoproturon	8/11/89	3	4.3	1.4	-0.49	8.4	15.0	0.25	10
	10/11/89	3	6.7	1.2	-0.75	13.7	8.0	-0.24	5
	13/12/89	3	3.2	0.93	-0.54	8.8	12.6	0.16	8
	13/12/89	1	3.3	3.9	0.07	5.4	13.9	0.41	12
	25/12/90	0	0.49	2.4	0.70	1.8	6.8	0.58	13
	25/12/90	1	10.6	4.2	-0.40	17.2	12.3	-0.14	2
	5/01/91	0	0.36	1.6	0.64	5.2	2.5	-0.32	20
	8/01/91	0	0.60	1.4	0.37	6.7	1.7	-0.60	20
	8/01/91	1	0.96	2.5	0.42	2.6	3.1	0.08	3
	8/01/91	5	0.14	2.7	1.30	0.40	5.9	1.17	7
	21/02/91	0	<0.02	0.24	>1.10	<0.02	0.30	>1.18	-
	21/02/91	1	0.92	0.43	-0.33	2.1	0.50	-0.62	2
	21/02/91	5	1.4	0.73	-0.28	2.6	1.2	-0.34	6
	4/03/91	5	1.7	0.53	-0.51	2.3	0.80	-0.46	24
Lindane	8/11/89	3	1.2	0.35	-0.54	4.6	3.5	-0.12	6
	8/11/89	5	20.85	0.90	0.02	1.9	8.8	0.67	10
	10/11/89	3	1.2	0.35	-0.54	4.1	2.7	-0.18	5
	13/12/89	1	0.12	0.67	0.74	0.30	2.4	0.90	10
	13/12/89	3	0.14	0.27	0.28	0.50	2.9	0.76	7
	16/12/89	0	20.16	0.17	0.02	0.40	0.50	0.10	-3
	16/12/89	5	20.57	0.64	0.05	2.5	4.6	0.26	-3
Simazine	24/02/89	0	22.4	32	0.15	68.0	101.0	0.17	5
	2/03/89	0	8.2	28	0.53	13.9	87.6	0.80	8
	24/02/89	1	0.50	4.4	0.96	12.8	1.8	0.85	12
	25/12/90	0	1.7	0.41	-0.62	4.1	1.4	-0.47	1
	5/01/91	0	0.90	0.35	-0.41	1.5	0.60	-0.40	8
	8/01/91	0	20.5	0.33	-0.20	0.70	0.40	-0.24	1
	21/2/91	0	0.26	0.17	-0.18	0.40	0.20	-0.30	5
	16/03/91	0	3.3	7.8	0.38	15.3	26.2	0.23	3
Mecoprop	15/5/90		0.30	0.78	0.42	1.4	5.2	0.57	16
Dichlorprop	15/5/90	1	0.35	0.23	-0.18	1.0	1.5	0.18	14
Trifluralin	11/11/90	5	3.7	0.64	0.76	14.1	14.9	0.03	2
	15/11/90	5	0.39	0.12	0.51	2.2	1.2	-0.26	1

Notes:

[1] Flow weighted mean
[2] Simple mean (no flow data available)
[3] More than one rainfall event during sampling period
[4] LOG_{10} (Predicted/observed), 0 is perfect fit, >1 or <-1 fit worse than order of magnitude

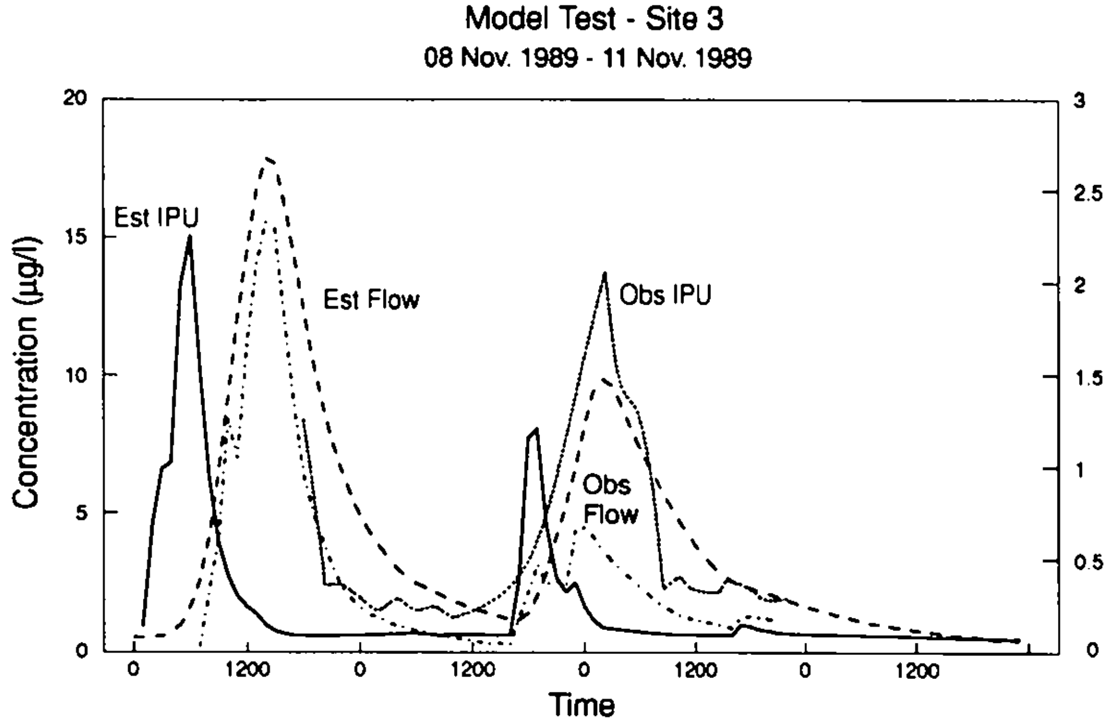


Figure 4.6 Observed and simulated flow and isoproturon concentrations as generated by the IH model for Site 3

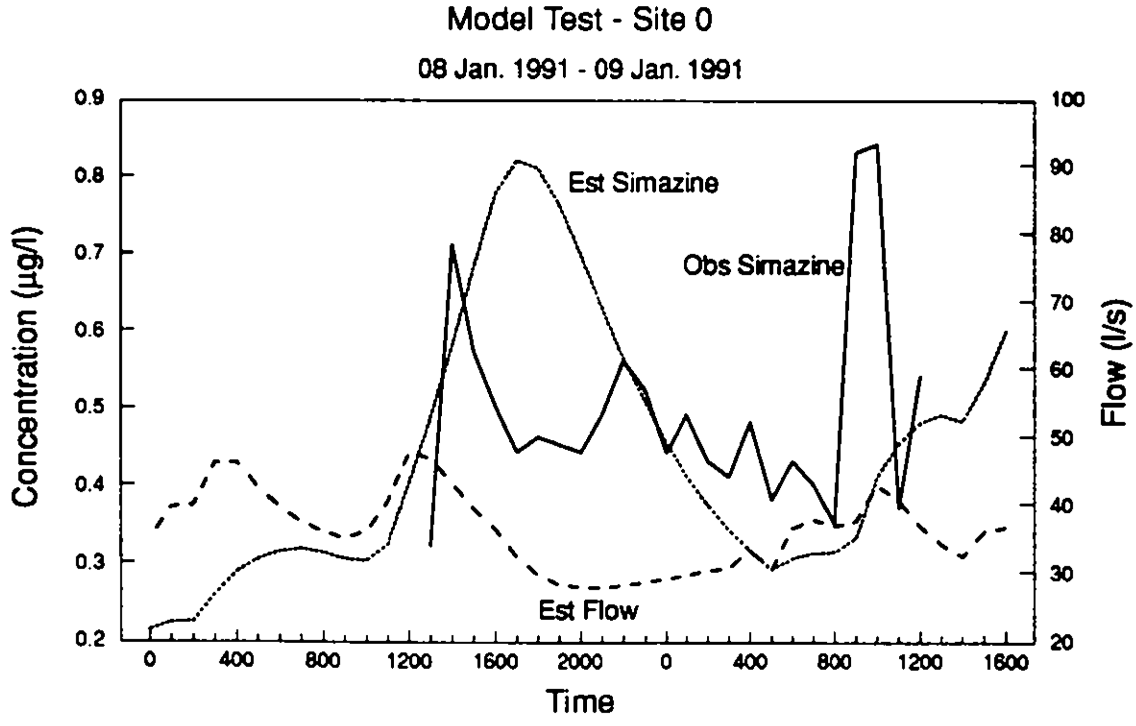


Figure 4.7 Observed and simulated simazine concentrations and simulated flow using the IH model at Site 0

***Table 4.3** Summary of the results of the simulation of pesticide concentrations using the IH model at ADAS Rosemaund during a number of rainfall events*

Pesticide	Date of event	Site no.	Observed mean[1] (µg/l)	Predicted mean[1] (µg/l)	Error[4]	Observed maximum (µg/l)	Predicted maximum (µg/l)	Error[4]	Time error (hours)
Isoproturon	8/11/89	3	4.3	1.4	-0.49	8.4	15.0	0.25	10
	10/11/89	3	6.7	1.2	-0.75	13.7	8.0	-0.24	5
	13/12/89	3	3.2	0.93	-0.54	8.8	12.6	0.16	8
	13/12/89	1	3.3	3.9	0.07	5.4	13.9	0.41	12
	25/12/90	0	0.49	2.4	0.70	1.8	6.8	0.58	13
	25/12/90	1	10.6	4.2	-0.40	17.2	12.3	-0.14	2
	5/01/91	0	0.36	1.6	0.64	5.2	2.5	-0.32	20
	8/01/91	0	0.60	1.4	0.37	6.7	1.7	-0.60	20
	8/01/91	1	0.96	2.5	0.42	2.6	3.1	0.08	3
	8/01/91	5	0.14	2.7	1.30	0.40	5.9	1.17	7
	21/02/91	0	<0.02	0.24	>1.10	<0.02	0.30	>1.18	-
	21/02/91	1	0.92	0.43	-0.33	2.1	0.50	-0.62	2
	21/02/91	5	1.4	0.73	-0.28	2.6	1.2	-0.34	6
	4/03/91	5	1.7	0.53	-0.51	2.3	0.80	-0.46	24
Lindane	8/11/89	3	1.2	0.35	-0.54	4.6	3.5	-0.12	6
	8/11/89	5	20.85	0.90	0.02	1.9	8.8	0.67	10
	10/11/89	3	1.2	0.35	-0.54	4.1	2.7	-0.18	5
	13/12/89	1	0.12	0.67	0.74	0.30	2.4	0.90	10
	13/12/89	3	0.14	0.27	0.28	0.50	2.9	0.76	7
	16/12/89	0	20.16	0.17	0.02	0.40	0.50	0.10	-3
	16/12/89	5	20.57	0.64	0.05	2.5	4.6	0.26	-3
Simazine	24/02/89	0	22.4	32	0.15	68.0	101.0	0.17	5
	2/03/89	0	8.2	28	0.53	13.9	87.6	0.80	8
	24/02/89	1	0.50	4.4	0.96	12.8	1.8	0.85	12
	25/12/90	0	1.7	0.41	-0.62	4.1	1.4	-0.47	1
	5/01/91	0	0.90	0.35	-0.41	1.5	0.60	-0.40	8
	8/01/91	0	20.5	0.33	-0.20	0.70	0.40	-0.24	1
	21/2/91	0	0.26	0.17	-0.18	0.40	0.20	-0.30	5
	16/03/91	0	3.3	7.8	0.38	15.3	26.2	0.23	3
Mecoprop	15/5/90		0.30	0.78	0.42	1.4	5.2	0.57	16
Dichlorprop	15/5/90	1	0.35	0.23	-0.18	1.0	1.5	0.18	14
Trifluralin	11/11/90	5	3.7	0.64	0.76	14.1	14.9	0.03	2
	15/11/90	5	0.39	0.12	0.51	2.2	1.2	-0.26	1

Notes:

Flow weighted mean

[2] Simple mean (no flow data available)

[3] More than one rainfall event during sampling period

[4] LOG_{10} (Predicted/observed), 0 is perfect fit, >1 or <-1 fit worse than order of magnitude

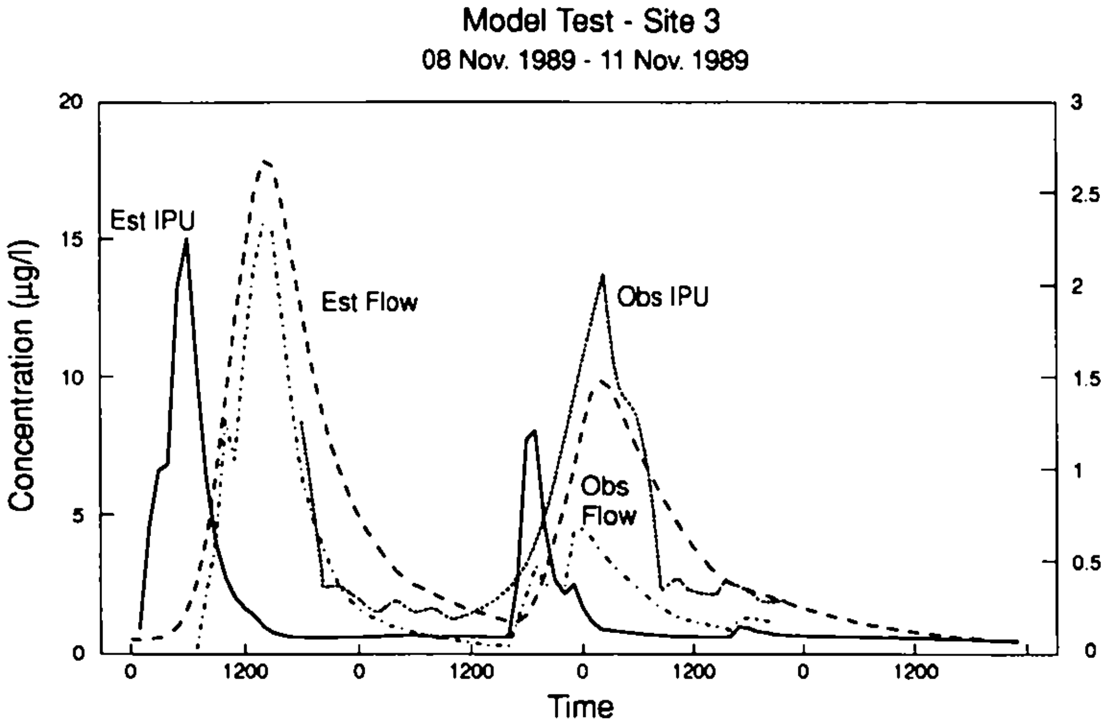


Figure 4.6 *Observed and simulated flow and isoproturon concentrations as generated by the IH model for Site 3*

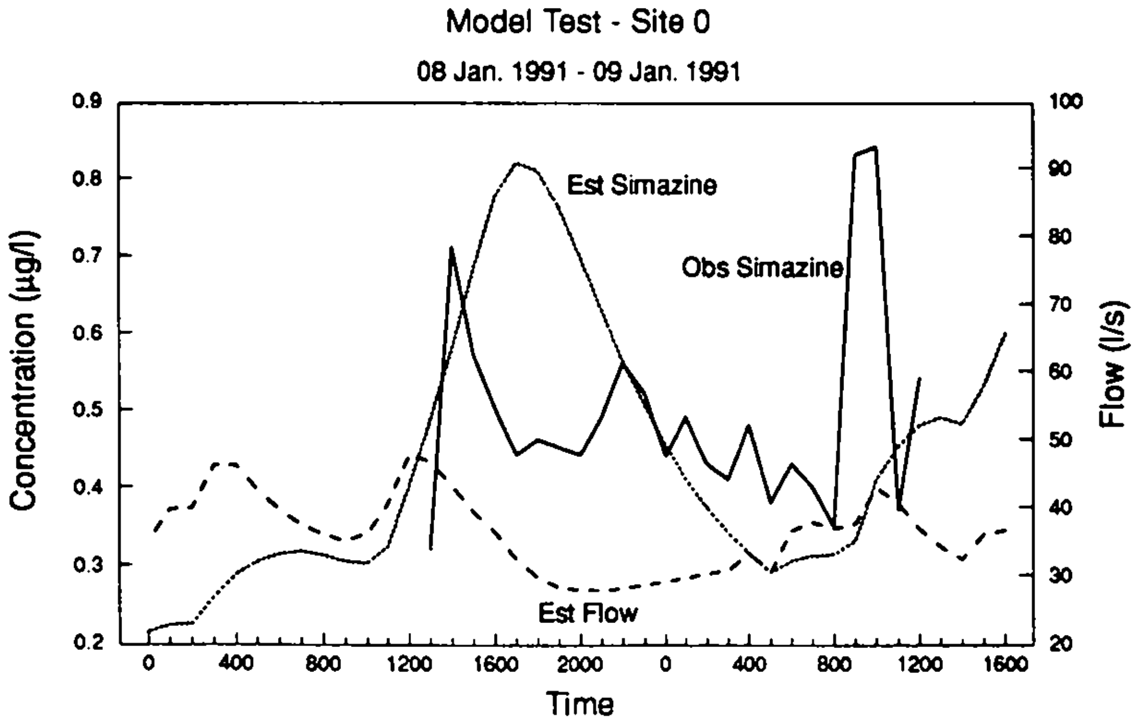


Figure 4.7 *Observed and simulated simazine concentrations and simulated flow using the IH model at Site 0*

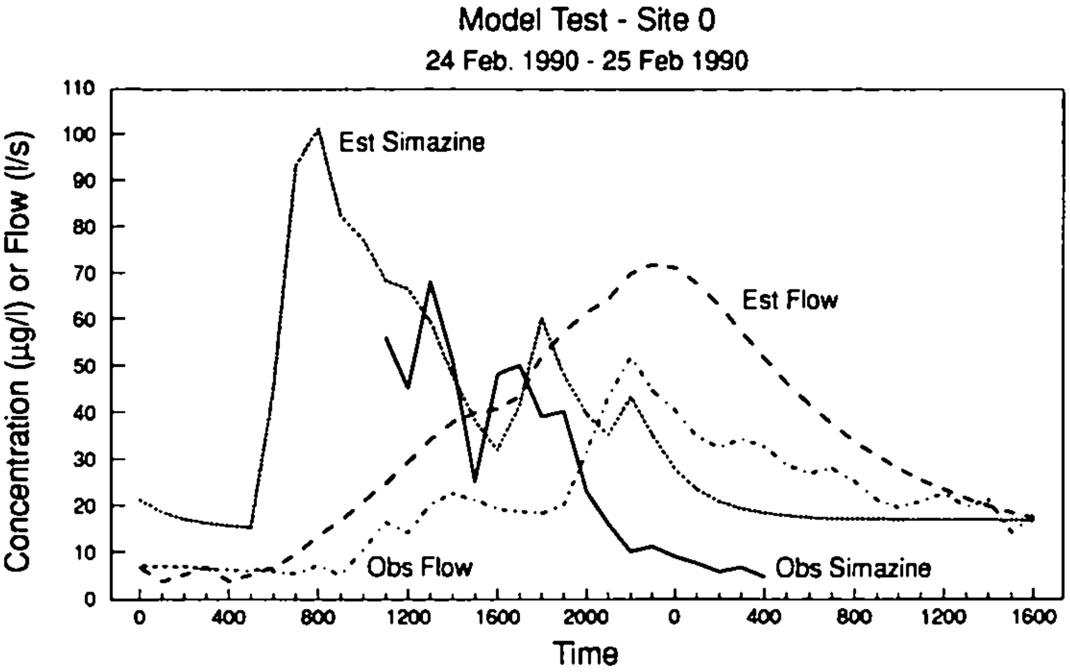


Figure 4.8 *Comparison between observed flow and simazine concentration and values simulated using the IH model*

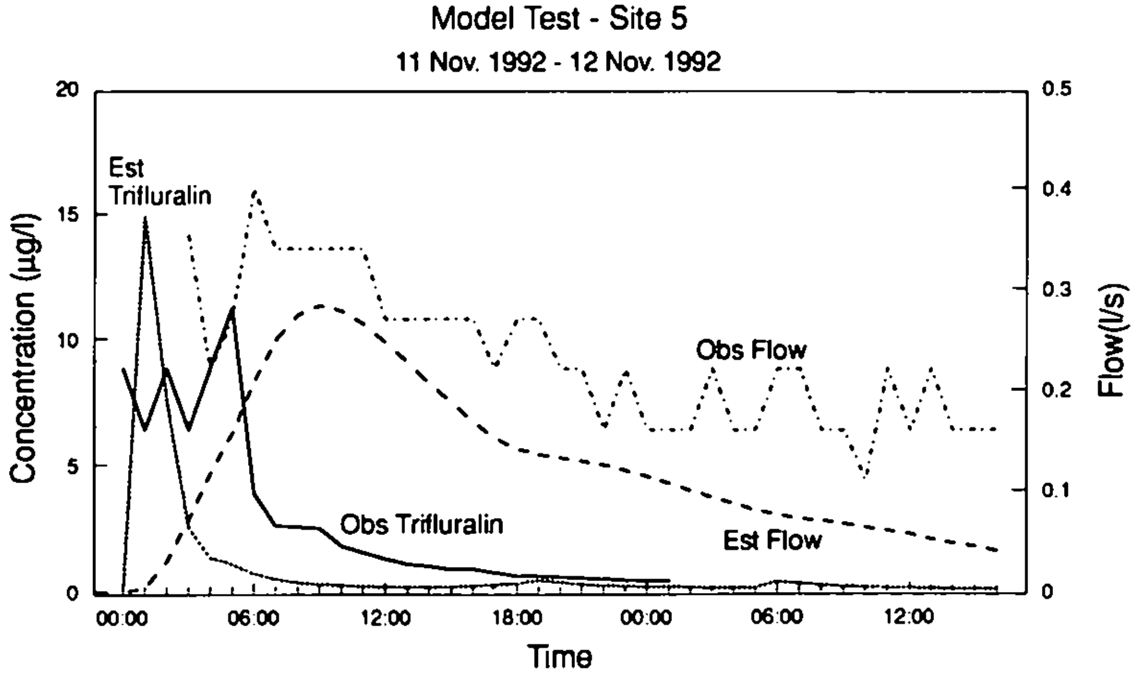


Figure 4.9 *Comparison between observed flow and trifuralin concentration and values simulated using the IH model*

water movement between them. This level of detail means that the model may be calibrated to different situations through suitable observations. Questions such as for how long the stream concentration would remain above a concern level as a result of various use patterns could be addressed, and the response time of the system investigated.

The modelling work carried out in this study has identified modelling approaches which go a long way towards meeting the aims identified at the start of the project. A model such as SoilFug could be used in initial assessments of agrochemicals and other substances where a release route to soil is identified. The properties of the soil and drainage at Rosemaund tend to maximise the appearance of chemicals in the stream water, and so a scenario based on these conditions would give a reasonable worst case. The IH model provides the basis for a system to allow the assessment of pesticide usage strategies and the design of monitoring studies in a range of catchments. All of the models would benefit from further testing with data from different sites. The SoilFug model has been applied as part of its original development to two river basins in Northern Italy (Di Guardo *et al.*, 1994a). Further experience with the use of these models needs to be gained in a variety of circumstances to broaden our understanding of their performance and increase confidence in their use.

5 Discussion and conclusions

The ADAS Rosemaund study has established that the use of pesticides, even when applied according to the principles of good agricultural practice, can lead to the contamination of surface waters in the catchment into which they drain. In doing so this study was amongst the first to establish the importance of bypass flow, the episodic nature of pesticide transport to surface waters and the potential biological importance of these events.

The magnitude of the concentrations observed in surface water varies, not only between pesticides, but also for individual rainfall events. However, whenever rainfall occurs following a pesticide application some of the chemical will almost certainly be transported to nearby streams. One of the reasons ADAS Rosemaund was chosen was because its soil type and geology meant that the hydrological regime was likely to be surface water dominated. In this respect it is perhaps not surprising that rainfall transports pesticide from soil to the stream. However, similar highly structured soils with underdrainage form 45% of agricultural land in the UK (Cannel *et al.*, 1978) and 32% are hydrologically dominated by bypass flow (Boorman *et al.*, 1995). Thus while the results from this study may represent a worst case in terms of surface transport concentrations, they are of wide significance.

It has been demonstrated at ADAS Rosemaund that rainfall events generate flushes of pesticide which tend to reach the stream via field drains, coincident with or slightly ahead of the main surge of water. This gives rise to high but short lived concentrations in receiving waters. The significance of these concentrations to aquatic life will obviously depend on the toxicity of the pesticide and the duration of exposure. However, in situ bioassays in the stream at ADAS Rosemaund have shown that observed carbofuran and chlorpyrifos concentrations can be fatal to *Gammarus pulex*, a freshwater shrimp (Matthiessen *et al.*, 1995). It is clear therefore, that transiently high concentrations in headwater streams, resulting from the use of products at approved rates, are of potential significance to the ecology of streams. Some recognition of such transient exposures and potential bioaccumulation needs to be built into future pesticide assessments if headwater streams are to be protected fully. Protection of these waters should ensure protection of habitats throughout the river network, as dilution, degradation and sorption of pesticides on to sediments progressively reduces their concentration downstream.

Almost all the applied pesticide stayed in the soil at ADAS Rosemaund and was degraded there. However, high concentrations of pesticide were generated in the stream at the sub-catchment level by very small amounts of transported pesticide. In the ADAS Rosemaund study the estimated maximum transfer of pesticide to the stream in a single event was 60.6 g and the maximum amount as a percentage of pesticide applied was only 1.1%. It is almost inevitable that such small amounts will be lost from any catchment where pesticides are used, whatever the agricultural practice. It is the short duration pulses of high pesticide concentrations in surface waters, which have been clearly demonstrated in this study, which are of potentially greatest environmental concern. The period during which the risk of pollution by peak concentrations exists may be reduced, but probably not eliminated, by using chemicals that are rapidly degraded. However, such chemicals will by their nature have little residual pesticidal effect and may therefore lead to multiple applications where before one would have sufficed.

Concentrations of the highly sorbed herbicide, trifluralin, have been measured in the dissolved and particulate phases in samples from three rainfall driven transport events. These measurements have shown that in the majority of cases the dissolved fraction carries more than 50% of the pesticide load. This is because the mass of water moving from the fields is so much greater than the mass of sediment. Therefore, even pesticides as sorptive as trifluralin (K_{oc} = 8000 mg/l) may be considered to be transported in the dissolved phase and should not be described as immobile. However, a small amount of trifluralin (and larger amounts of sorbed pesticides such as deltamethrin) will be transported on particulates via the field drains to the stream where some will be deposited on the stream bed. Pesticides so deposited may become bio-available, either through desorption into the water column, or ingestion by benthic feeders resulting in possible bio-accumulation.

The above discussion is most relevant to the upper reaches of small catchments where the main land use is agricultural production. Looking at the larger catchment scale it is likely that, in most catchments, the proportion of land used for crop production will be less. Thus a dilution of pesticide load would occur and this dilution is the first line of defence in preventing high concentrations occurring in main rivers, where important fisheries exist from which most potable water abstractions are made. There is clearly a need to assess the extent of pesticide usage in water supply catchments with a view to estimating the maximum acceptable usage (MAU). The MAU would be set to guarantee both the quality of raw waters used for potable abstraction and to meet any environmental quality standards that may exist.

The only practicable way to move towards an estimate of maximum acceptable usage is through the use of models. A combination of models would be required to achieve this including a model to estimate diffuse transport from source area catchments and a river network model to integrate the inputs throughout the extent of the catchment. The source area model would require reasonably accurate data on pesticide usage within the catchments, as it changes from year to year. It is unlikely that the actual data would be available for whole catchments so estimates would have to be made, based on cropping patterns and general pesticide use.

Once such a modelling structure has been set up for a particular catchment it would prove a powerful tool for a variety of additional applications. For example, a pesticide sampling strategy may be developed which could provide a true picture of pesticide contamination in the most cost effective way. The location of pesticide 'blackspots' could be predicted and targeted for increased monitoring. The use of different groups of pesticides is seasonal and the pesticide analysis suite could be tailored to meet predictions of the temporal variability of pesticides within a year.

The IH model developed in this study has shown itself to be a good predictor of pesticide concentrations at ADAS Rosemaund. Perhaps its most limiting feature is that it is only valid under conditions of winter and early spring drainage. However, these are the times of peak pesticide usage when the surface waters are at most risk from pesticide transport and therefore this should not prove to be a problem.

A new predictive fugacity model, SoilFug, has been tested on the ADAS Rosemaund data and good agreement has been obtained when calculating the average pesticide concentrations during rainfall events. However, these concentrations tended to be overestimated to some extent. In 67 simulations of neutral or undissociated pesticides, 49 were estimated within one order of magnitude of the actual mean concentrations. The parameters required by this model, in order that it can be applied to new chemicals for the purpose of risk assessment, are generally easy to obtain or estimate from existing procedures. The BRE model produced not dissimiliar results to the SoilFug model, but requires considerably greater information. The portability of the IH and BRE models to other catchments has yet to be tested. Also the SoilFug model was not developed for this study and although it has been validated with data from two Italian catchments, its portability needs further testing before it is verified for use in the UK.

While a complex model, with its explicit links between the physico-chemical properties of the pesticide and the hydrological flow paths, was the desired end product of this study, there is a half-way house represented by empirically derived indices of pesticide contamination. One such index, I_m, based on half-life and the timing of rainfall events after application, has been developed for the ADAS Rosemaund data. This approach gives quick, easily calculated estimates of when pesticides are likely to be a problem. Although there was no well correlated relationship between the I_m index and maximum pesticide concentration, there was a qualitative increase in the observed concentration with increasing value of the index. However, the general problem with empirical relationships is that they are not valid outside the range of data for which they were estimated and should not therefore be used for other applications.

As noted in the introduction, this study was carried out in a period of significant changes in agricultural pesticide usage. Therefore, although still directly relevant, the preceding results and discussion must be viewed in the context of these changes. There has been an improvement in the properties and application of pesticides, which may combine to reduce the level of contamination and its consequent biological impacts on the whole environment, including surface water. Also there has recently been a reduction in pesticide inputs in agriculture (see Introduction) which additionally may act to reduce the possibility of pesticide transport and its biological impacts. Current and future factors which may reduce agricultural pesticide inputs still further are:

(i) General Agreement on Tariffs and Trade (GATT) and EC (European Commission) Common Agricultural Policy (CAP)

GATT and CAP create the economic environment in which British agriculture has to operate. These agreements will challenge European farmers to compete with imports at world prices and to export their surplus production at world prices and still remain viable. The CAP and GATT agreements will act to reduce unit costs of production. As a result pesticide usage must be questioned and optimized.

Also there are constraints on intensive arable production, e.g. introduction of set-aside. Set-aside will automatically reduce the pesticides applied on arable farms, although there are derogations for particular herbicide uses.

(ii) Pesticide legislation

Statutory pesticide approval data requirements under the UK Food and Environment Protection Act 1985 (FEPA) and the more recent EU pesticide harmonisation directive 91/414, are comprehensive with regard to environmental fate and behaviour. New pesticides with long persistence characteristics and potential for leaching and damage to the aquatic environment are looked at very critically. Also, the review programme of older pesticides should over time improve the environmental safety of available pesticides.

The Codes of Practice for safe use of pesticides on farms and holdings, and the protection of soil, water and air are all contributing to an improvement in farm pesticide management and the avoidance of point source pollution, and overspraying of watercourses.

Additionally, although not a direct effect on pesticides in water, legislation controlling pesticide residues in food (maximum residue limits, MRLs) is also having an effect on the pesticides available and their rates of use. Some supermarkets are imposing nil limits for pesticide residues in the produce they are buying.

(iii) Pesticide development

The agrochemical industry is contributing to this reduction in pesticide use and safety by finding new molecules which are active at a much lower rate (g ha^{-1} rather than kg ha^{-1}), are more selective (particularly insecticides) and have a better profile of fate and behaviour in the environment.

Formulation technology is also improving. The move to suspension and emulsifiable concentrates from wettable powders has improved handling. Better design of containers has improved pouring characteristics with less risk of concentrate spillage.

(iv) Engineering developments

Better nozzle design, air assistance and closed transfer systems, which may well in future be linked to direct injection, have aided the minimisation of pesticide applications. Futuredevelopments, such as linking satellite tracking technology to field mapping techniques, should allow pesticide application only where it is required in a field.

(v) Integrated crop management (ICM)

The objective of ICM, through integrated pest management (IPM), is to control crop damage from pests, diseases and weeds, to economically acceptable levels with minimum impact on the environment. The use of pesticides is integrated with other cultural methods, such as:

- *Varietal resistance/tolerance*: Minimises pesticide use by limiting pest or disease damage.
- *Crop rotations*: To prevent the build-up of specific crop pests, diseases and weeds and lessen the reliance on pesticides.
- *Cultivations*: Appropriate cultivation buries weed seed and diseased plant material and reduces future pest problems. Mechanical weeding may also replace the requirement for herbicide applications.
- *Decision Support Systems*: Ensure a pesticide is only used when it is needed, and is then applied at the correct time, and at the appropriate rate for maximum effect.
- *Novel Methods of Control*: Naturally-occurring parasites and predators are already being used in glasshouse crop pest control systems and other agents including bacteria, fungi and nematodes are becoming available. Development for outdoor crops apart from fruit is some time away. Also at the early stage of evolution are biopesticides and semiochemicals, the latter affecting insect behaviour and their ability to damage their crop host. Each may offer scope for reducing pesticide inputs.
- *Encouragement of Natural Enemies*: By enhancing habitats around and within the field, and avoiding the use of non-selective pesticides.

There are also a range of factors, outside the scope of this project, but worthy of consideration, which may have a significant influence on pesticide transport and which can be controlled. Harris *et al.* (1993) has demonstrated the impact of tillage methods on pesticide transport. Also the type of crops grown and the way in which they are grown could have significant effects on the amount of pesticide that is transported to surface waters. If models are to give a complete picture of the pesticide story, then they must build in links between agricultural practice and pesticide transport. This link may be primarily concerned with the different water pathways that are promoted by a range of cultivation methods and how this changes the interaction between the soil and pesticide.

In summary the ADAS Rosemaund pesticide study has produced one of the best data sets of the field and catchment scale movement of pesticides in the

UK. The study has established the importance of bypass flow, the episodic nature of pesticide transport to surface waters and the probability of resultant biological impacts in headwater streams. This data set has allowed an improved understanding of how pesticides move to surface waters and the environmental concentrations that result from this movement. This has permitted existing and new mathematical models to be developed and tested and their performance assessed. The output from this project has taken our knowledge of pesticide behaviour a major step forward and laid the foundation for more accurately predicting pesticide behaviour and targetting pesticide monitoring programmes.

6 Recommendations

1. This project has raised the possibility that aquatic life in headwater streams in agricultural areas where field-drained soils are prone to by-pass flow may be at risk from transported pesticide residues. Circumstantial support for this supposition is provided by an NRA report (Ashby-Crane *et al.* 1994) which has identified a number of small streams in agricultural areas where the benthic invertebrate community is inexplicably impoverished. The report points to pesticides as possible causative agents, but firm links are not made because other factors such as nutrients could be involved.

> **Recommendation 1** Using NRA data, a number of headwater streams which show inexplicable degradation be targeted for fully integrated studies to establish, or refute, these links. This research would simultaneously monitor pesticide concentrations after rain storms, responses of in situ bioassays (both plant- and animal-based), and responses of the benthic invertebrate and plant communities in the streams. Although such work will never provide absolute 'proof' that pesticides are responsible for the observed effects, the combined weight of evidence should be sufficient to give pesticide regulators some useful new insights into the potential environmental effects of these substances.

2. The project has shown that a simple predictive model (SoilFug) of mean pesticide concentrations in a headwater stream, and a more complex catchment-specific model (IH model), are both able to predict the concentrations appearing in ADAS Rosemaund stream with a reasonable degree of accuracy, although dissociated herbicides give some problems. The predictive model has already received successful validation with data from two other catchments (in Italy), but it is felt that further field validation of both models is required before they can be used with confidence and flexibility by the regulatory authorities.

> **Recommendation 2** We therefore recommend that both SoilFug and the IH model should be tested and possibly developed further using additional pesticide translocation data from a number of other types and sizes of agricultural catchment. It is possible that this could be arranged in conjunction with the field programme outlined in Recommendation 1, as well as by using existing data.

3. More monitoring data on pesticide concentrations are needed from headwater streams generally to assess compliance with Environmental Quality Standards, where they exist. Monitoring should be targeted on streams in agricultural areas, and should focus on the periods in November to April after heavy rainfall. Software such as the IH model will be able to assist in the most cost-effective targeting of this monitoring effort.

> **Recommendation 3** The National Rivers Authority should consider extending its aquatic monitoring programmes to include pesticides in small agricultural streams, because it appears likely that Environmental Quality Standards are being exceeded in some of these situations.

4. Despite the need for additional information outlined above, it is already clear that the fauna and flora in headwater streams are at some degree of risk from transported pesticide residues. Such streams are often of conservation significance, and they provide a reservoir of organisms which can recolonise the larger rivers into which they feed when, occasionally, industrial and sewage pollution incidents wipe out whole riverine communities. It is therefore essential that pesticide regulatory authorities should consider how to take more account of vulnerable headwater streams when conducting aquatic risk assessments. At present, the probability that streams of this nature will, in certain areas, experience episodic peaks of many different pesticides at μg/l concentrations is not fully taken into account (at least in the UK) when the risks for aquatic life are evaluated.

> **Recommendation 4** Pesticide regulators should consider making greater efforts to predict the risks which transported residues may pose to headstream fauna and flora, and should bear in mind that most pesticides are likely to appear briefly in many such streams at μg/l concentrations. This implies that some of the more acutely toxic and bioavailable substances may have to be restricted in their use in vulnerable areas, even though classic tests for leaching suggest that they are not leach-prone, and present aquatic risk assessments give them a clean bill of health.

5. The field data clearly demonstrate that almost all the significant pesticide translocation events at ADAS Rosemaund occurred in the period November to April inclusive, with the majority (67%) of events whose maxima exceeded 10 μg/l occurring

in the period November to January. There may therefore be some scope for encouraging farmers on soils prone to by-pass flow to minimise their use, during the early winter, of the pesticides which are of high toxicity to aquatic life and reasonably bioavailable.

> **Recommendation 5** After further research to establish the extent of underdrained soils where by-pass flow is a major factor in the hydrological regime, consideration should be given to discouraging the use of the more aquatically toxic and bioavailable pesticides during the early winter on land which is underdrained and prone to by-pass flow. For example, this could be achieved by modifying Codes of Practice and pesticide label information.

6. It may well be that other changes in land management practices (e.g. ploughing and planting) could also help to minimise pesticide transport to water on vulnerable soils. This requires investigation and possibly research.

> **Recommendation 6** A review should be conducted of land management practices to identify changes which could be made to minimise the translocation of pesticides via by-pass flow paths and field drains.

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Note: References shown in **bold** originate from the work of the present project.

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