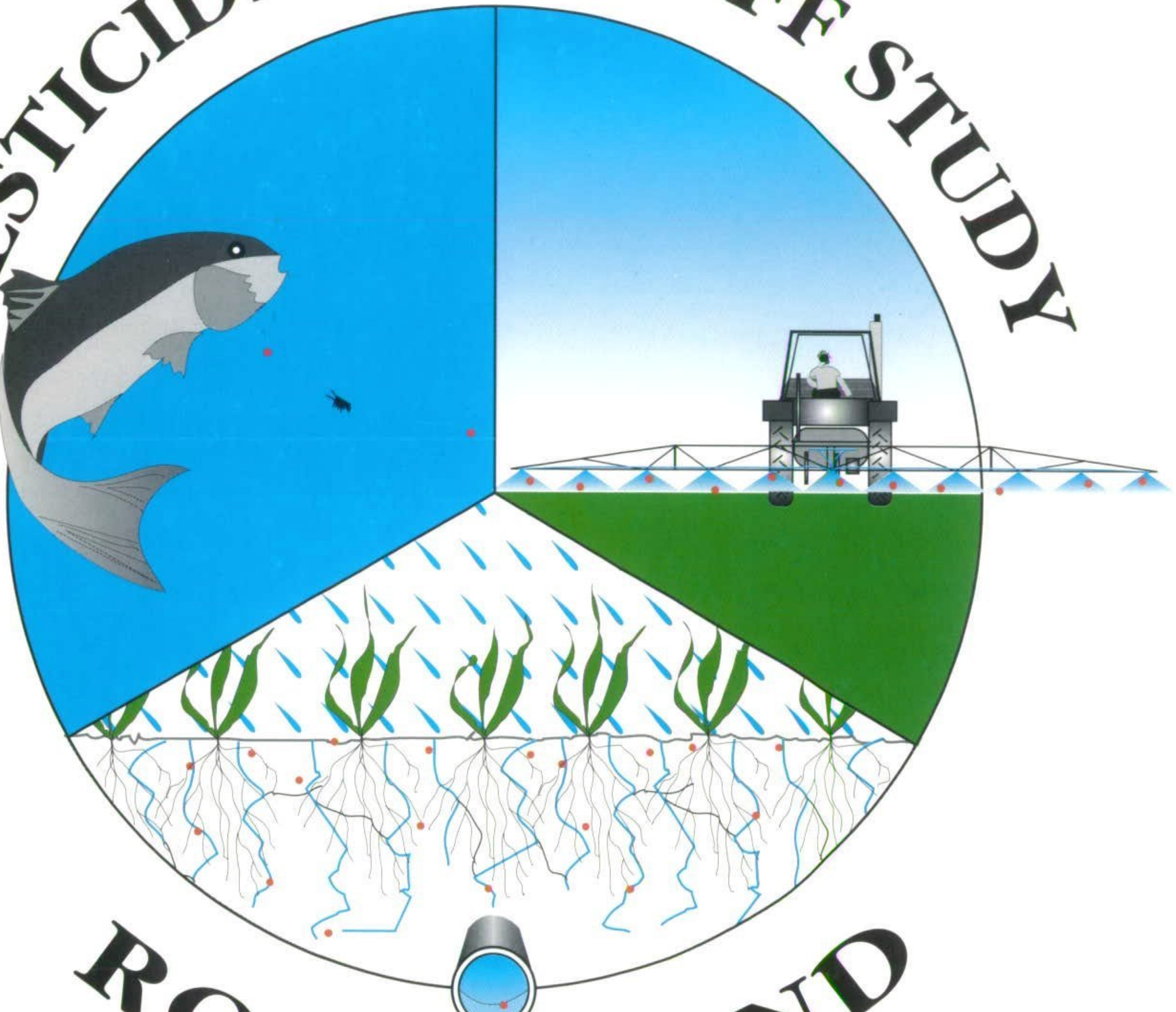
PESTICIDE RUN - OFF STUDY



ROSEMAUND

[redacted]

MAFF

ADAS
FOOD, FARMING, LAND & LEISURE

Institute of Hydrology

NRA

bre

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THE UNIVERSITY
OF BIRMINGHAM

PESTICIDE RUN-OFF STUDY
AT ADAS ROSEMAUND

Report of Years 5 to 6
Autumn 1992 to Spring 1993

Editor: R D J Mitchell

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CONTENTS

APPENDICES

1. EXECUTIVE SUMMARY

1.1 ADAS Rosemaund is an agricultural research centre in Herefordshire that encompasses an entire small water catchment which ultimately drains into the River Lugg. The majority of this largely arable catchment is field-drained, and it is underlain by impervious strata, thus maximising the amount of rainwater and associated agrochemicals which translocate into the stream.

1.2 Since 1987, the collaborating organisations listed at the front of this document have been conducting a research and monitoring programme to measure the translocation of operationally applied pesticides from the fields into the stream. Data for the years Autumn 1987 to Spring 1992 have been fully covered in the first three Pesticide Runoff Reports. The field programme of the project finished in Spring 1993, and this report presents the remainder of the data (Autumn 1992 - Spring 1993). The complete data set comprises of information on 19 pesticides (herbicides, fungicides and insecticides), some of which were monitored after several different applications.

1.3 The whole series of reports is intended primarily as a repository of the raw data, although it also contains some interpretation. A final summary report, including a full evaluation of the project's implications for pesticide risk assessment and management, will be published by the Institute of Hydrology (IH) in 1995.

1.4 The main purpose of the Rosemaund Pesticide Runoff Project was to provide reliable data on the environmental concentrations of pesticides which can occur through normal use in what might be considered a 'worst case' catchment. 'Worst case' in this context means that the potential for translocation of pesticide to the stream is high, a feature which is exacerbated by the presence of considerable by-pass flow in the main soil types. However, a hydrological regime of this nature is by no means rare; approximately 28% of UK soils are also prone to by-pass flow, so the results have implications for a large number of catchments.

1.5 The primary aim of this comprehensive collection of data is to provide raw material for the validation of computerised models of pesticide behaviour, either predictive models for pesticide risk assessment, or catchment-specific models which can assist in pesticide and water management. Some of this validation work has already been successfully completed for the SoilFug predictive model (Di Guardo *et al.*, 1994b), and a summary of the modelling results is given in this report. The modelling work with SoilFug has shown that, for many pesticides, it is possible to successfully predict the average concentrations which appear in the Rosemaund stream during and after rainstorms. Furthermore, it has also proved possible with the IH catchment model to predict mean and peak pesticide concentrations in the stream by combining a hydrological model with a pesticide behaviour model.

1.6 The data presented in this report concern records of rainfall, water flows and pesticide concentrations seen in the soil, drains and stream at Rosemaund. They focus on the dynamic situation during rainfall events, although some data are also presented for the 'background' levels between events. The main difference from previous years is that most of the pesticides reported on are not of the type which would be expected to leach through soils. The insecticides deltamethrin and chlorpyrifos, the herbicide trifluralin, and the fungicide fenpropimorph are all, to a greater or lesser extent, adsorbed to soil particles and therefore are traditionally considered as non-leachers. However, it is known that soil particles are easily carried through macropores and field drains and thence into the Rosemaund stream, so it was not unreasonable to suppose that adsorptive pesticides might also travel by this route.

1.7 Despite the fact that the pesticides under consideration tended to become adsorbed to soil particles, their behaviour appeared to be similar to the water soluble pesticides studied in previous years. Soon after rainstorms, transient peak pesticide concentrations appeared in the stream, generally coincident with or just before peak water flow rates. Concentrations (measured as dissolved and suspended combined) usually declined to baseline levels within 12 hours, and the overall picture is consistent with the view that by-pass flow is the dominant pesticide translocation mechanism. The implication, therefore, is that a proportion of the translocated material was adsorbed to mobile particulates. Limited measurements with trifluralin showed that up to half was present on particulate material, and it is expected that almost all the deltamethrin (which is very strongly adsorbed) would have been in the particulate phase. Some trifluralin was also shown to be present in overland flow, but it is unlikely that this contributed significantly to the concentrations seen in the stream.

1.8 The soil data for trifluralin and chlorpyrifos indicated little disappearance during the period of the experiments, while deltamethrin was always below detection limits, and fenpropimorph was not monitored. Peak concentrations of the adsorptive pesticides seen in field drains were 14.1 µg/l (trifluralin), 2.9 µg/l (chlorpyrifos), 0.02 µg/l (deltamethrin) and 1.2 µg/l (fenpropimorph). Equivalent peak concentrations seen in the stream were 0.9 µg/l (trifluralin) and 1.9 µg/l (deltamethrin) but there are no stream data for chlorpyrifos and fenpropimorph. The results for deltamethrin are particularly surprising because it was only applied to the field at 0.005 kg/ha, whereas the other pesticides were applied at rates at least 140 times greater. Isoproturon, a herbicide studied in previous years, was also monitored in a field drain and reached a record maximum of 340 µg/l.

1.9 Bioassays were used to measure the potential biological effects of certain translocated pesticides in the stream. As deltamethrin was expected to be translocated with particulates, mobile and bedded stream sediment was collected after the event in which a peak of 1.9 µg/l (total residues) was measured in the stream water. These sediments were tested in the laboratory with sensitive midge larvae (*Chironomus riparius*) and shown not to exert any chronic toxicity. This implies that deltamethrin residues, although present in the stream at potentially toxic concentrations, were too tightly bound to be bioavailable to sediment-feeding midge larvae.

1.10 An *in situ* bioassay which had been used in previous years to monitor the effects of pesticide runoff at Rosemaund (see third report), measured the feeding rate of caged amphipod crustacea (*Gammarus pulex*) during the chlorpyrifos experiment. As in an earlier experiment with the carbamate insecticide carbofuran, chlorpyrifos reaching the stream via the field drains was shown not just to cause reductions in feeding rate, but also substantial mortality of the test organisms. These results confirm that biologically significant concentrations of certain pesticides are able to leach into streams via field drains, and emphasise the need to consider bioavailability before drawing conclusions about potential environmental impacts.

1.11 In summary, the results described in the present and foregoing reports have shown that, almost irrespective of physicochemical properties or application rates, most pesticides can translocate after rainstorms through field drains into the Rosemaund stream at concentrations which peak in the range 0.5 to >25 µg/l. These peaks do not tend to persist for more than a few hours, and are almost exclusively the result of by-pass flow, although overland flow and seepage cannot be ruled out as infrequent contributory factors. Despite these observations, the amount of pesticide translocating into the stream during any single rainfall event was never more than 0.7% of the applied dose, and concentration declines in the soil could generally be explained in terms of known biodegradation rates. Mean and peak concentrations in drains and stream could generally be predicted with simple models, although the concentrations of some pesticides (notably the phenoxy acid herbicides) were over-estimated. The limited use of bioassays to monitor the potential biological effects on stream organisms of the observed concentrations has shown that the transience of pesticide peaks is no guarantee that effects will not occur. In the case of two insecticides (carbofuran and chlorpyrifos), heavy mortality of bioassayed crustacea was observed. On the other hand, the strongly adsorbed insecticide deltamethrin did not cause toxic effects in a sediment bioassay. For technical reasons, plant-based bioassays were not deployed, but in several cases (most notably with isoproturon, trifluralin and atrazine) herbicides reached concentrations in the stream which would have been expected to damage macrophytes or algae.

1.12 These results originate from a single catchment, so caution must be used when extrapolating to other locations. This implies the need for similar research on a number of other soil types, but it should not prevent tentative conclusions being made about the potential contribution to surface water contamination by pesticides translocated via by-pass flow. It seems likely that the presence of field drains on soils prone to by-pass flow will generally lead to similar phenomena to those described above. This has many implications for pesticide design, regulation and management, not the least being that headwater streams appear at particular risk of damage by leaching residues. Scattered and inconclusive evidence already exists that some headwater streams may have been damaged by diffuse pesticide inputs, but much more research is required to document the extent and causes of such phenomena. In the meanwhile, it would be prudent for pesticide manufacturers and regulators to take note of the Rosemaund data set and assume that it probably represents the upper limit of pesticide leaching to surface waters.

2. INTRODUCTION

The use of pesticides in agriculture has risen dramatically in recent years. This has been mainly due to the introduction of effective annual grass weed herbicides and more effective cereal fungicides in the 1970s. This increase in pesticide usage has led to serious concern about possible contamination of the environment by these chemicals. The effect of pesticides in water, both to aquatic life and potable water supplies are of particular concern.

Reviews of pesticides in drinking waters sources in England and Wales (Lees and McVeigh, 1988: Drinking Water Inspectorate, 1992) have indicated that a number of sources may contain individual pesticide levels greater than the Maximum Acceptable Concentrations (MAC) laid down in the European Community 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 μg/l and a MAC of 0.5 μg/l for total pesticides. Although these MACs 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 EC Directives. It is therefore vital that the movement and fate of pesticides in the aquatic environment is well understood and predictable so that the NRA can seek to control diffuse inputs of such chemicals and ensure compliance with the statutory objectives. Without such information it is difficult to envisage how compliance with such standards could be achieved.

Pesticide registration authorities in the UK are reacting to this with increasingly stringent acceptance criteria for new pesticides and by reviewing the use of existing pesticides which already occur in water. Before such risks can be assessed it is necessary to know and/or be able to predict the concentrations and the toxicity of pesticides which may occur in the aquatic environment as a result of normal agricultural practice. The processes and mechanisms involved in the translocation of pesticides from the areas of application to the aquatic environment are poorly understood. There is for example a lack of knowledge on the movement of pesticides through the soil to drains and also on movement of pesticides adsorbed onto eroded soil particles.

Field 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). In addition to this, in most cases details of the 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 does, therefore, exist a need to study agrochemical mobility under experimental conditions in controlled catchments in the UK.

In addition to the need for field data on pesticide concentrations in the aquatic environment there is also a requirement for accurate predictions of run off patterns of currently used products from particular watersheds 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 Boards in Scotland.

It was for these reasons that a joint study was initiated in 1985-86 by the Welsh Water Authority (subsequently the Welsh Region of the NRA) and the Institute of Hydrology (IH) based at and supported by personnel of the ADAS Rosemaund Research Agency (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 Resource Centre (SSLRC) began investigations into pesticides movements and their effects at Rosemaund and ADAS Soil and Water Research Centre (SWRC) carried out investigations on the drainage of selected fields on the farm.

The site at Rosemaund is a catchment which is almost completely within the boundaries of the farm. This allows the study of pesticide mobility under experimental conditions in a controlled catchment situation. Within the constraints of Good Agricultural Practice, the pesticides can be selected and applied in known amounts to suit the experiments. In addition, the geology and soil structure prevent significant loss of rainfall to ground water, thus maximising chemical transport to the outflowing stream.

The principal aims of all of the studies were to investigate and model the sources of pesticides in an agricultural catchment and their translocation to, and distribution and effect in, the receiving watercourses. The emphasis of each study was different and, to a degree, specific to the interests of the organisations concerned.

The NRA/IH study is largely a catchment-based investigation of the transport and fate of pesticides and nutrients, whilst the MAFF and other associated investigations are more concerned with the development of predictive models of the movement and fate of pesticides through soils and receiving watercourses and their subsequent ecological impact. The different approaches are complementary and to a large extent interdependent, but each aspect of the study has its own specific aims and work programme.

This report is the fourth and final joint compilation of progress to date by all of the organisations which have collaborated in the Pesticide Run-Off Study at ADAS Rosemaund between Autumn 1992 to Spring 1993. A final summary document will be published in 1995. Individual organisations have reported, and will continue to report their findings separately and independently according to the contractual requirements of their respective funding bodies. Each contribution to this report has been produced as it was submitted. Joint publications in scientific journals have also been, and will continue to be produced as appropriate.

3. OBJECTIVES

3.1 MAIN OBJECTIVES

There are two main objectives of this study:-

(a) To investigate, develop and validate hydrodynamic models of the movement and fate of agricultural pesticides between the place of application and the receiving watercourses, on a whole catchment basis.

(b) To assess the movement, distribution and environmental impact of selected pesticides in surface waters.

Whilst all participating organisations are committed to and contribute to achievement of the overall objectives, each has its own detailed contractual aims and objectives which are pitched at varying levels of complexity and scale, but which nevertheless are complementary.

3.2 DETAILED OBJECTIVES OF EACH PARTICIPATING ORGANISATION

3.2.1 NRA/IH

The NRA is primarily involved as a funding organisation and, although it does provide analytical support, the study is largely undertaken under contract by IH which also has internal research objectives of its own. The detailed objectives of the NRA/IH study are:-

(a) To monitor the run-off of pesticides from an agricultural catchment managed using best agricultural practice.

(b) To understand the processes that control pesticide run-off at the field and catchment scale.

(c) To understand the soil water system at the Longlands field site and extrapolate this to the rest of the catchment.

(d) To identify the pathways that contribute to storm flow generation.

(e) To produce and validate a simple model to estimate the pesticide runoff from the catchment.

(f) To develop management recommendations for pesticide use strategies.

(g) To derive appropriate sampling strategies for pesticides in surface waters.

3.2.2 MAFF/BRE/SSLRC/University of Birmingham

(a) To generate field data of pesticide leaching and runoff from the upper Rosemaund catchment in order to validate predictive models of the transport of pesticides and other chemicals.

(b) To test the ability of existing models to predict 'worst case' stream concentrations for new pesticides and industrial chemicals.

(c) To assess the impact of pesticides on the general biological quality of the receiving stream using sensitive bioassays (e.g. *Gammarus* feeding assay).

(d) To improve the accuracy of predictions of chemical hazard to aquatic life which may result from the use of new chemicals.

3.2.3 ADAS

(a) To co-ordinate the joint effort of the study; to provide and manage suitable sites; to apply necessary treatments; to provide technical assistance to the collaborators in meeting the objectives of their studies.

(b) To provide expertise from the SWRC to ensure that hydrological data is of the highest quality, and standardised on a single database.

A list of participating workers and departments is given at the front of this document.

4. STUDY SITE

4.1 LOCATION

ADAS Rosemaund is located in the West Midlands mid-way between Hereford and Bromyard, near the village of Preston Wynne at an average altitude of 84m above sea level. The farm covers 176 ha of an undulating valley which is dissected by a stream running from east to west, which ultimately drains into the River Lugg. The farm comprises a catchment area for the stream, with very little of the catchment area of 180 ha lying outside the farm boundary. Location and field plans showing the boundary of the catchment can be found in Appendix I.

4.2 CLIMATE

The climate is typical of much of Herefordshire and is intermediate in character between the mild oceanic type of western Britain and the more extreme, but drier semi-continental climate of East Anglia. The mean annual rainfall is 662 mm and is fairly evenly distributed throughout the year. Mean monthly rainfall figures are given in Table 4.1. The figures show a fairly even distribution throughout the year with a slight peak in late summer and a winter maximum in November and December. Weather data summaries for the years 1990-92 are given in Appendix II.

Table 4.1. Mean monthly rainfall (mm) 1951-1992

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
62	43	49	43	52	52	53	62	60	56	66	64	662

4.3 GEOLOGY AND SOILS

Rosemaund is underlain almost entirely by Devonian rocks composed of soft siltstones and mudstones of the Devonian age. There are thin interbedded soft fine micaceous sandstones and sands within the succession but they have little influence on the soil pattern. The farm is generally free of drift deposits. A narrow strip of clayey or silty alluvium flanks the stream that runs through the farm. A soil map of the farm was made in 1989 and has been supplemented by auger bores in some areas. Most of the farm is covered by the reddish silty clay loams of the normal and shallow Bromyard series, but heavier soils are found in seasonally waterlogged hollows and valley bottoms. Soil and drainage maps of the farm are given in Appendices III and IV respectively.

Table 4.2. Classification of Soils of Rosemaund

Soil sub-group	Soil series	Top soil characteristics	Definition
Typical brown earths	Bromyard	Stoneless silty clay loam	Reddish-medium silty material passing to soft siltstone or shale, at about 100 cm depth
	Bromyard (shallow phase)	Stoneless silty clay loam	Reddish-medium silty material passing to soft siltstone or shale, at about 35 cm depth
Stagnogleic argillic brown earths	Middleton	Stoneless silty clay loam	Reddish-medium silty material passing to soft siltstone or shale
Gleyic brown gley soils	Mathon	Stoneless silty clay loam	Reddish-clayey river alluvium
Pelo-alluvial gley soils	Compton	Stoneless silty clay loam	Reddish-clayey river alluvium

4.4 AGRICULTURE

The deep and fertile soils at Rosemaund are capable of producing high yielding crops when carefully managed. A range of crops is grown, mostly in a six year rotation (see table 4.3), designed to maximise the research and development opportunities whilst retaining an agriculturally valid rotation. For example the area of oilseed rape on the farm has increased as more research is carried out on the crop. Of the total farm hectarage, about one quarter is in grass (as pasture of sheep and red deer as well as some of silage production for the beef enterprise) and half is in cereal production (winter and spring wheat, barley and oats). The remainder of the farm comprises a small hop enterprise, some forage crops and a range of break crops (winter and spring oilseed rape, peas, beans and linseed).

Table 4.3. Typical Arable Rotation at Rosemaund

Year	Crop
1	Oilseed rape
2	Winter wheat
3	Cereal (wheat, barley, oats)
4	Peas, beans, linseed
5	Winter wheat
6	Winter barley

Crops are grown according to Good Agricultural Practice and as much as is possible, all operations follow standard husbandry practices for the crop. The wide range of crops grown at Rosemaund inevitably leads to the use of a wide range of pesticides at different times of the year.

A cropping history of each field is listed in Appendix V.

4.5 GENERAL PESTICIDE USE AT ROSEMAUND

The use of pesticides on the farm follows the codes of Good Agricultural Practice advised by the Ministry of Agriculture, Fisheries and Food. The wide range of crops grown at Rosemaund leads to the use of a wide range of pesticides throughout the year. Winter sown arable crops receive on average one or two autumn pesticides (herbicides and insecticides) followed by further applications in the spring and summer (herbicides, fungicides and plant growth regulators). Spring sown arable crops receive similar spring and summer pesticide inputs. Hops, a high value, high risk crop, require numerous treatments to achieve a high value product at harvest. These treatments are, however, restricted largely to the summer months with only one or two winter applications of herbicides. Very little pesticide is used in grassland production.

4.6 LEACHING POTENTIAL AND SELECTION OF PESTICIDES FOR STUDY

Maximum leaching potential of pesticides tends to coincide with autumn and winter applications when rainfall, soil moisture and ground water levels are all high. The individual properties of applied pesticides are very important as some exhibit a much higher potential to leach into water than others. A number of physico-chemical factors; solubility in water, octanol-water partition and soil adsorption coefficients, persistence in both soil and water, and the rate, timing and conditions of its application affect the potential to leach. All of these factors combine to make the accurate prediction of pesticide leaching extremely difficult.

Before the selection of pesticides to be monitored in this study was made, a range of information was considered. Some pesticides, for example sulfonyl ureas are applied at such low rates that they may be difficult to detect in the water course, despite their high leaching potential. Others, like oxamyl, break down very quickly in the soil and are extremely difficult to trace.

A short list of pesticides was drawn up based on information similar to the examples above and a number of studies (e.g. Bird and Whitehead, 1985) confirmed which pesticides were widely found in UK waters. Pesticides less prone to leaching were also studied to provide a broad database for the validation of leaching models. A final short list of pesticides for the study at Rosemaund were drawn up in 1987, and further additions made as the study progressed (Table 4.4)

The pesticides of highest priority were considered to be the herbicides mecoprop, isoproturon and simazine all of which can be applied in the autumn and spring in relatively large amounts. Isoproturon is predominantly an autumn herbicide whereas mecoprop is mainly used in the spring.

Table 4.4. Pesticides monitored at ADAS Rosemaund

Herbicides	Isoproturon
	Simazine+
	Atrazine+
	Trifluralin+
Insecticides	Deltamethrin
	Chlorpyrifos
Fungicides	Fenpropimorph

+ on the Red List of Substances most dangerous to the aquatic environment

5. SUMMARY EXPERIMENT REPORTS

5.1 EXPLANATION OF SUMMARY REPORTS

The results from the experiments carried out between Autumn 1992 and Spring 1993 are reported below. They are reported in summary form to present an overall picture of the findings in this study. The pesticide monitoring summary reports have been placed in chronological order, each covering a season of experiments; autumn 1992 and then spring 1993.

Each summary is divided between the two main reporting groups (A) MAFF Fisheries and BRE, and (B) NRA and IH. Each group has different objectives (Section 3.2) but similar monitoring regimes. Group A summary reports are given first followed by Group B for each season.

The results of a benthic macroinvertebtrate survey are included in Appendix XI. This study was carried out independently by the National Rivers Authority (Welsh region) and the results are included for information only.

5.2 DETAILS OF PESTICIDE APPLICATIONS MONITORED IN THIS STUDY

All of the monitoring in this study concentrated on pesticides applied to a field at the upper end of the catchment. (Foxbridge and Longlands). Monitoring of pesticides followed their normal use as per cropping, timing and rates of application. They were applied using either a self propelled Chaviot dedicated sprayer or granular applicators. Details of the pesticides monitored are given in Table 5.1.

Table 5.1. Details of pesticides monitored in each season

Season	Pesticide monitored	Rate applied (kg/ha)	Product name	Fields	Crop	Date
Autumn 1992	Trifluralin	1.1	Atlas trifluralin	F&L	WW	6.11.92
	Isoproturon	2.5	Javelin Gold	F&L	WW	15.12.92
	Deltamethrin	0.005	Decis	F&L	WW	15.12.92
Spring 1993	Chlorpyrifos	0.72	Dursban 4	F&L	WW	19.3.93
	Fenpropimorph	0.75	Corbel	F&L	WW	19.3.93

F&L Foxbridge and Longlands WW Winter wheat

5.3 MONITORING AND SAMPLING SITES

The differences between the initial objectives of the two main reporting groups, MAFF/BRE and NRA/IH, resulted in separate sampling sites and monitoring regimes for both. In general MAFF/BRE monitored the movement of pesticides down the soil profile and into the stream, and NRA/IH concentrated on the whole catchment.

A detailed plan of all sampling and monitoring sites can be found in Appendix VI. Each site has an eight digit Ordnance Survey reference number, as well as being referred to by a descriptive name in the reports and tables of data. These sites are listed in Table 5.2.

Table 5.2. Sampling sites - Ordnance Survey reference numbers and descriptive names

OS reference numbers	Descriptive name
SO 5582 4789	Main gauging site (IH)
SO 5665 4841	Upper gauging site 1 (MAFF)
SO 5667 4842	Stream Site 1A (MAFF)
SO 5668 4843	Stream Site 1B (MAFF)
SO 5672 4843	Ditch, Site 2 (MAFF)
SO 5672 4842	Drain, Site 3 (MAFF)
SO 5688 4847	Foxbridge & Longlands drain outfall: Site 4 - left hand drain (MAFF) Site 5 -right hand drain (IH, MAFF) Site 6 - middle drain (MAFF & IH)

5.4 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS - TRIFLURALIN/DELTAMETHRIN EXPERIMENT - AUTUMN 1992 TO SPRING 1993

5.4.1 Introduction

This experiment was part of a series whose major aim is to validate predictive models of pesticide translocation from fields into the Rosemaund stream. However, unlike in previous experiments which focused on pesticides whose relatively high water solubility's and low soil adsorption coefficients predisposed them to leaching, the present experiment studied substances which might not have been expected to leach.

The dinitroaniline herbicide trifluralin has a fairly high soil organic carbon adsorption coefficient (Koc = 8000), with low water solubility (0.3 mg/l) and a long soil half-life (DT50 = 60 days). The pyrethroid insecticide deltamethrin is extremely strongly adsorbed to soil particles (estimated Koc = 72,000), has negligible water solubility (<0.002 mg/l) and a fairly short soil half life (5-19 days). Deltamethrin is also highly toxic to aquatic life (especially insects and crustacea), but is generally so strongly adsorbed to sediments that the toxicity is not likely to be expressed in practice. Nevertheless, it was decided to conduct an insect larval bioassay on sediments from the stream. If soil acted like a chromatographic column, neither of these substances would be expected to leach into the Rosemaund stream. However, it has now been well-established that the soil hydrological regime at Rosemaund is dominated by by-pass flow. It was therefore thought possible that pesticide residues adsorbed onto fine particulates could be carried rapidly through the soil profile via cracks and other macropores.

Trifluralin was applied as Treflan (480 g/l EC) to 4.58 ha of Foxbridge and Longlands at 1.1 kg a.i./ha on 6 November 1992. This was followed up on 15 December 1992 with deltamethrin applied as Decis (25 g/l EC) at 0.005 kg a.i./ha to the same area of Foxbridge and Longlands. The crop was winter wheat.

5.4.2 MAFF/BRE experiment

5.4.2.1 Methods

Water sampling

As in previous years (see Reports for Years 2-4 and 3-5 - 2nd and 3rd Project Reports), stream and drain water samples were taken automatically by peristaltic pump-driven samplers during rainfall events whose intensity exceeded approximately 10 mm/24 h. However, in recognition of the fact that much of the pesticide during this experiment would be translocated while adsorbed to fine suspended soil particles which tend to be mobilised only during the most intense phase of water flow, the automatic sampling period was shortened to 12 h and the frequency increased to every 30 minutes. On a few occasions, measurements were also made of the suspended solids load in the Site 3 drain by means of filtration and oven-drying followed by weighing.

Soil sampling

Soil samples were taken with a stainless steel corer. Sampling sites were chosen to lie on the different soil types present in the field. Samples were taken at 3 sites on each of 3 soil types (Bromyard, Bromyard Shallow and Middleton) and at 1 site on the Compton. At each site 3 depth samples were taken, 0-25 cm, 25-50 cm, and 50-100 cm. For those soil types where 3 sites were sampled, the 3 samples for a particular depth were pooled and analysed as 1 sub sample. Hence there are 3 concentrations measured for each soil type corresponding to the three depths.

Water analysis

The 11 water samples were "fixed" at the experimental site by the addition of 50 ml hexane, transported to Birmingham University, and stored at 4°C in the dark. The samples were prepared by a double liquid/liquid extraction into hexane (two periods of mechanical shaking of 15 minutes with 50 ml hexane). The organic extracts were then filtered through Whatman GF/C glass fibre filters and dried over $NaSO_4$. The extracts were then reduced to approximately 400 µl under a stream of oxygen free nitrogen and the precise volume determined by weight. The final extracts were transferred to 2 ml screw top vials and stored at -20°C ready for analysis.

Analysis of the trifluralin and deltamethrin residues was by gas chromatography with Electron Capture Detection (ECD). The instrument used was a Hewlett Packard 5890 GC fitted with a bonded phase capillary column (60m x 0.2 mm DB-5; 5% phenyl methyl silicone). The chromatographic conditions used are listed below.

Chromatographic Parameters Used for Trifluralin and Deltamethrin analysis of Water Samples

Initial oven temperature	50°C	hold for 1 minute
temperature ramp A	3°C per min	
final temperature	120°C	hold for 0 minutes
temperature ramp B	5°C per min	
final temperature	200°C	hold for 0 minutes
temperature ramp C	30°C per min	
final temperature	300°C	hold for 5 minutes
Injector temperature	track oven temperature	
Detector Temperature	325°C	

Quantification was achieved by use of external calibration standards which were obtained from Promochem, UK. Peak heights were measured manually from an integrator chart print out. The integration parameters were initially applied but found to be inaccurate, especially for lower concentrations and where uneven baselines occurred.

The results shown below have not been corrected for extraction efficiency. A test for extraction efficiency of trifluralin using environmental water from the Rosemaund site gave a mean recovery of 77% +/- 6% (n=4). This was determined by spiking one litre of stream water with the trifluralin reference standard to a concentration of 0.4 µg l^{-1}. Two blanks indicated no detectable trifluralin. The limit of detection for this method was 1 ng l^{-1} for water samples of 1 litre. In all tables "0" indicates not detected and "-" indicates no sample available for analysis.

Extraction efficiency for deltamethrin was determined to be 92% +/- 10% (n=4) at a level of 0.4 µg l^{-1} . These results were obtained by spiking Rosemaund water in parallel with the trifluralin recovery tests referred to above. The detection limit for deltamethrin was determined to be 1 ng l^{-1}. Two blank samples were also analysed which contained no detectable deltamethrin.

It should be noted that the extraction method used for trifluralin and deltamethrin would have stripped off all material adsorbed on suspended matter, so the results given are for 'total' residues, not merely the dissolved fraction.

On two occasions, stream sediments from Sites 1, 2, 3, and 4-6 (single location) were sampled and then bioassayed in the laboratory using a chronic whole-sediment test based on the growth of larvae of the midge *Chironomus riparius*. Sediments for the growth bioassay were sampled 24 hours after the first rainfall event following the application of trifluralin or deltamethrin ie 12/11/92 and 17/12/92. Sediments were sampled from the top 2 cms of the stream bed or when flow gauging chambers were present, from the surface of the sediment which had accumulated in the chamber. For the post-deltamethrin bioassays, sediments were also taken from buckets which had been forced into the stream bed at two of the sites (2 and 3) in order to collect freshly mobilised sediment by passive sedimentation.

Sediments were returned to the laboratory, sieved through a 500µm sieve and stored at 4°C for up to 2 weeks. For the growth assay 150 cm^3 of sediment was allocated to replicate 1 litre pyrex beakers. Reconstituted laboratory water was added to the beakers and they were left to settle for one day. Four replicates of each sediment collected were used. The overlying water was aerated for two days before the addition of 20 2nd instar *Chironomus riparius* larvae to each. A sediment collected in early October 1992 and stored frozen was used as a control. Larvae were maintained in the aerated beakers of sediment at a temperature of 20°C for a period of 10 days from the time of addition. Ground "Tetramin" was added to each beaker as food at a rate of 5 mg every three days.

After this time the larvae were placed in clean water for 24 hours to allow their guts to be purged of sediment. They were then blotted dry and weighed individually.

Soil analysis

Trifluralin

A sample of soil (40 g) was shaken for 60 minutes with 100 ml of a methanol-water mixture (9:1 v/v) and then centrifuged. The supernatant liquid was filtered and a 50 ml aliquot (≡20 g soil) taken. This was diluted with a 10% sodium chloride solution in water (100 ml) and then shaken with 25 ml of dichloromethane for 1 minute. The organic layer was removed and dried through anhydrous sodium sulphate; this procedure was repeated with 2 further 25 ml aliquots of dichloromethane. The sodium sulphate was washed with 15 ml of dichloromethane, the extracts combined and evaporated to dryness. The residue was dissolved in toluene (5 ml) and quantified using gas-liquid chromatography. Equipment and conditions used: Hewlett Packard 5890 Series II GC with electron capture detector and HP 7673A autosampler, 2% Carbowax 20M + 5% DC 200 on Diatomite GLQ (80-100 mesh) packed column; injector temperature 250 °C; column temperature 170 °C; detector temperature 250 °C. The detection limit was 0.003 ppm wet weight soil.

To determine soil moisture content, subsamples were weighed into glass jars, heated in an oven overnight and, when cool, re-weighed.

Deltamethrin

A sample of soil (40 g) was shaken for 60 minutes with 100 ml of an acetone-water mixture (9:1 v/v) and then centrifuged. The supernatant liquid was filtered through glass wool and a 50 ml aliquot (≡20 g soil) was evaporated to the aqueous phase. After dilution with 20 ml water the aqueous phase was extracted with 25 ml dichloromethane, the organic phase then being filtered through sodium sulphate to dry. This process was repeated with two further 25 ml aliquots of dichloromethane; the three extracts were combined, together with 15 ml of dichloromethane used to rinse the sodium sulphate. The bulk extract was evaporated to dryness and the residue dissolved in toluene (10 ml).

A column was prepared in hexane using 5% deactivated Florist (8 g) capped with anhydrous sodium sulphate. The sample was added to the column and eluted. Hexane (10 ml) was used to rinse the sample flask, then added to the column and eluted. An aliquot of 5% ethyl acetate in hexane (15 ml) was added to the column and eluted. All fractions up to this point were discarded. A further aliquot (50 ml) of 5% ethyl acetate in hexane was added and eluted. This fraction was collected, evaporated to dryness, and the residue was then taken up into toluene (5 ml) for quantification by gas-liquid chromatography. Equipment and conditions used: Hewlett Packard

5890 GC with an electron capture detector and HP 7673A autosampler; injector temperature 275 °C; column temperature 240 °C; detector temperature 300 °C. The detection limit established was 0.003 ppm wet weight soil.

5.4.2.2. Results and Discussion

Water

Manual water samples

The results from the samples collected manually are shown in Table W1 (Appendix 7). Note that pre-spray levels of both deltamethrin and trifluralin were in the range 0-4 ng/l, ie essentially negligible. In the stream, concentrations of trifluralin between rainfall events were in the range 8-64 ng/l, with the higher levels observed during the month after spraying. Trifluralin concentrations in the stream were higher (31-345 ng/l) during 16-18 December 1992, but stream flow rates were elevated during this period due to a 9 mm rainfall event on 16/12/92 and a 20 mm event on 18/12/92. Maximum between-event trifluralin concentrations in field drains ranged up to 371 ng/l (Site 5), while reaching 1422 ng/l (Site 4) during the 16/12/92 event. Between-event trifluralin concentrations in drains and stream did not exceed 133 and 28 ng/l, respectively, after the end of 1992.

By contrast with trifluralin, between-event concentrations of deltamethrin were generally much lower, in the range 0-3 ng/l in the stream and 0-4 ng/l in the field drains.

This is partly explained by the much lower application rate of deltamethrin, but also by the fact that the sediment onto which it was probably all adsorbed is only mobilised during rainfall events. Background levels of suspended solids measured in the Site 3 drain were generally below 10-20 mg/l, but could peak at 800 mg/l at the peak of the hydrograph. The data in Table W1 for the period 16-18/12/92 when flow rates were high shows that deltamethrin concentrations jumped to a peak of 250 ng/l in the stream and 984 ng/l (Site 4) in the field drains.

Rainfall event on 11 November 1992 (Tables W2 and W3, Appendix 7)

This was the first significant rainfall event (10.5 mm) after trifluralin was sprayed on 6/11/92, having been preceded by a total of 5.5 mm rain in the form of intermittent showers. Figure W1 shows that trifluralin peaked in the stream at Site 1 at 954 mg/l within 2 hours of peak rainfall and only declined slowly over the following 12 hours. Trifluralin concentrations in the Site 3 drain (Figure W2) peaked at 3010 ng/l, but declined more rapidly than in the stream. These peak concentrations were well below the UK Environmental Quality Standard (EQS), expressed as a maximum allowable concentration, of 20,000 ng/l. They exceeded the annual average EQS of 100 ng/l but that should not have posed any threat to aquatic life because the peak in the stream was probably back to the background value after about 24 h.

Rainfall event on 15 November 1992 (Tables W4 and W5, Appendix 7).

This 8 mm event actually started at 07.00 on 14/11/92. Figure W3 shows that it resulted in a 384 ng/l biphasic peak of trifluralin in the stream at Site 1 which was approximately coincident with the peak of the hydrograph. Trifluralin concentrations declined within 8 h to below 100 ng/l. In the drain at Site 3 (Figure W4) the peak trifluralin concentration (638 ng/l) was almost double that in the stream, but as with the 11/11/92 event, concentrations dropped more quickly than in the stream.

Rainfall event on 24-25 November 1992 (Tables W6 and W7, Appendix 7)

The samplers failed to trigger during the peak hydrograph (Figure W5) on 25/11/92, but were triggered manually at 12.00 on 26/11/92. The total rainfall during the 2 days was 30 mm. The highest trifluralin concentrations measured in the stream at Site 1 (Figure W5) and drain at Site 3 (Figure W6) were 134 and 109 ng/l respectively, but it is likely that higher concentrations occurred earlier during the main hydrograph.

Fig. W1 Rosemaund Site 1: Trifluralin Experiment 11 11 92.

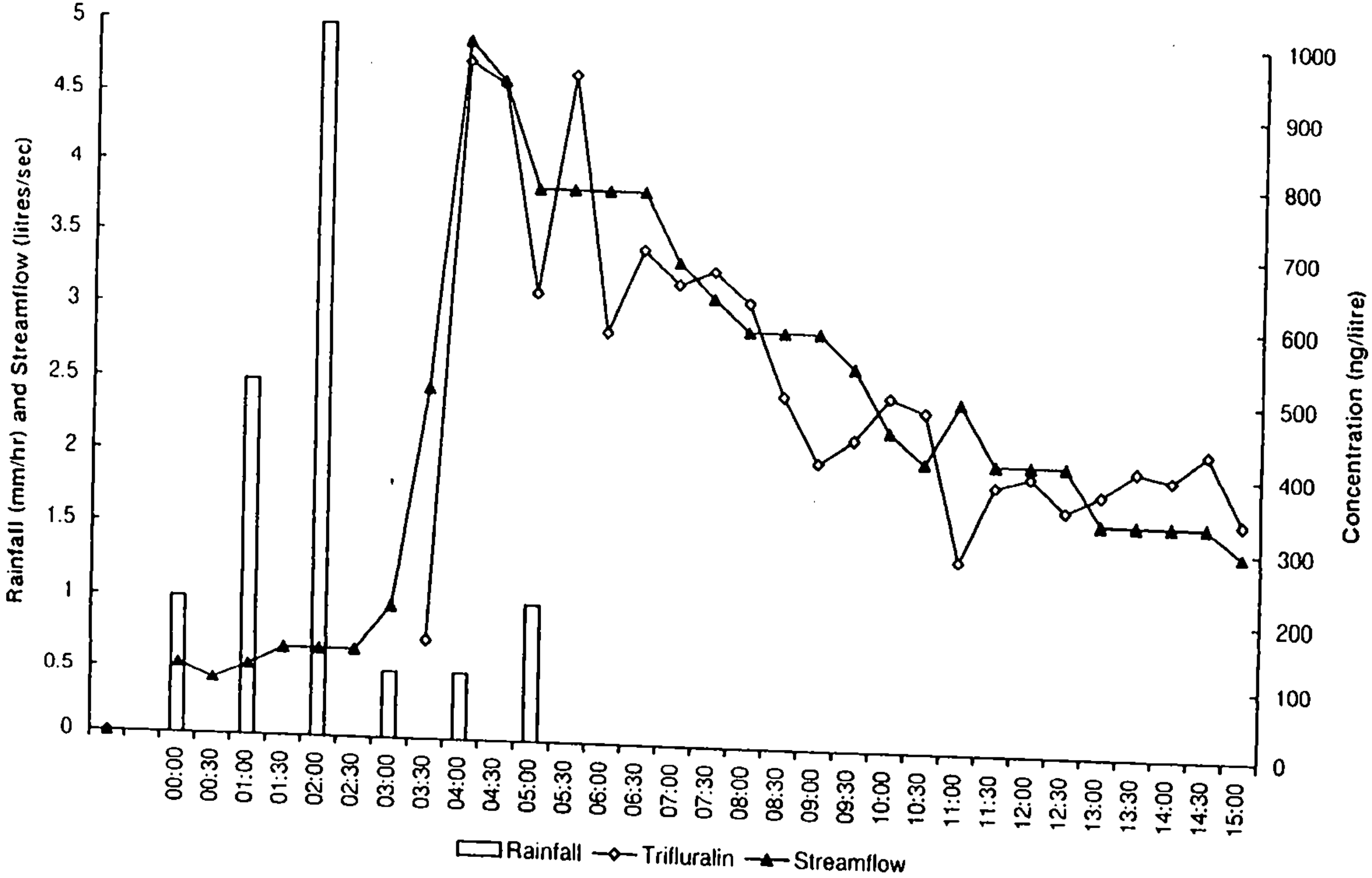


Fig. W2 Rosemaund Site 3: Trifluralin Experiment 11 11 92.

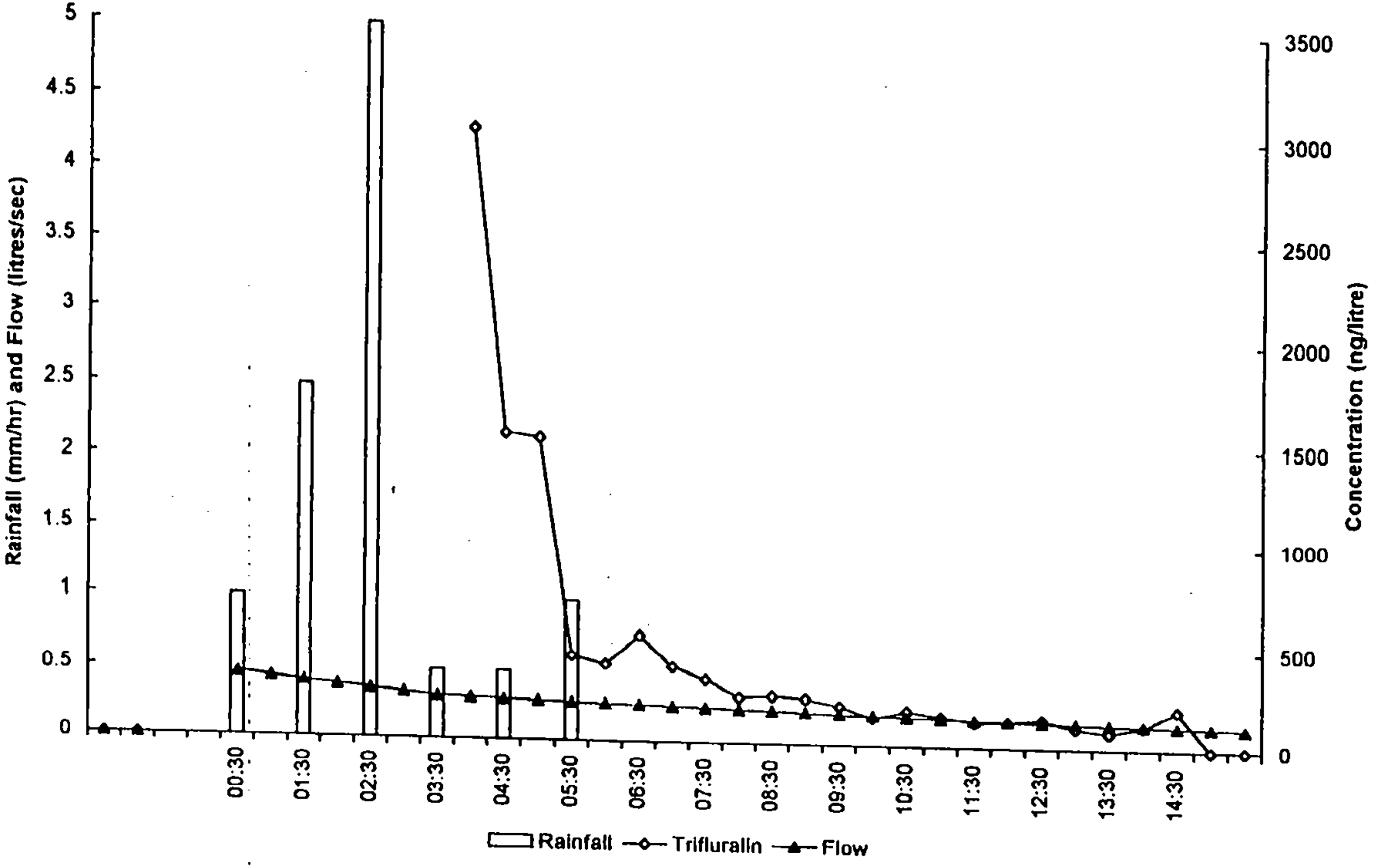


Fig. W3 Rosemaund Site 1: Trifluralin Experiment 15 11 92.

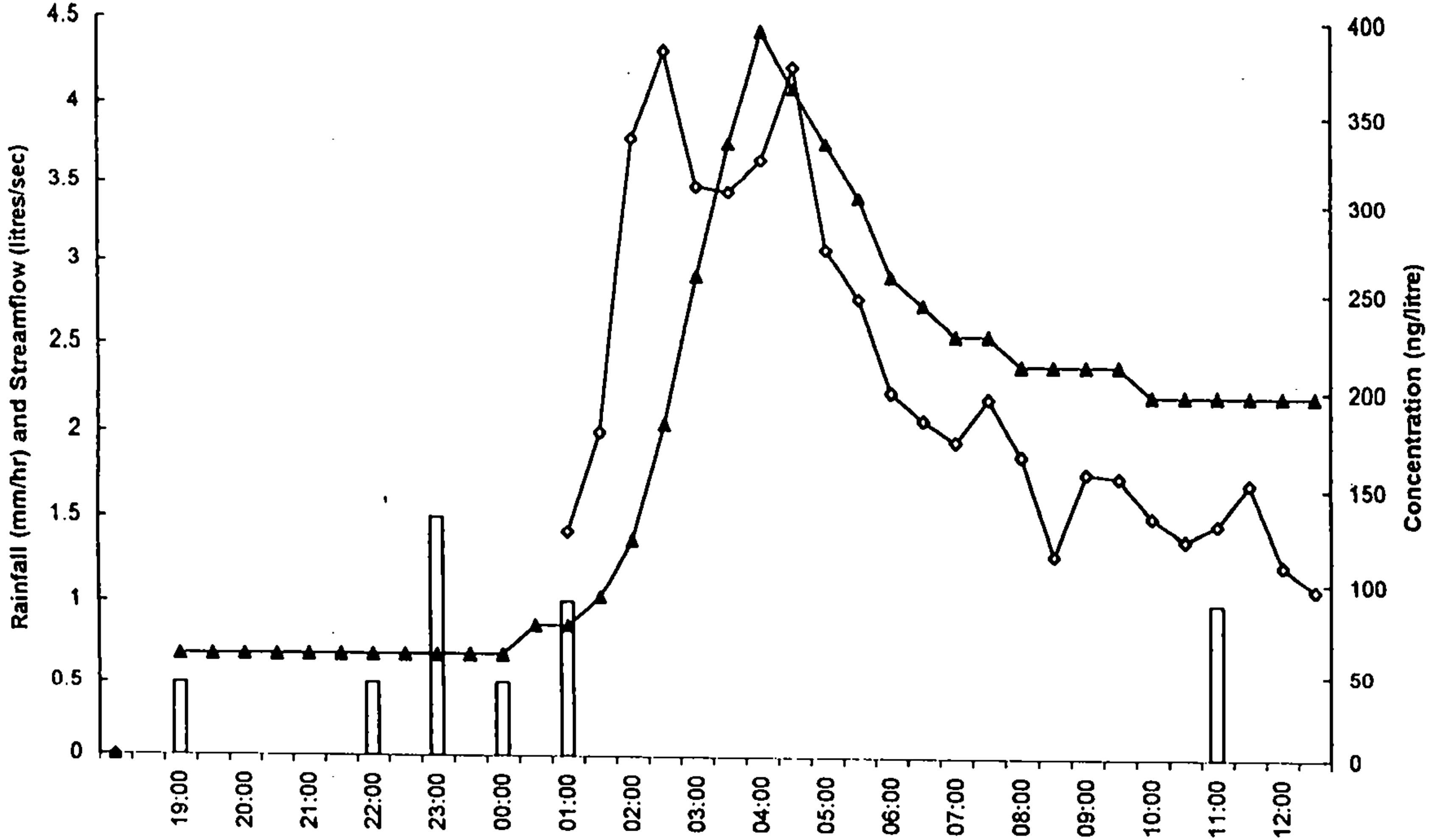


Fig. W4 Rosemaund Site 3: Trifluralin Experiment 15 11 92.

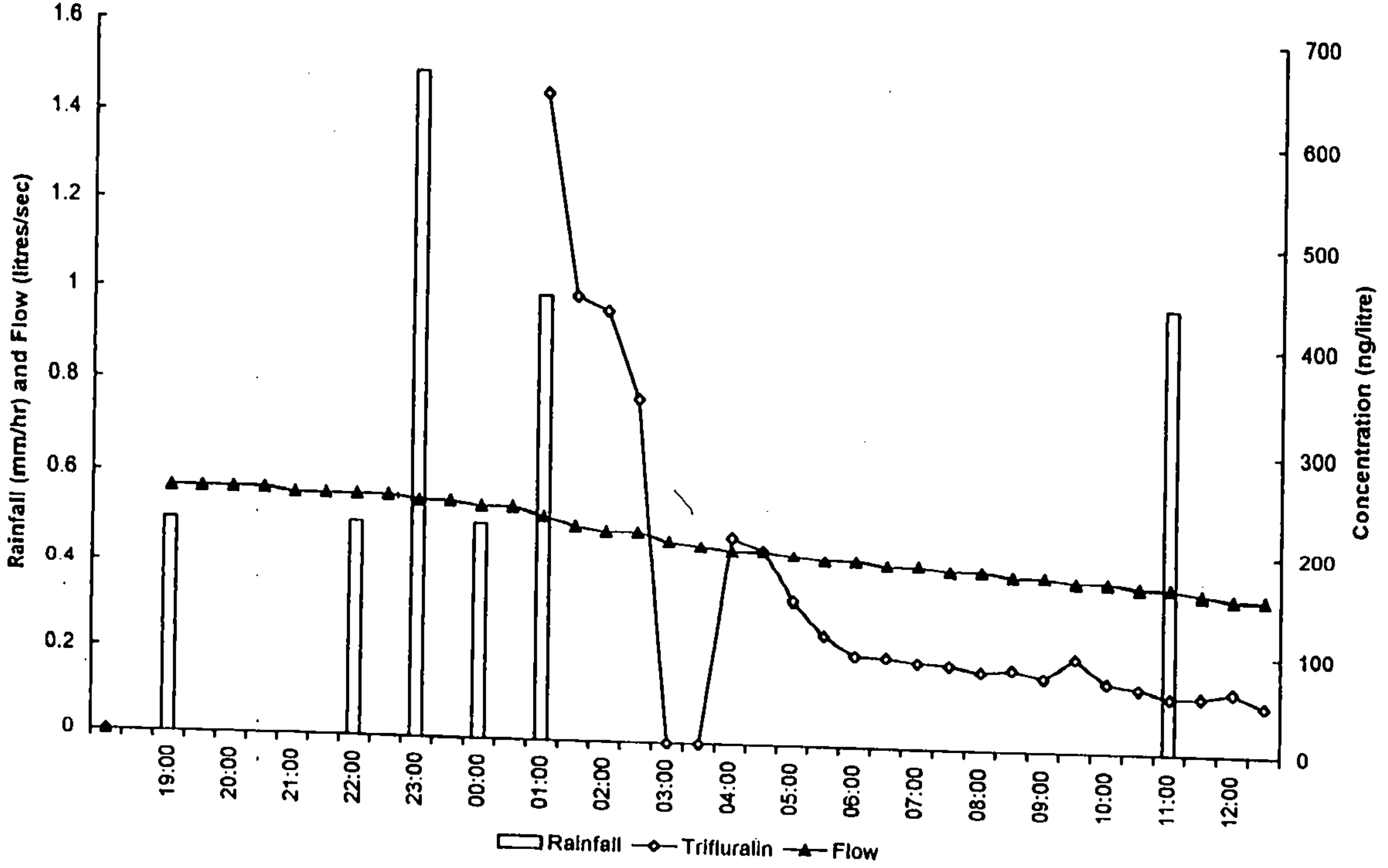


Fig. W5 Rosemaund Site 1:Trifluralin Experiment 26 11 92.

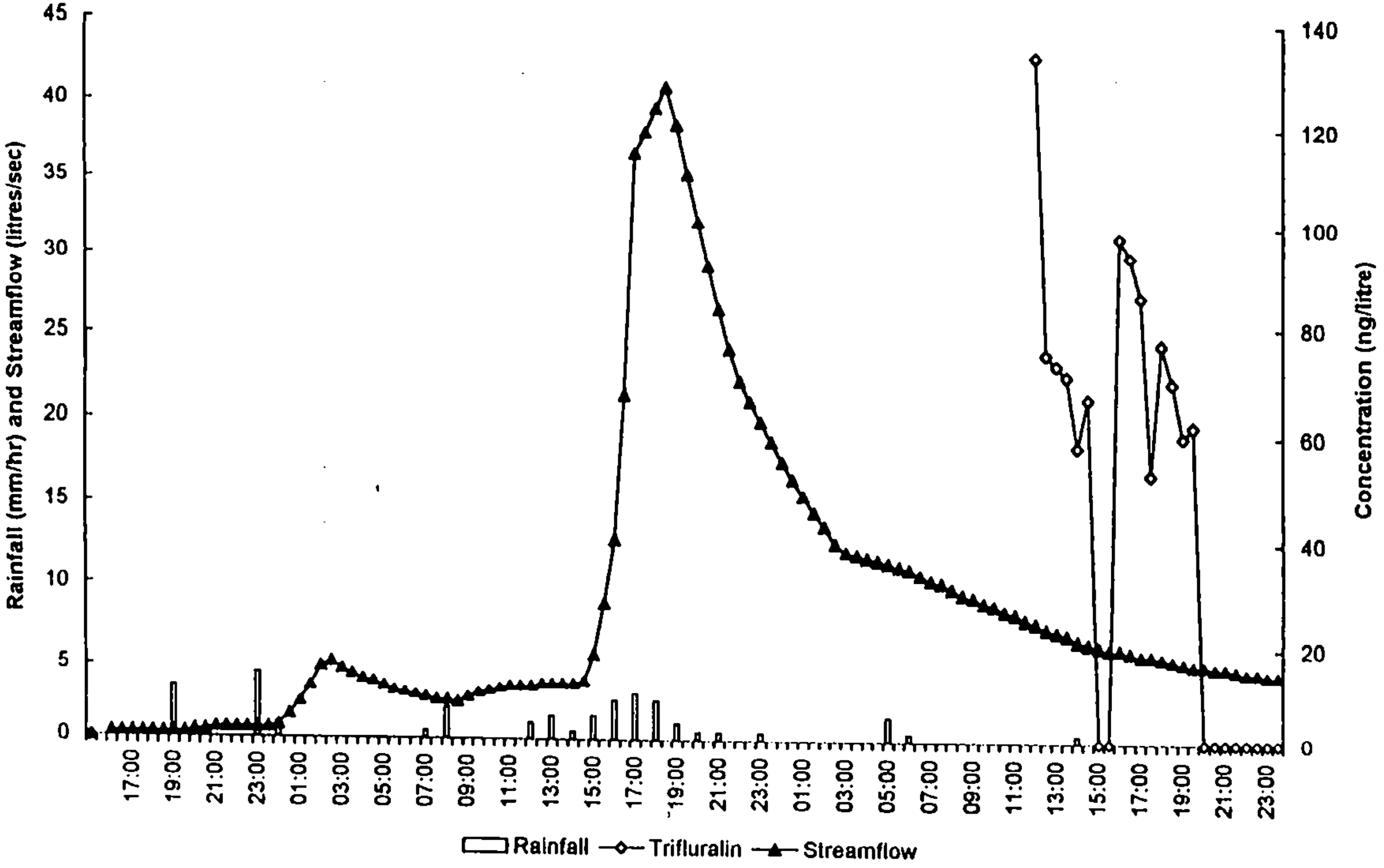
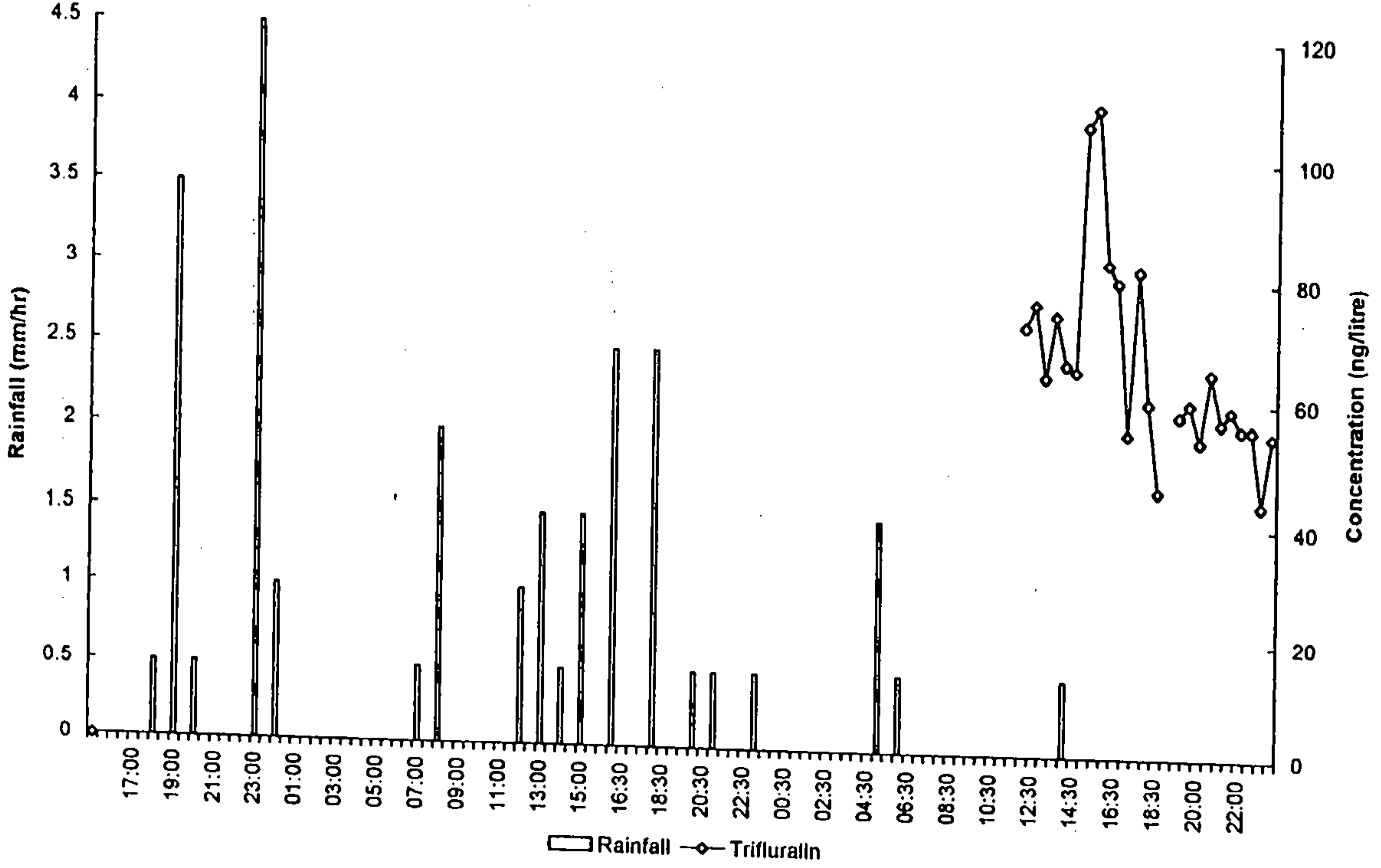


Fig.W6 Rosemaund Site 3: Trifluralin Experiment 26 11 92.



Rainfall event on 16 December 1992 (Tables W8 and W9, Appendix 7)

This 9 mm event was the first to occur after the deltamethrin was applied on 15/12/92, but it had been preceded in the previous 3 weeks by a total of 67 mm of rain, of which at least 2 portions (on 28-29/11/92 and 1/2/92) should have triggered the samplers. However, no samples were in fact taken during this period. Figure W7 shows a very small peak (8 ng/l) of deltamethrin in the stream just before the peak of the hydrograph on 16/12/92. This was similar to background levels seen during earlier events before deltamethrin was sprayed, and probably indicates that this event was not sufficiently large to mobilise soil particulates into the field drains. Unfortunately, no suspended solids data are available. Trifluralin (Figure W8) peaked at 78 ng/l in the stream, approximately 5 h after the peak of the hydrograph. No data from the Site 3 drain are available for this event.

Rainfall event on 18 December 1992 (Tables W10 and W11, Appendix 7)

This event was more substantial (20 mm) than the one on 16/12/92 and suspended solids in the drain at Site 3 reached over 500 mg/l at 12.00. However, suspended solids data are not available from the peak of the hydrograph. Deltamethrin in the stream at Site 1 (Figure W9) peaked at 1872 ng/l, about 2 $^1/_2$ hours before the peak of the hydrograph. Deltamethrin concentrations then declined within an hour to the 30-130 ng/l range, but did not decline further to background levels within 12 hours. Trifluralin in the stream (Figure W10) also peaked before the hydrograph (1040 ng/l) and rapidly declined below 100 ng/l. It is difficult to explain why pesticide concentrations peaked so early, but it is possible that pesticide-laden silt had already been carried down the soil profile by the event on 16/12/92, and was then flushed out into the stream by the flow at the very start of the 18/12/92 event. Peak deltamethrin concentrations in the Site 3 drain only reached 19 ng/l (Figure W11), indicating that the residues seen in the stream must have originated from one of the other drains which take water solely from Foxbridge and Longlands. Trifluralin peaked at 389 ng/l in the drain (Figure W12) and rapidly declined below 50 ng/l.

Fig. W7 Rosemaund Site 1: Deltamethrin Experiment 16 12 92.

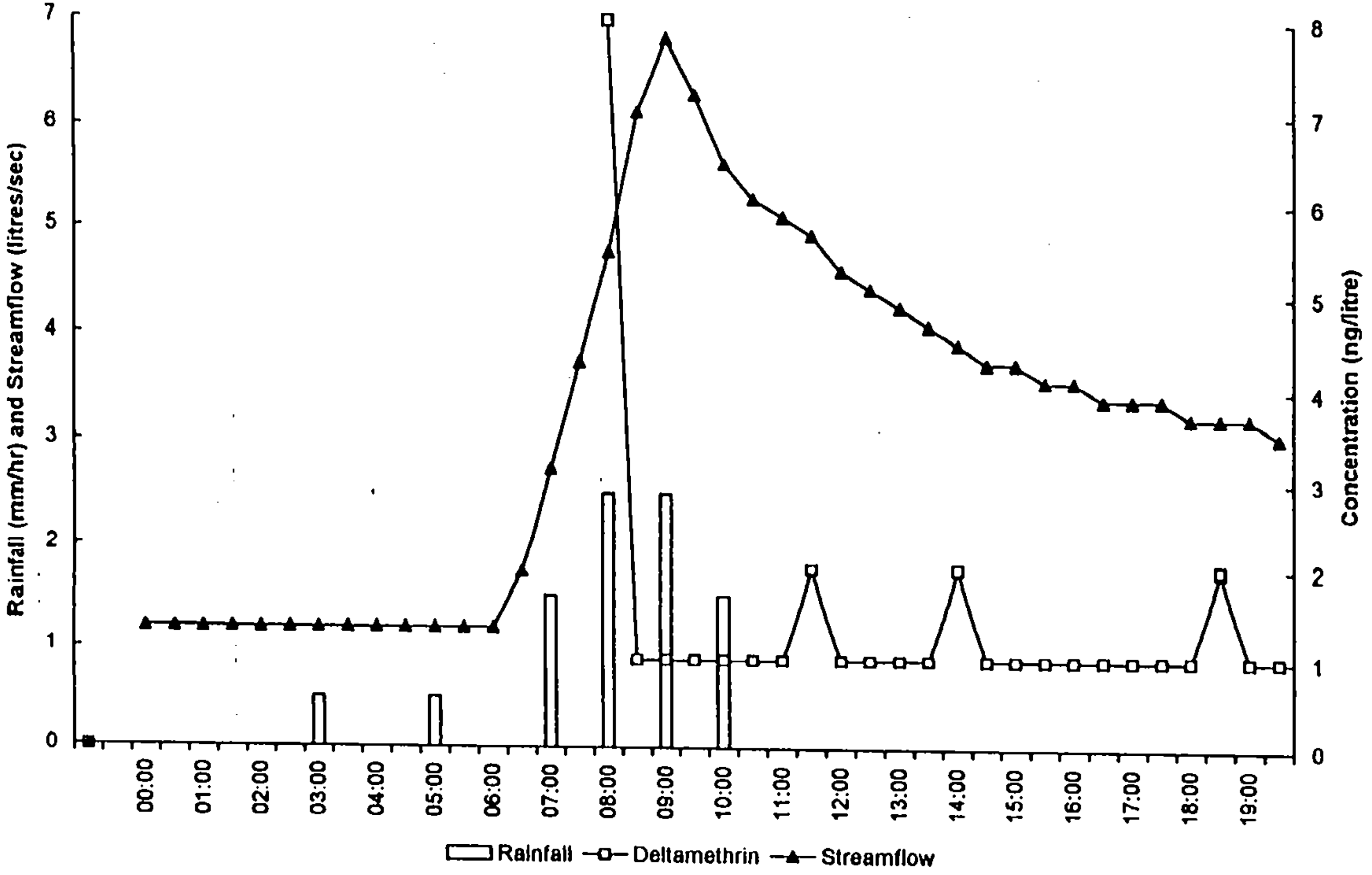


Fig. W8 Rosemaund Site 1: Trifluralin Experiment 16 12 92.

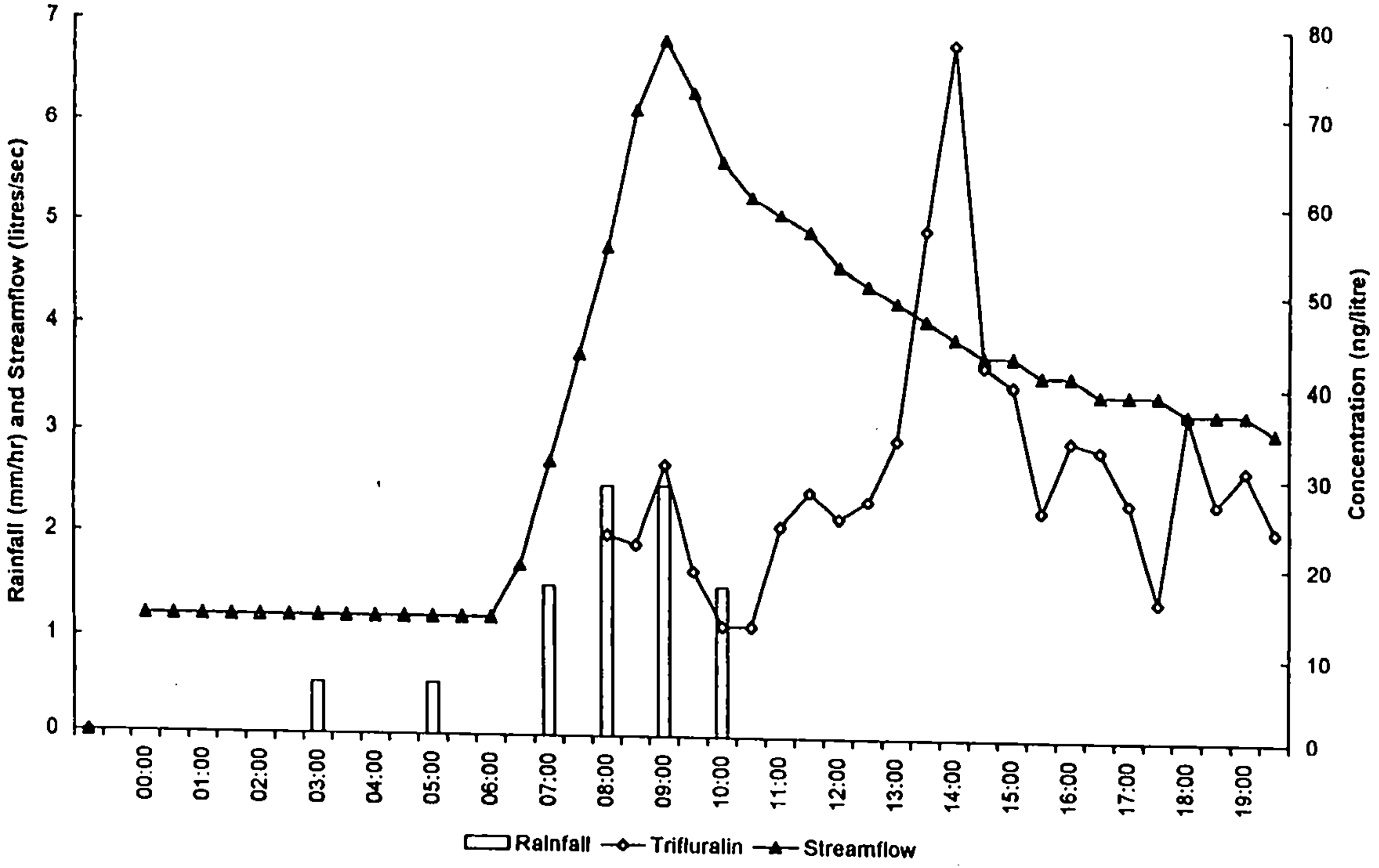


Fig. W9 Rosemaund Site 1: Deltamethrin Experiment 18 12 92.

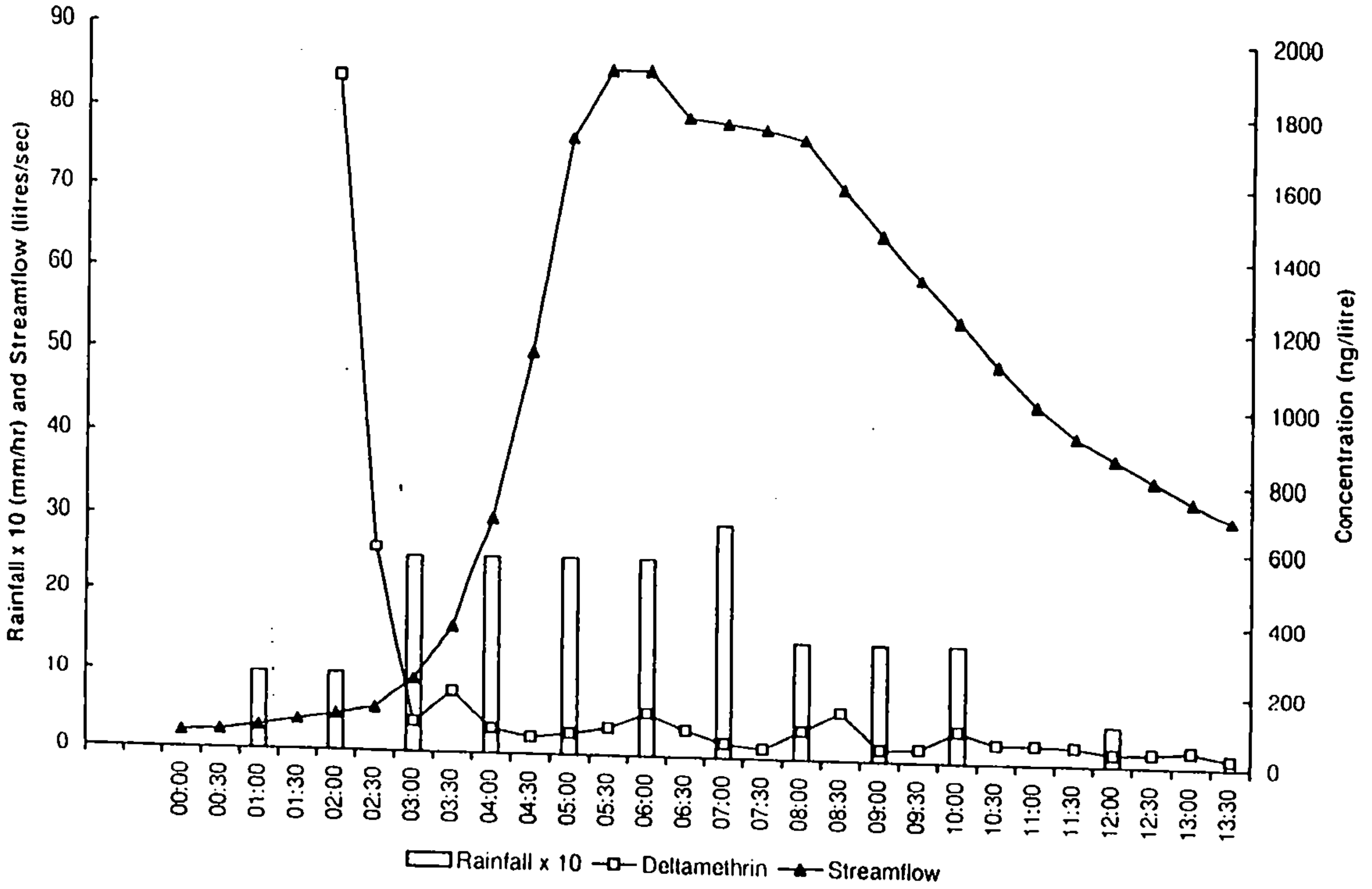


Fig. W10 Rosemaund Site 1: Trifluralin Experiment 18 12 92.

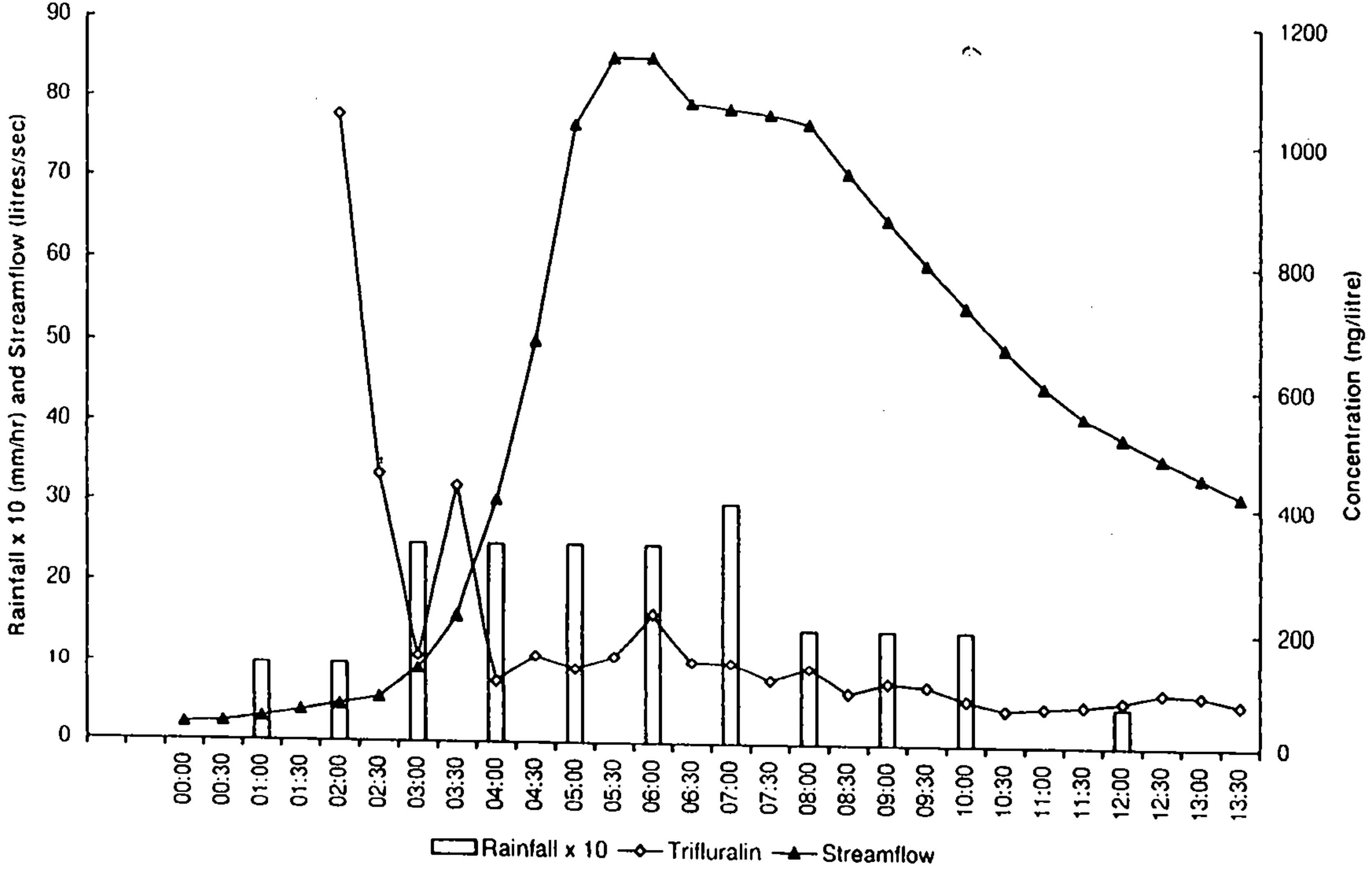


Fig. W11 Rosemaund Site 3: Deltamethrin Experiment 18 12 92.

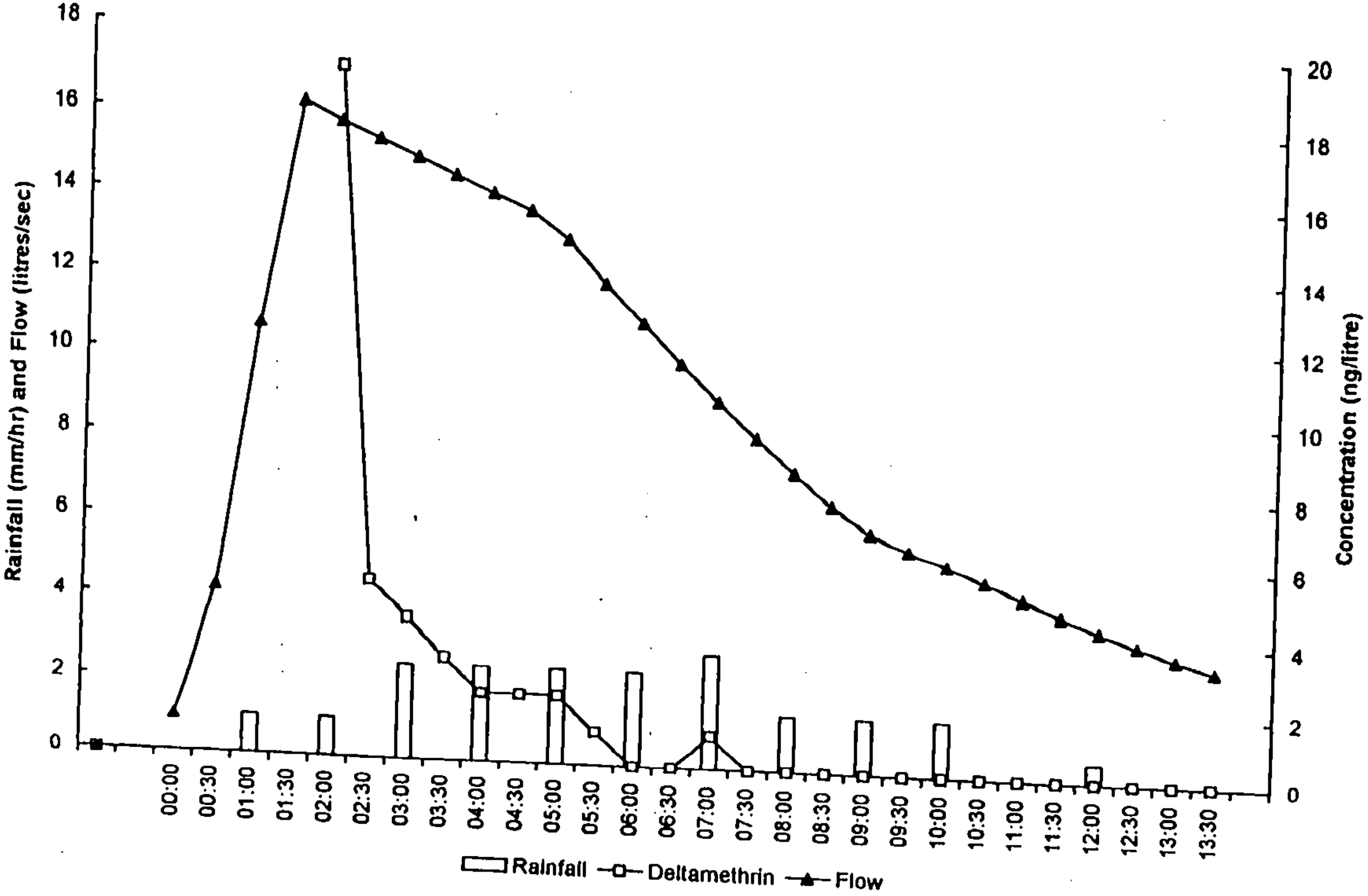
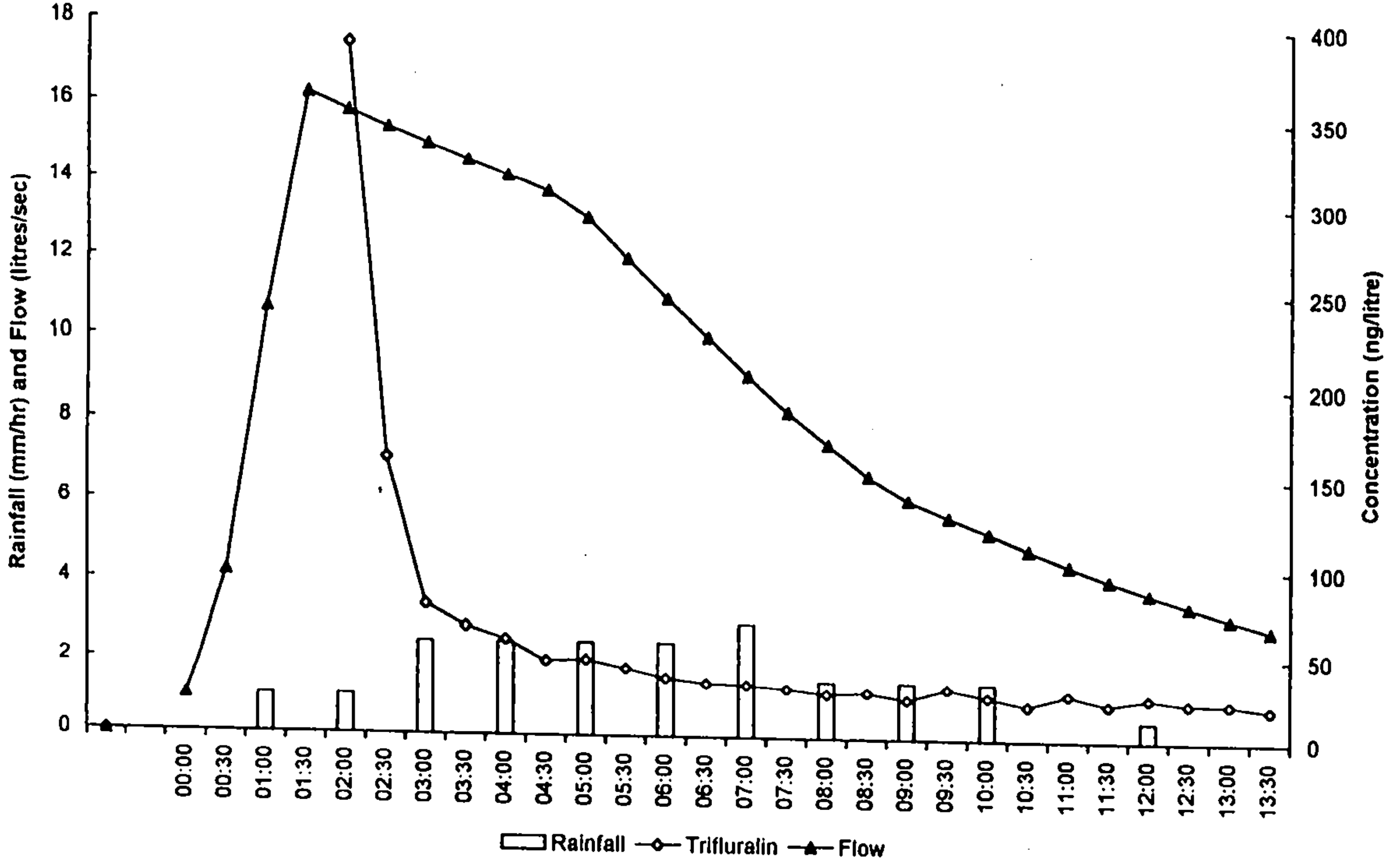


Fig. W12 Rosemaund Site 3: Trifluralin Experiment 18 12 12.



Rainfall event on 5 January 1993 (Tables W12 and W13, Appendix 7)

This was a very small event (6 mm) but it had been preceded on the previous day by a further 2 mm of rain. Before that, almost no rain had fallen since 18/12/92. As a consequence of low flow rates, deltamethrin barely rose above background (to 11 ng/l) in the stream at Site 1 (Figure W13), and trifluralin only peaked at 95 ng/l (Figure W14). Flow rates barely increased above baseline in the drain at Site 3 and deltamethrin did not increase at all. However, trifluralin peaked at 177 ng/l (Figure W15).

Rainfall event on 7 April 1993 (Table W15, Appendix 7)

By this time, trifluralin and especially deltamethrin had degraded considerably in the soil, but were still detectable in the field drain at Site 3 (no samples were obtained from the stream at Site 1). This 11 mm event produced a deltamethrin peak in the drain of 12 ng/l (Figure W16) and a trifluralin peak of 114 ng/l (Figure W17).

Rainfall event on 9 April 1993 (Table W16, Appendix 7)

This 12 mm event was the last to be monitored, and again, samples were only obtained from the drain at Site 3. Deltamethrin peaked in the drain at 10 ng/l (Figure W19), showing that residues of this insecticide had effectively returned to pre-spray levels. Trifluralin, as one might expect from its longer half-life, was still present above background, peaking at 109 ng/l (Figure W20).

Sediment bioassays

No significant differences were observed between the growth rates of *Chironomus riparius* larvae held in control sediment and those held in any of the sediments collected after the trifluralin and deltamethrin applications. Unfortunately, there was insufficient analytical resource to permit analysis of the relevant sediments for pesticide residues, so it is not known to what extent they were contaminated.

Fig. W13 Rosemaund Site 1: Deltamethrin Experiment 5 1 93.

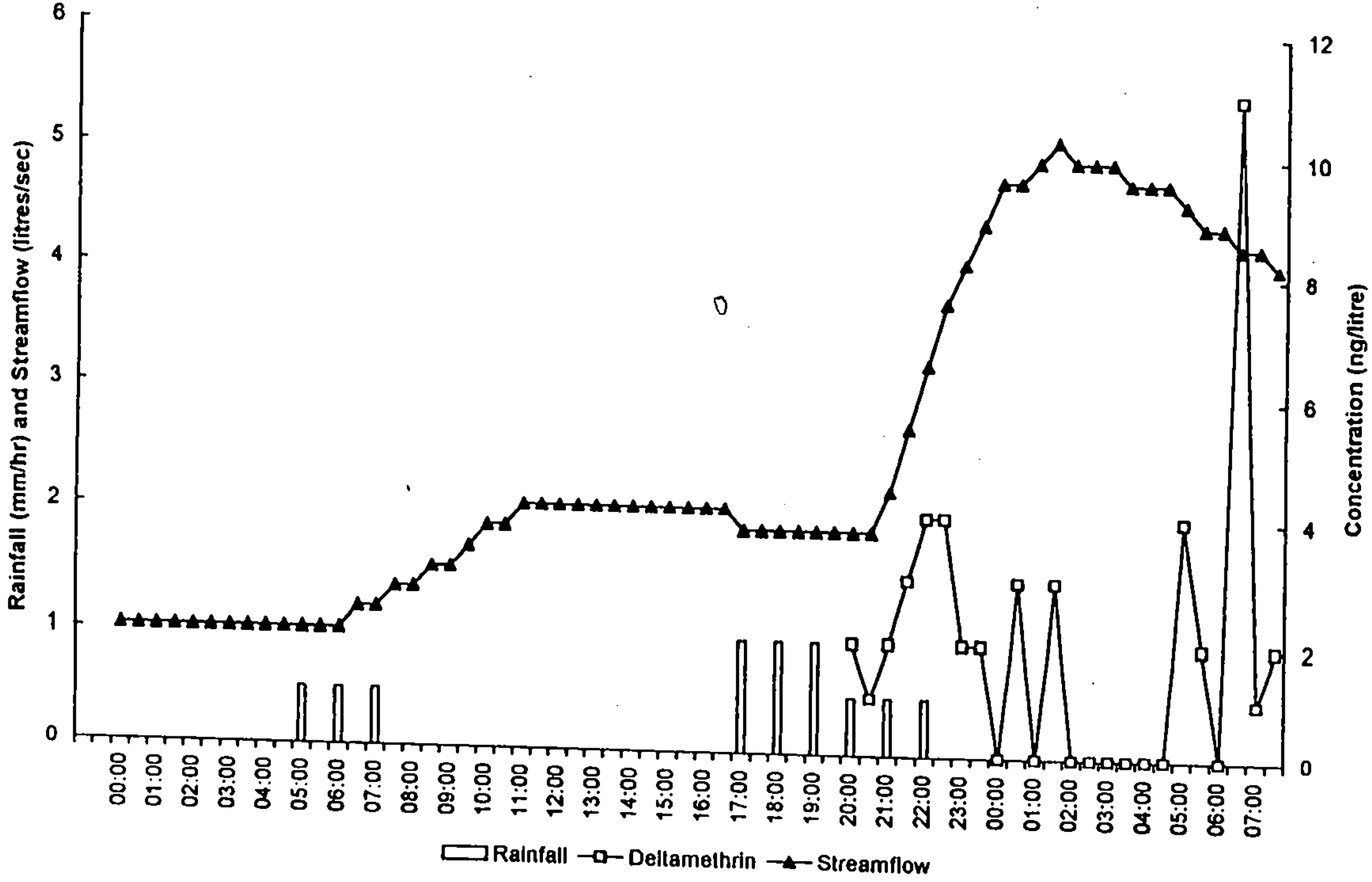


Fig. W14 Rosemaund Site 1: Trifluralin Experiment 5 1 93.

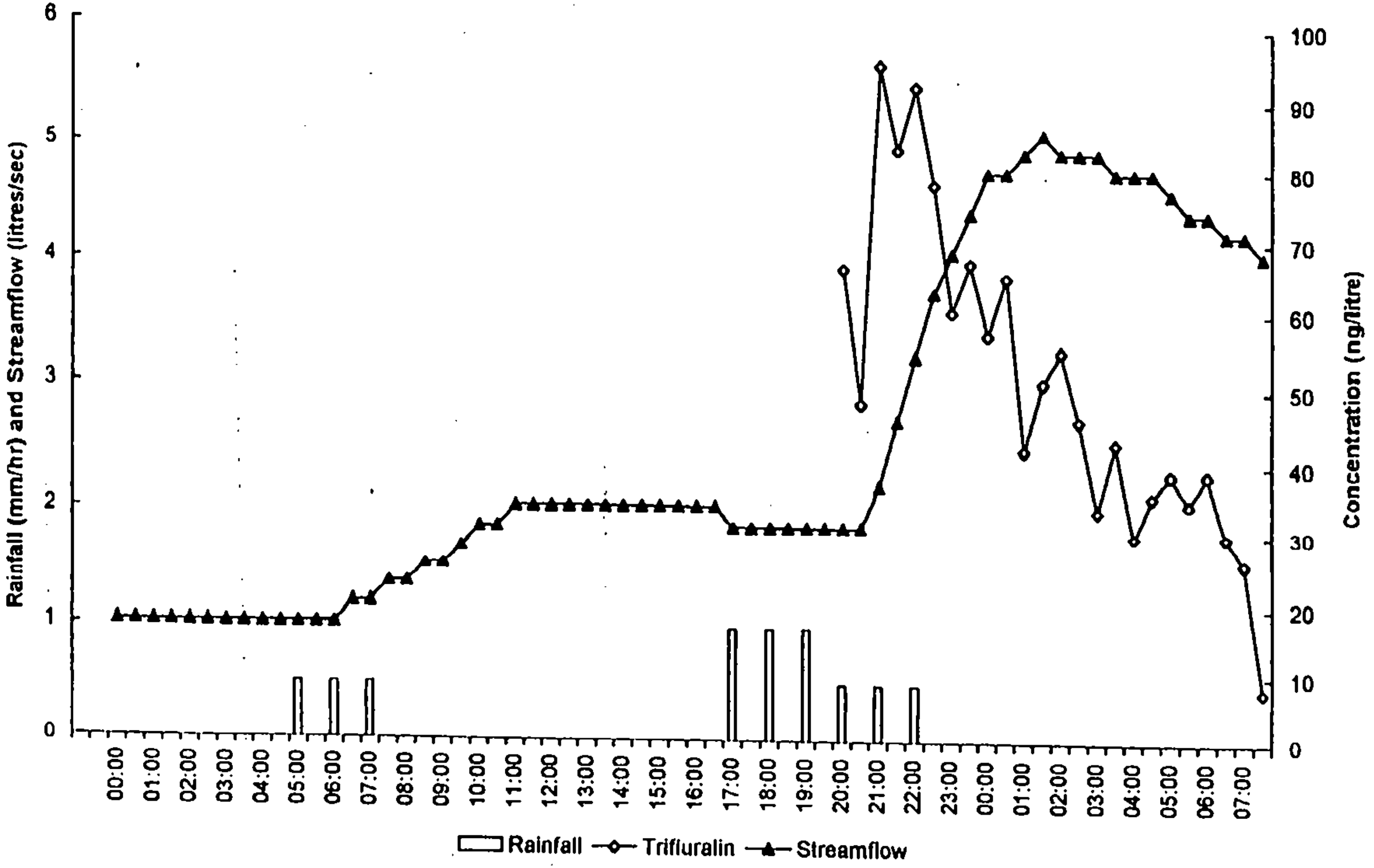


Fig. W15 Rosemaund Site 3: Trifluralin Experiment 5 1 93.

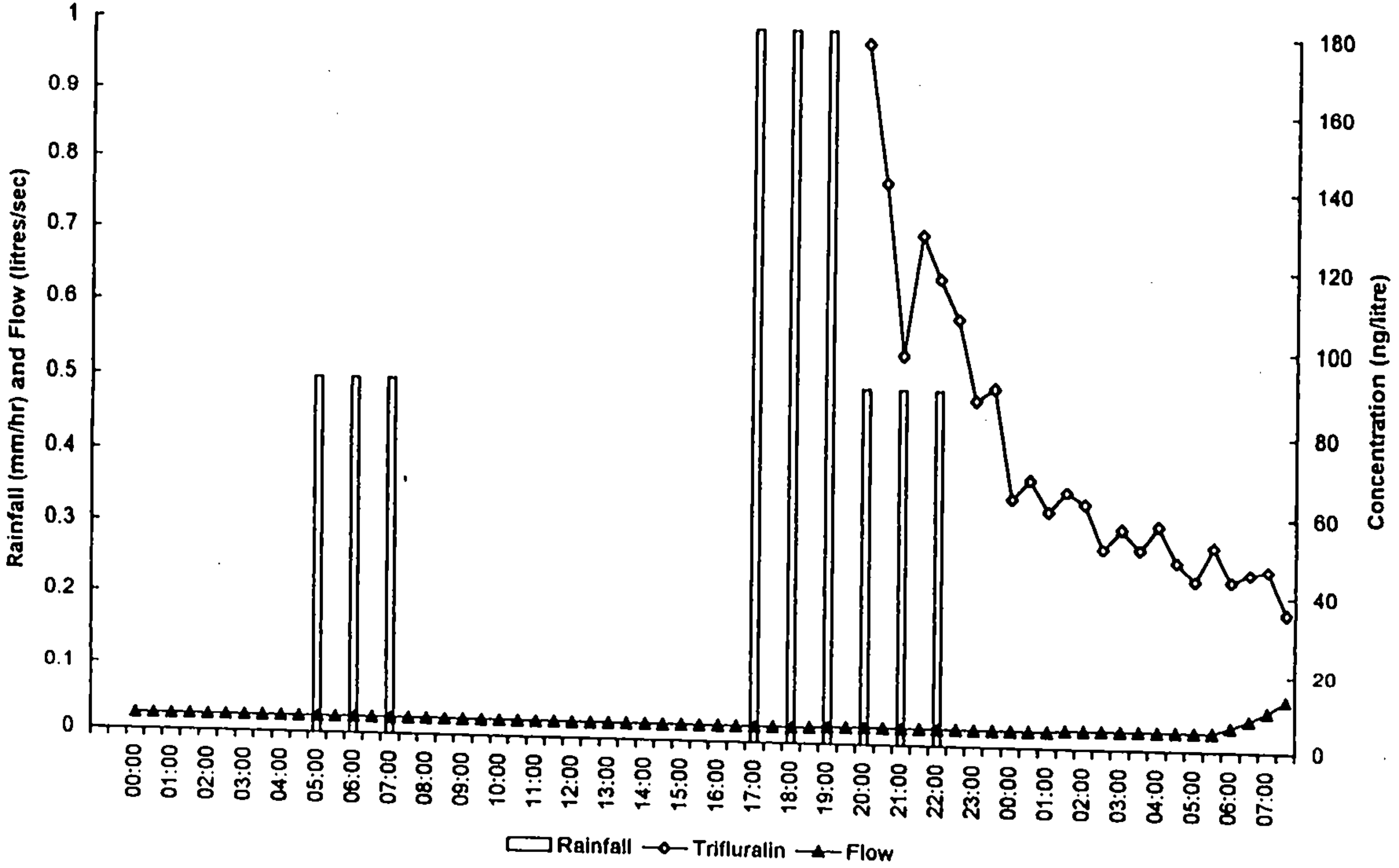


Fig. W16 Rosemaund Site 3: Deltamethrin Experiment 7 4 93.

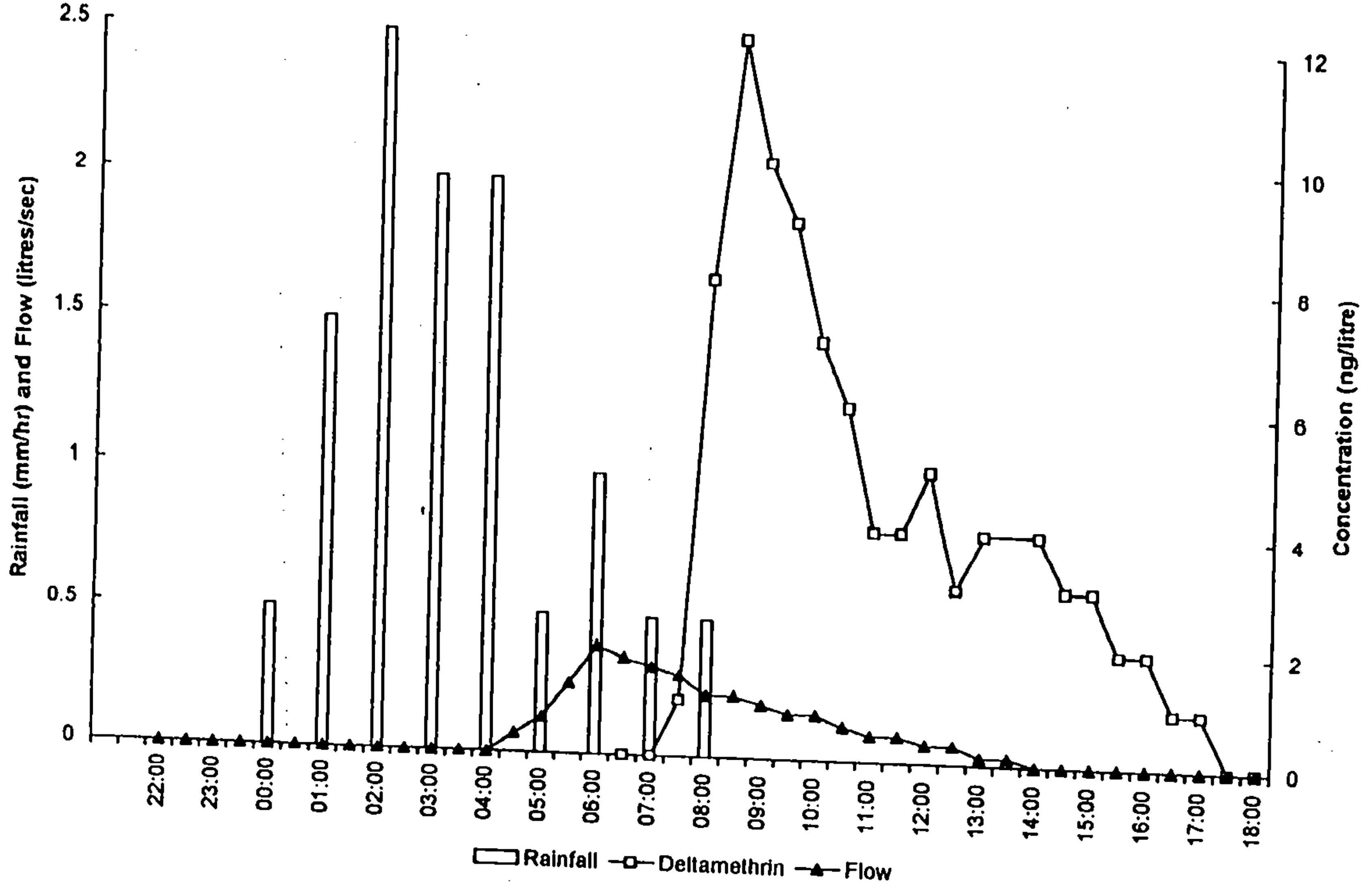


Fig. W17 Rosemaund Site 3: Trifluralin Experiment 7 4 93.

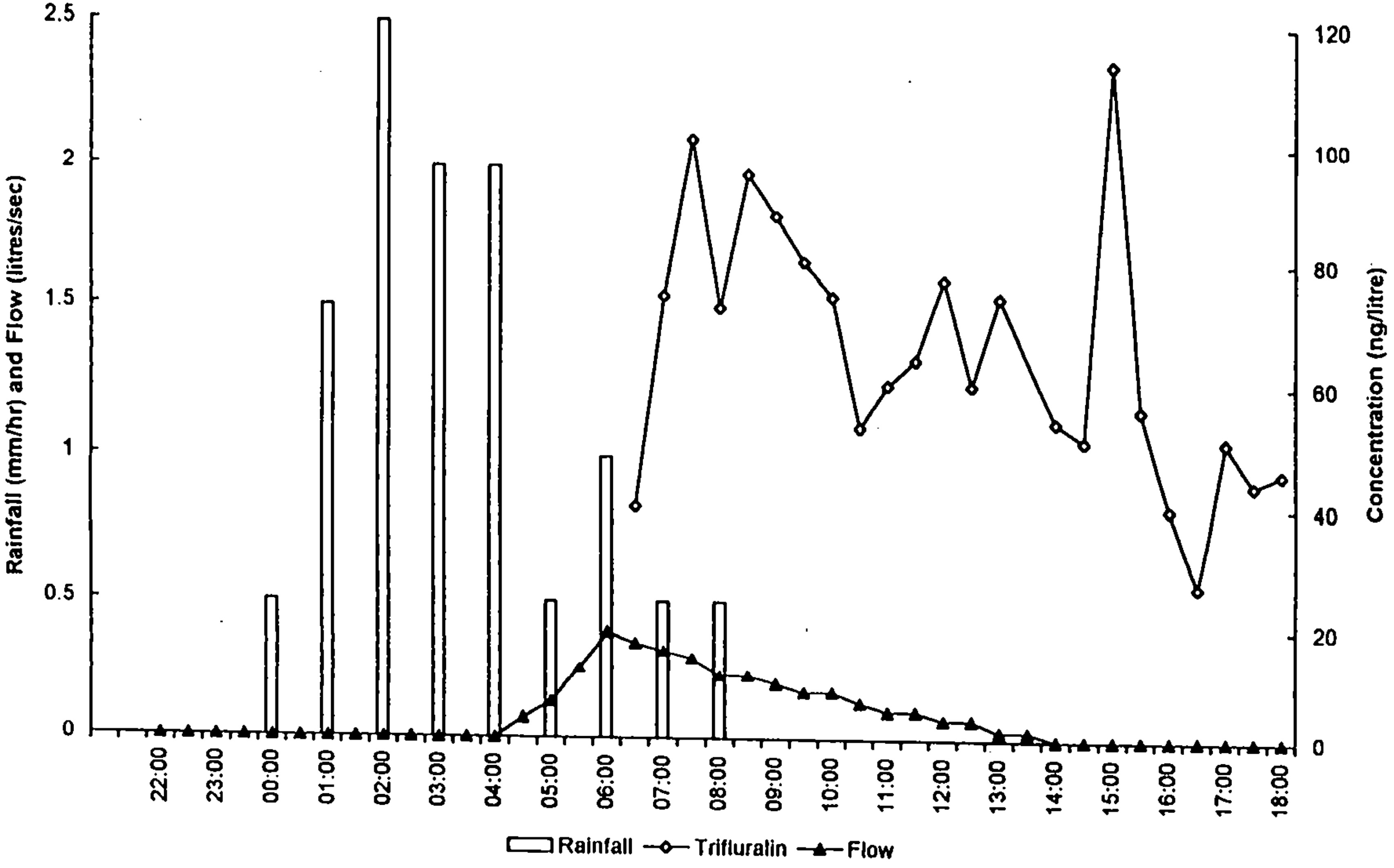


Fig. W19 Rosemaund Site 3: Deltamethrin Experiment 9 4 93.

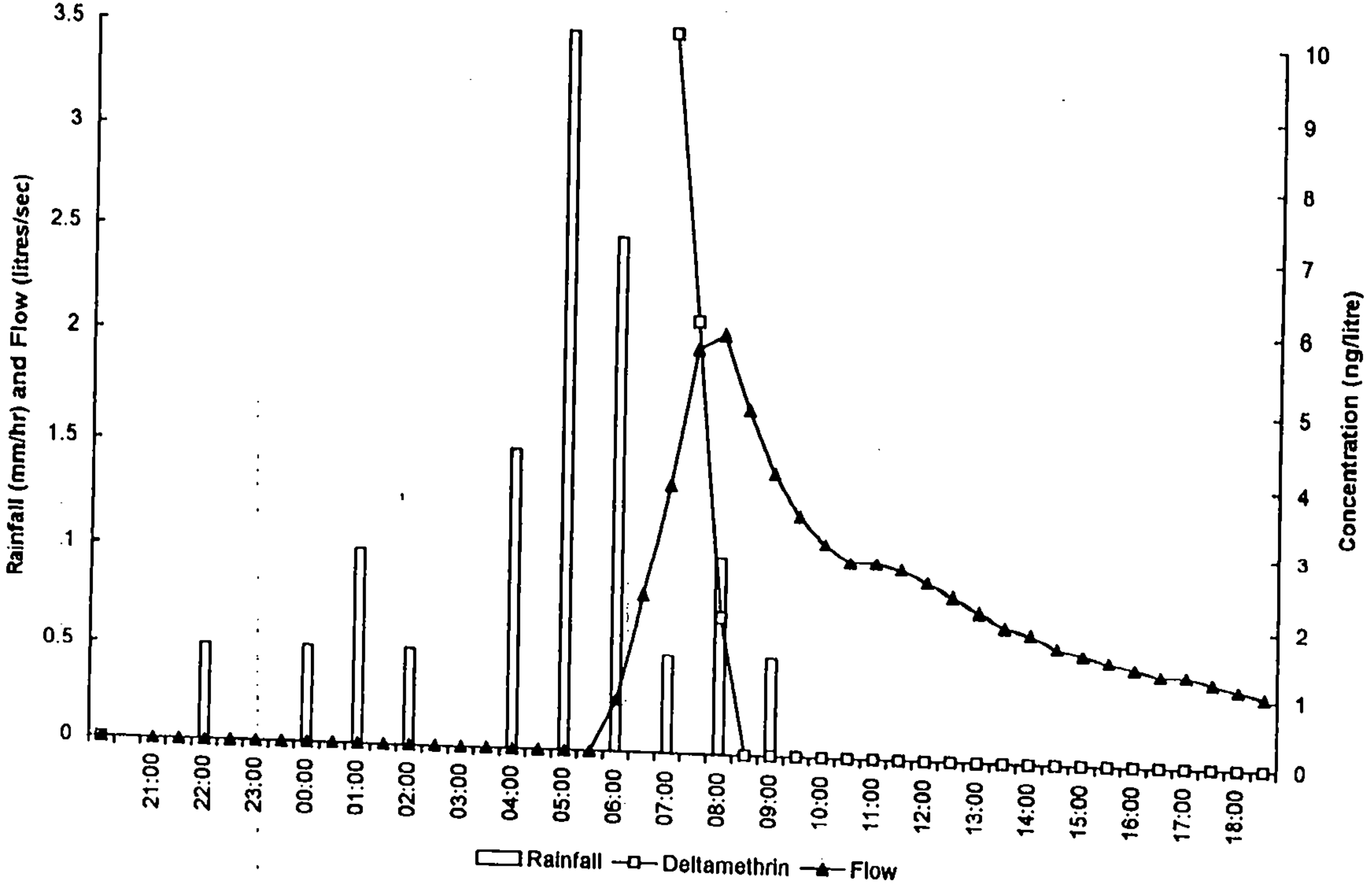
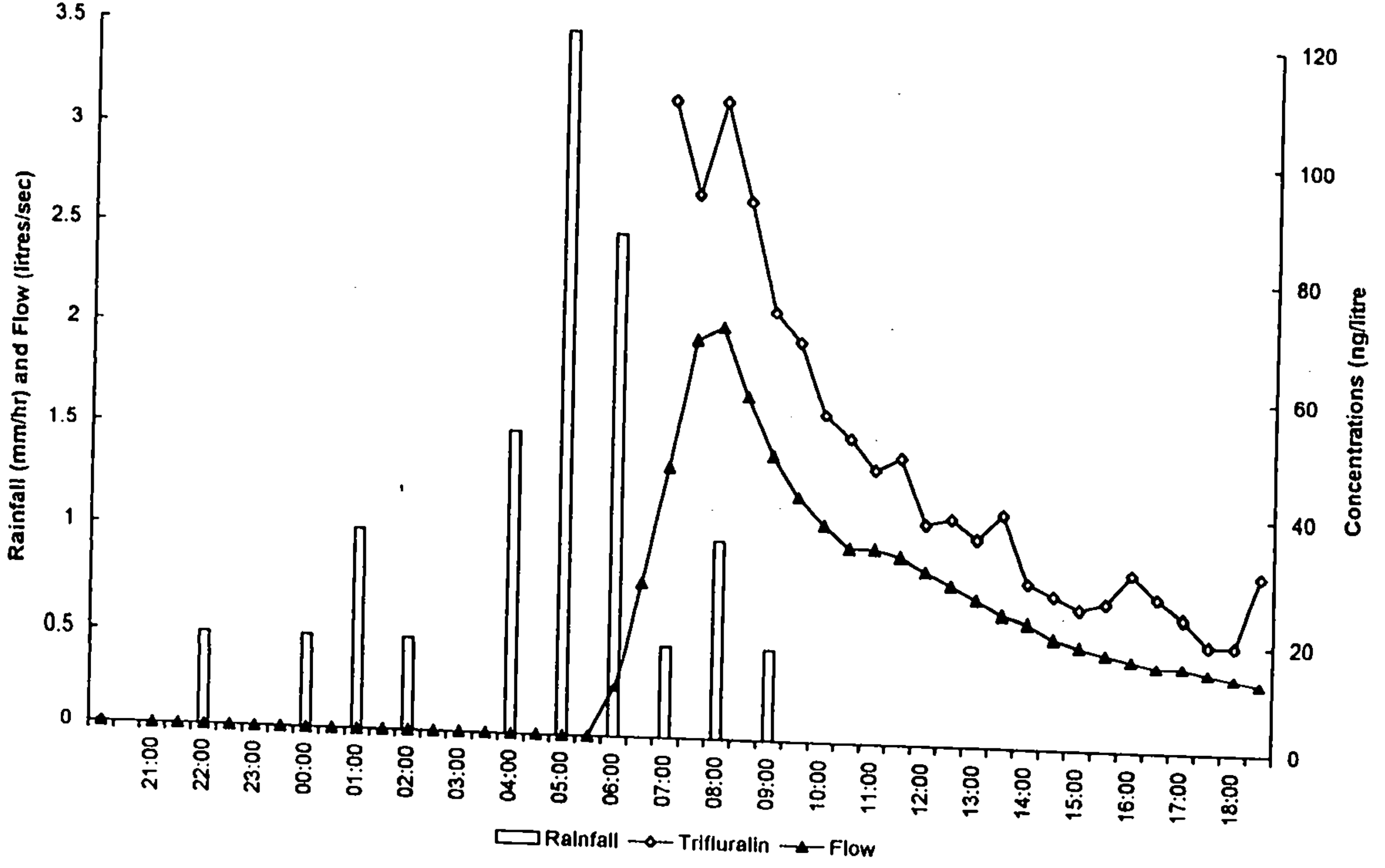


Fig. W20 Rosemaund Site 3: Trifluralin Experiment 9 4 93.



Soil

Trifluralin

Background samples taken on 1 October 1992 contained less than the detection limit, 0.003 ppm wet weight.

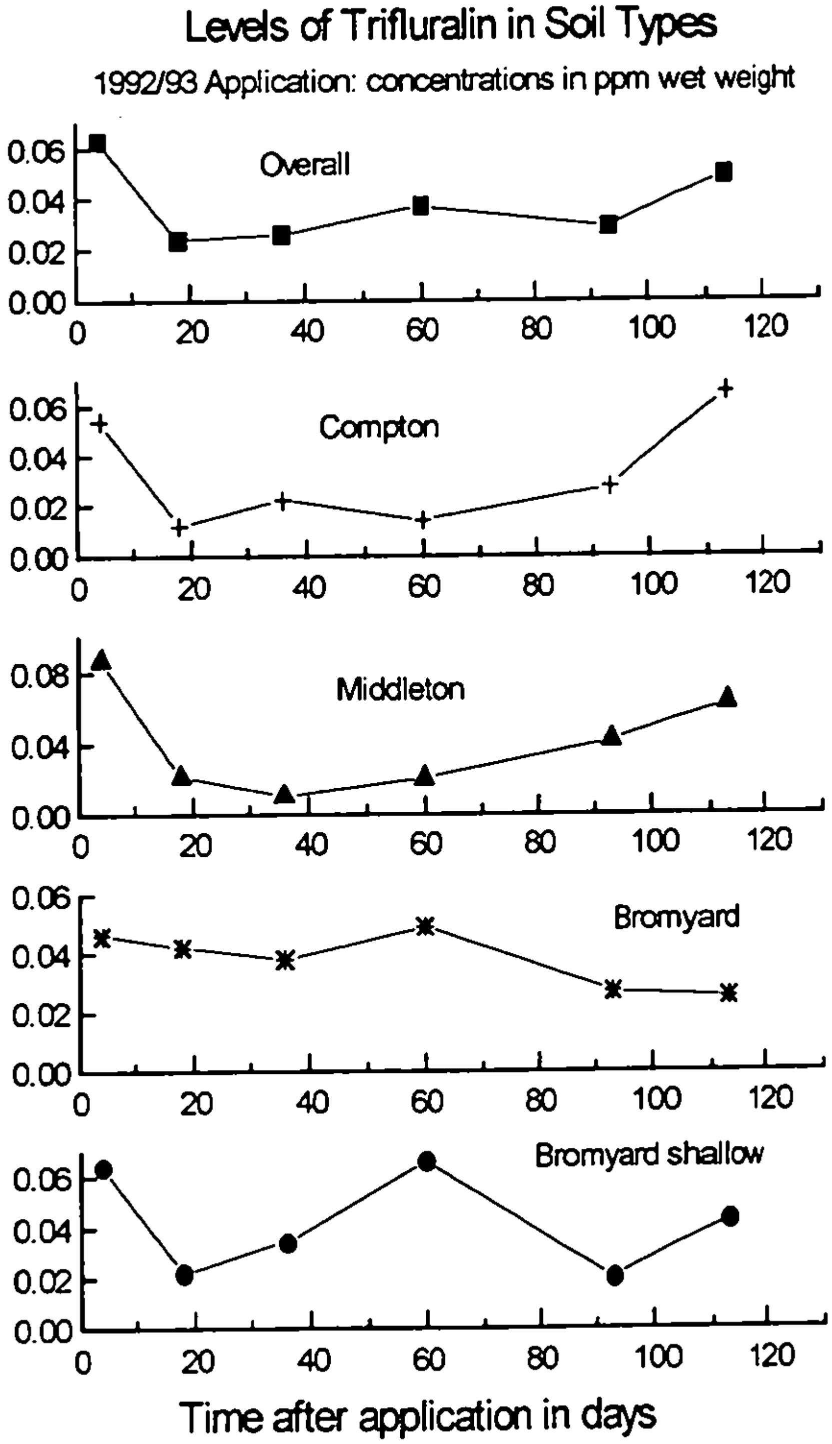
Individual results and derived average concentrations are given in Tables B1 to B6 in Appendix 8. Trifluralin was applied at 1.1 kg/ha on 8 November. The initial concentration expected over the top 1 metre depth for this application would be 0.073 ppm, which compares well with the measured value of 0.063 ppm 4 days later. The subsequent variation in the measured levels was somewhat erratic as shown in the plot (Figure 5.1). Initially the overall concentration decreases as would be expected, but later measurements show an increase. The individual soil types show similar patterns, in general having higher levels in the later samples. The exception is the Bromyard soil, which shows the expected approximately exponential decrease.

If the degradation was first order, plots of $\log_e$(conc) versus time should be linear with a negative slope. For most of the soil types, the correlation coefficient of such plots is low and the slope is either positive or close to zero. The Bromyard is the exception, with a slope corresponding to a rate constant of 5.4×10^{-3} day^{-1}.

It is difficult to deduce much from this data. It may be that the smaller number of sampling sites used meant that the results are affected more by uneven distribution. However the later high levels are found at most of the sites. Another possibility is that overland flow may have carried pesticide from the slopes of the catchment down to the valley bottom. This would have the effect of transferring trifluralin from the sites on the Bromyard soils to those on the Middleton and Compton soils which occupy the lower slopes and the valley bottom, leading to the increased levels of the chemical at these lower sites. The depth profiles in the main showed higher levels in the top layer and lower levels at depth at all sites; hence movement of top soil would carry the largest load of chemical.

Deltamethrin

FIGURE 5.1 TRIFLURALIN LEVELS IN FOXBRIDGE AND LONGLANDS



Samples were taken on 14 December 1992, 6 and 21 January, 3 and 25 March 1993. All samples contained less than the detection limit of deltamethrin (0.003 ppm wet weight) except for the 0-25 cm sample of the Bromyard soil on 6 January (0.004 ppm) and the 50-100 cm sample of the Middleton soil on 3 March (0.005 ppm). The failure to detect deltamethrin is not unexpected given the very low level of application of this chemical and the relatively high detection limit.

5.4.2.3 Conclusions

This experiment showed conclusively that two pesticides which have not been traditionally considered prone to leaching can nevertheless translocate rapidly via field drains into the Rosemaund stream. Peak concentrations in the stream at site 1 for trifluralin and deltamethrin were 1040 and 1872 ng/l, respectively, showing that they translocate at levels comparable to many more water-soluble substances. The fact that the strongly-adsorbed deltamethrin was only applied at a rate of 5g/ha suggests that neither application rates nor chemical properties are of over-riding importance in determining the transient concentrations which may appear in headwater streams. These observations therefore reinforce the view that peak pesticide levels are more a function of soil properties, in particular the presence of by-pass flow.

On the other hand, the sediment toxicity data show that the contaminated soil particles which settled in the stream after rainfall events were not acutely toxic to sensitive insect larvae. This was to be expected with trifluralin which is not especially strongly bound to soil and is also not very toxic to arthropods. However, it is of major importance for the safe use of deltamethrin which in its unadsorbed form is highly toxic to this phylum. It can be confidently asserted that the concentrations of deltamethrin observed in the stream after certain rainfall events would have been lethal for many stream fauna if present in solution.

5.4.3 IH/NRA - Autumn 1992

5.4.3.1 Methods

Sample collection methods for stream and drain water samples were fully described in the Report for years 1-3. Additional sampling was introduced into the field programme to monitor aspects of sediment transport which should be more important with the highly sorbed chemicals studied in these experiments. The additional monitoring covered surface runoff from Longlands Field, pesticide concentrations in the mobile phase of stream sediments and the dissolved and particulate fractions in selected water samples. The methods employed are described below.

Surface Runoff Samples

Surface runoff samples were collected using SSLRC surface runoff traps. The traps were 1 m wide steel troughs with 3 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 bottles. 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 centimetres 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 bucket 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. These bottles were 0.5 l wide mouthed jars. Any remaining sediment was 'swept' into the bottle, using a PTFE spatula. The bottles were sealed and labelled.

Chemical Analysis

Water Samples

Water samples were analysed at the Institute of Hydrology: routine samples for atrazine, simazine, isoproturon and trifluralin, storm event samples for trifluralin only. The methods for atrazine, simazine and isoproturon were fully described in the Report for years 2 to 4. All samples were stored below 4°C prior to analysis.

Trifluralin was extracted sequentially from the water samples with 100, 50 and 30 ml of dichloromethane. The combined extract was dried with anhydrous sodium sulphate and evaporated to dryness in a rotary evaporator. The residue was redissolved in 2 ml of pesticide grade ethyl acetate.

Analysis of the extract was by HPLC using a Zorbex C18 column using a acetonitrile/water solvent at 0.8 ml/min. Detection was by UV at a wavelength of 255 nm. Calibration using external standards gave a detection limit of 0.08 µg/l.

Surface Runoff

Surface runoff samples were analysed at the Institute of Hydrology for trifluralin following the same method as for water samples.

Bed Sediments

The bed sediments were analysed at the Institute of Freshwater Ecology (IFE) River Laboratory, Wareham. The sediments arrived frozen and were allowed to thaw. Samples that were coarse in nature were sieved through a 2 mm stainless steel sieve. The samples were then frozen overnight and then 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).

Suspended Solids

Samples for suspended solids analysis were also sent to IFE, Wareham. The water samples were stored in the dark at 5 °C and separated as soon as possible after arrival. The suspended solids were separated 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 in the aqueous phase and μg/kg (dry weight) for solids.

5.4.3.2 Results and Discussion

Routine Samples

Manual samples were taken throughout the year covered by this report. Details of the results of the analysis of these samples are given separately for Longlands Drain Site and the Main Gauging Site in Tables A1 and A2 in Appendix 9.

Rainfall Event on 11 November 1992

A rainfall event of 10.5 mm on 11 November 1992 caused an increase in river level sufficient to trigger the samplers on both Longlands field drain and at the Main Gauging Site. At Longland Drain Site the sampler triggered at 0350 and samples were taken half hourly for the following 12 hours. The details of the event are given in table A3. in Appendix 9. The sampler at the main gauging site triggered at 0300 and a sample taken each hour for 21 hours. The details of this event are given in Table A4. Appendix 9.

The rainfall produced only a small response in drain flow, however, the trifluralin concentrations showed a dramatic response. (Fig. IH1). The first sample showed the highest trifluralin concentration (14.12 µg/l) which declined rapidly over a period of a few hours. This type of response has been typical of those observed during rainfall events at Rosemaund.

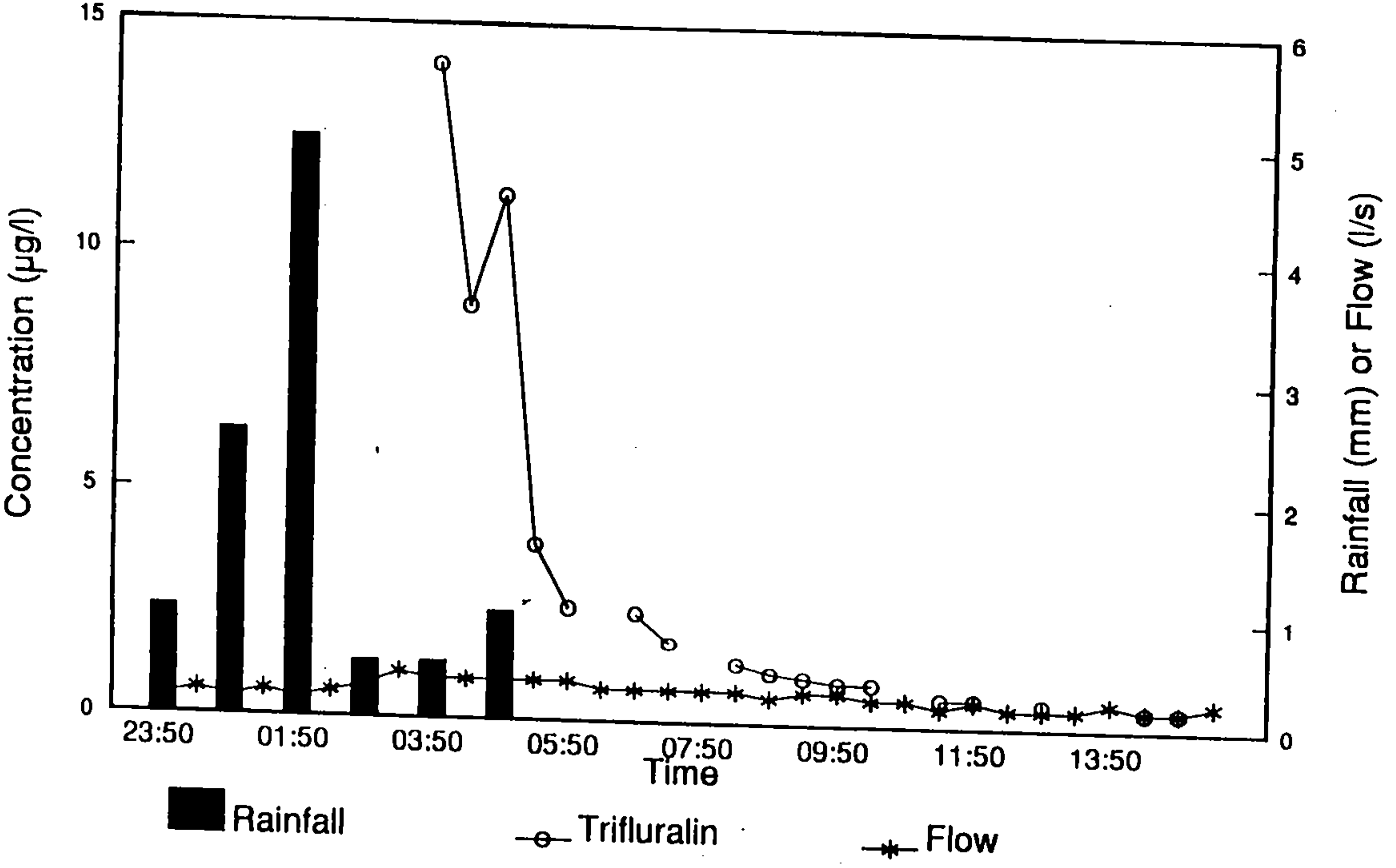
The Main Gauging Site drains a much larger area than Longlands Drain and thus the rainfall resulted in a more obvious response in river flow. The trifluralin concentrations during the event were much lower due to dilution of pesticide runoff by trifluralin free water from untreated fields. Of the 21 samples taken 15 were below the detection limit. Of the others the peak value recorded was 0.37 µg/l.

Rainfall Event on 15 November 1992

Between 2100 on 14 November 1992 and 0100 the next day 4 mm of rainfall was recorded causing sufficient rise in river level to trigger the samplers at both Longlands Drain and the Main Gauging Site. During the sampling run a further 1 mm of rain fell in the hour from 1000 on 15 November 1992. The sampler at the Longlands Drain Site triggered at 0050 on 15 November 1992 and a sample was taken every half an hour for the next twelve hours. The details of the event are given in Table A5. Appendix 9. The sampler at the Main Gauging Site was started at 0300 on 15 November 1992 and took a sample every hour for a period of 24 hours. Details of this event are given in Table A6. Appendix 9.

This small rainfall event produced only a small and ill-defined flow response at both Longlands Drain and the Main Gauging Site. The trifluralin concentrations recorded in the discharge from

Fig III 1.



Longlands Drain, Site 5

11 Nov. 1992

Longland Drain showed a similar response to the previous event only with lower concentrations (Fig. IH2). At the Main Gauging Site all the concentrations measured were at or below the detection limit.

Rainfall Event on 25 November 1992

In the 18 hours between 1200 on 25 November 1992 and 0600 the following day 17 mm of rainfall was recorded in the catchment. Neither of the samplers triggered automatically, however, the sampler on Longlands Drain was started manually at 1200 on 26 November 1992. A series of 24 samples were taken at half hourly intervals, details are given in Table A7. Appendix 9.

The response of the stream to the rainfall event can be seen clearly in figure IH3. It is also clear from this graph that the automatic sampling occurred only over the recession of the hydrograph. The concentrations were lower that in the two previous events and showed no clear relationship to rainfall or flow. The general decline in the trifluralin concentrations during the recession was interrupted by a peak of concentrations arising from six samples. No explanation can be given for these observations.

Rainfall Event on 18 December 1992

A rainfall event of 9 mm occurred between 0345 and 1045 on 16 December 1992 which caused sufficient increase in flow to trigger the autosampler at Longlands Drain Site. A series of 21 samples were taken at half hourly intervals and analysed for trifluralin and isoproturon. Isoproturon analysis was included because it had been applied to the catchment on 15 December 1992. The details of this rainfall event are given in Table A8. Appendix 9. The autosampler at the main site was not triggered.

The discharge from the Longlands Drain showed a small but significant response to the rainfall. Trifluralin concentrations also followed a clear pattern (Fig. IH4). The first value was below detection limits (0.08 µg/l) but rose quickly before the main flow of water arrived. During the main flow period the trifluralin concentrations fell but then rose again as the flow rate decreased. It could be suggested that there was a dilution of the trifluralin during the main

Fig IH2

Longlands Drain, Site 5

14 Nov. 92 - 15 Nov. 92

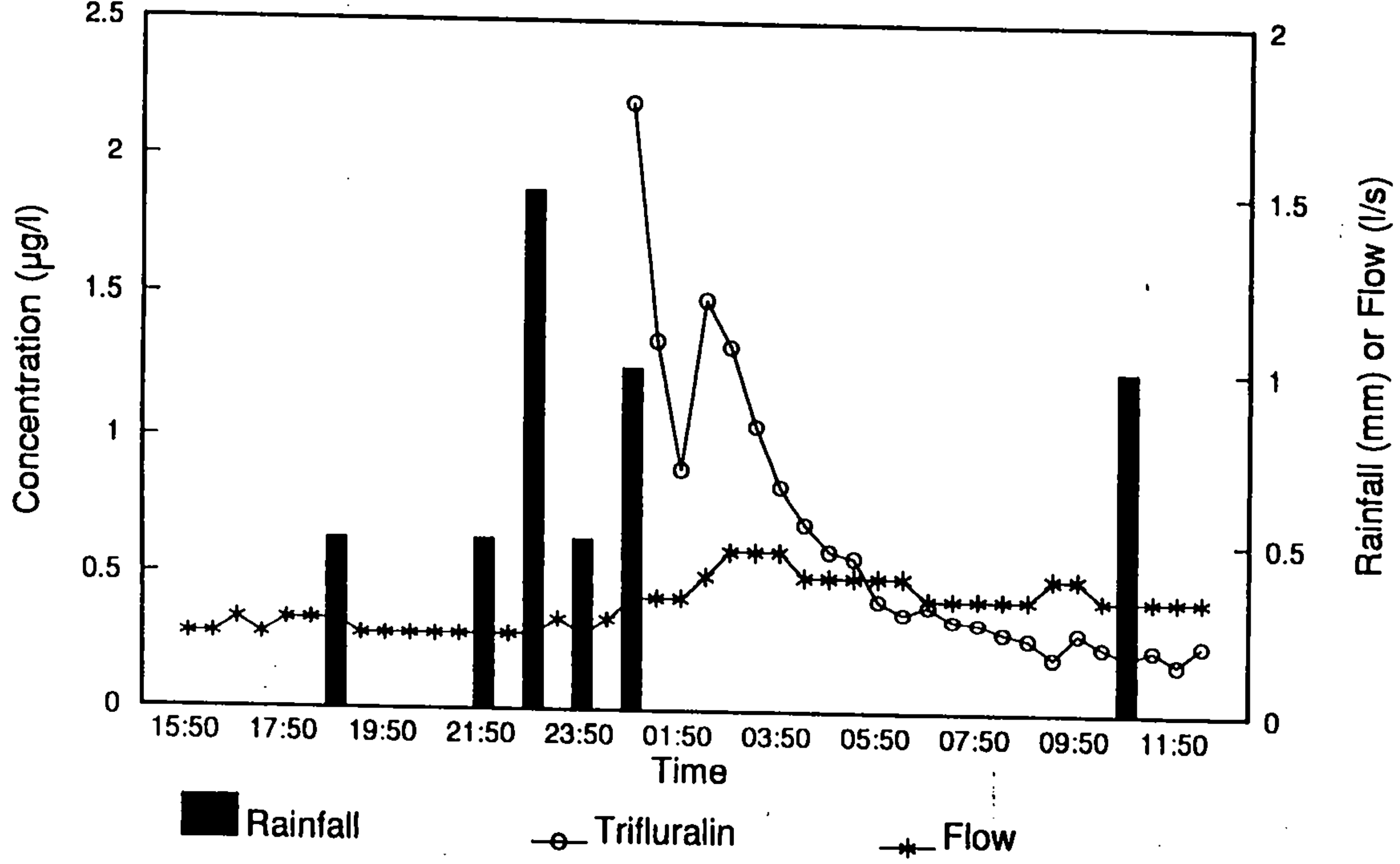


Fig 1H3

Longlands Drain

25 Nov. 92 - 26 Nov. 92

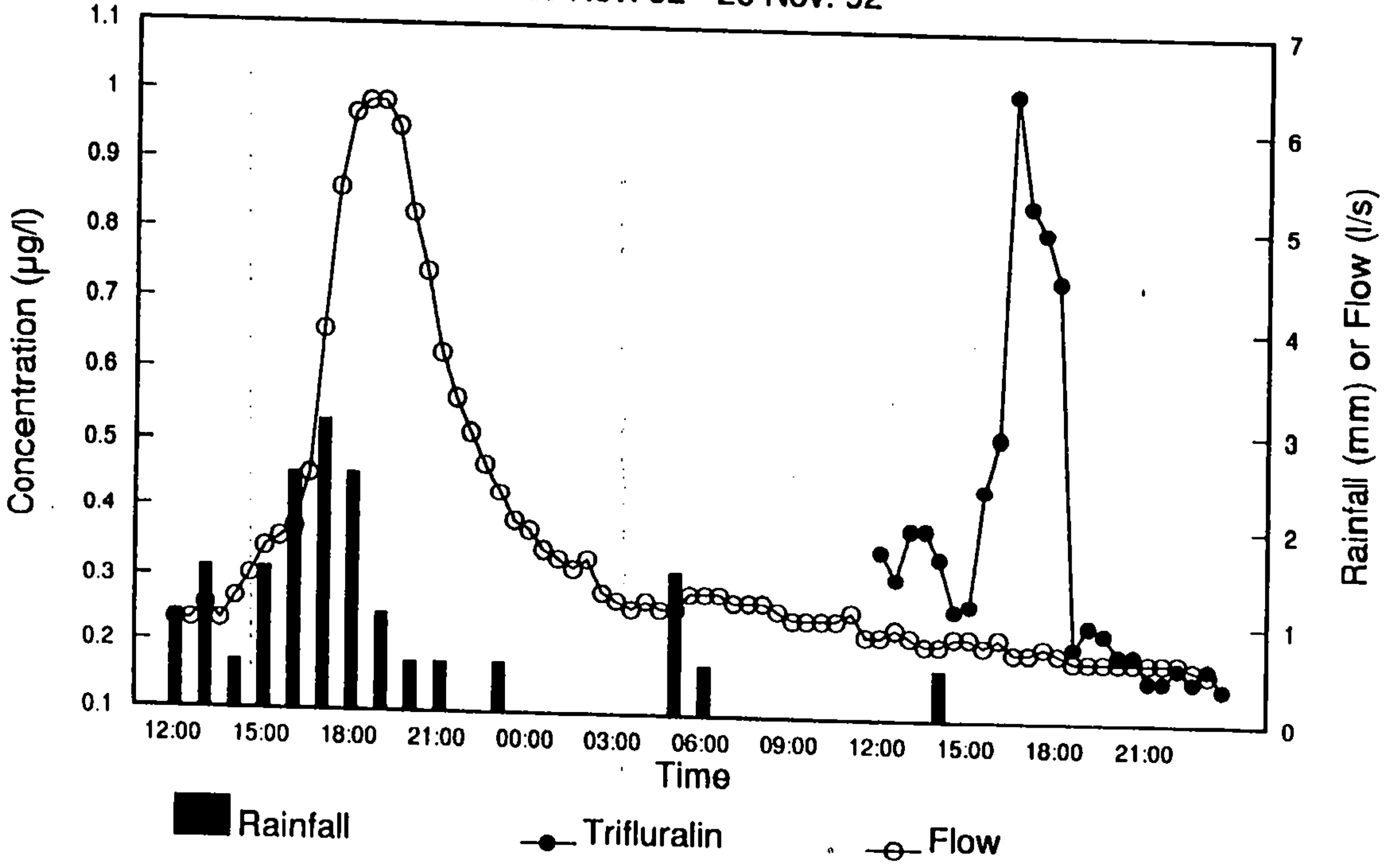
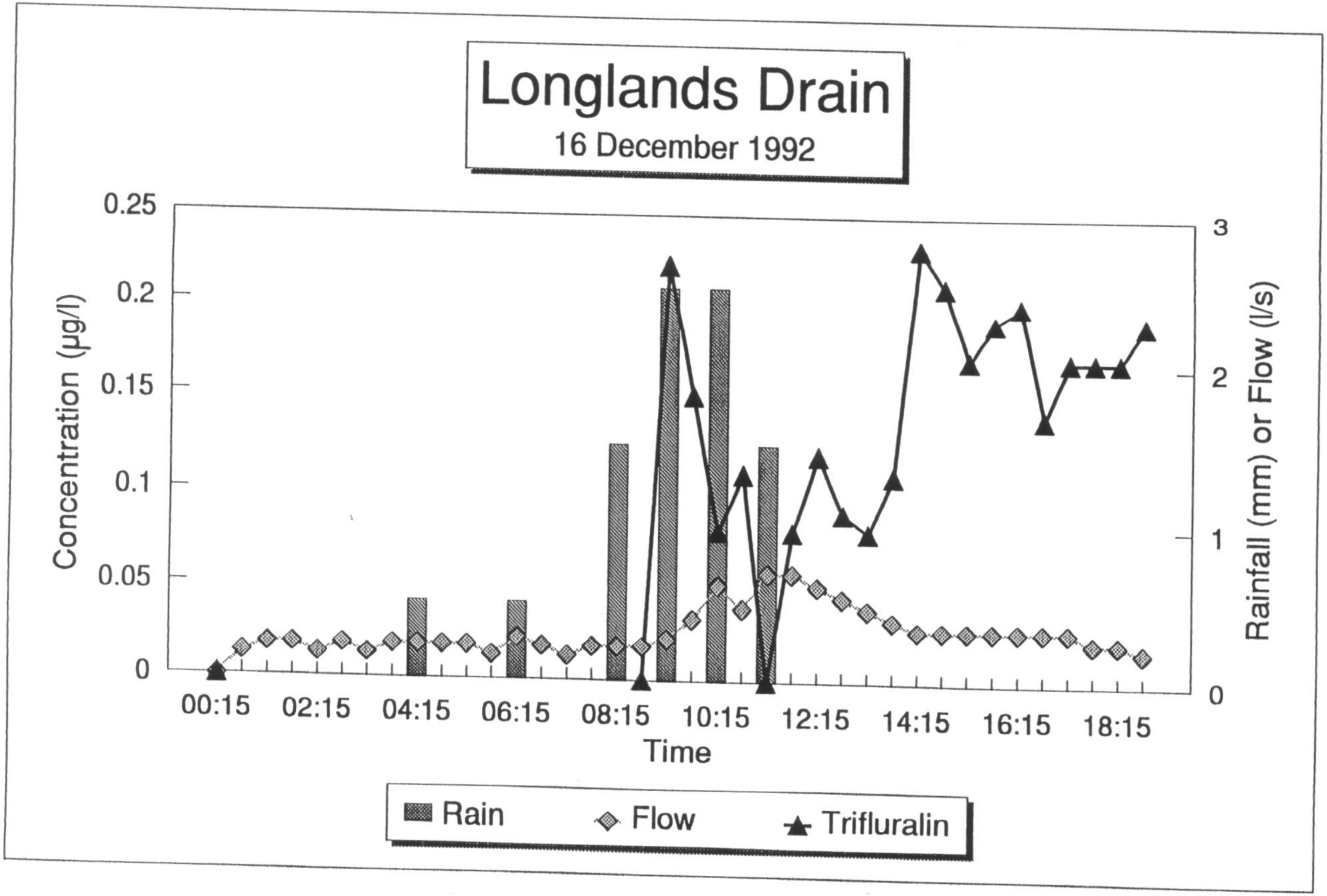


Fig 1H4


Longlands Drain
16 December 1992
Concentration (µg/l)
0
0.05
0.1
0.15
0.2
0.25
Rainfall (mm) or Flow (l/s)
0
1
2
3
00:15
02:15
04:15
06:15
08:15
10:15
12:15
14:15
16:15
18:15
Time
Rain
Flow
Trifluralin

flow event. However, the concentrations were fairly low (maximum 0.23 µg/l), and caution should be employed when interpreting such small changes on small values.

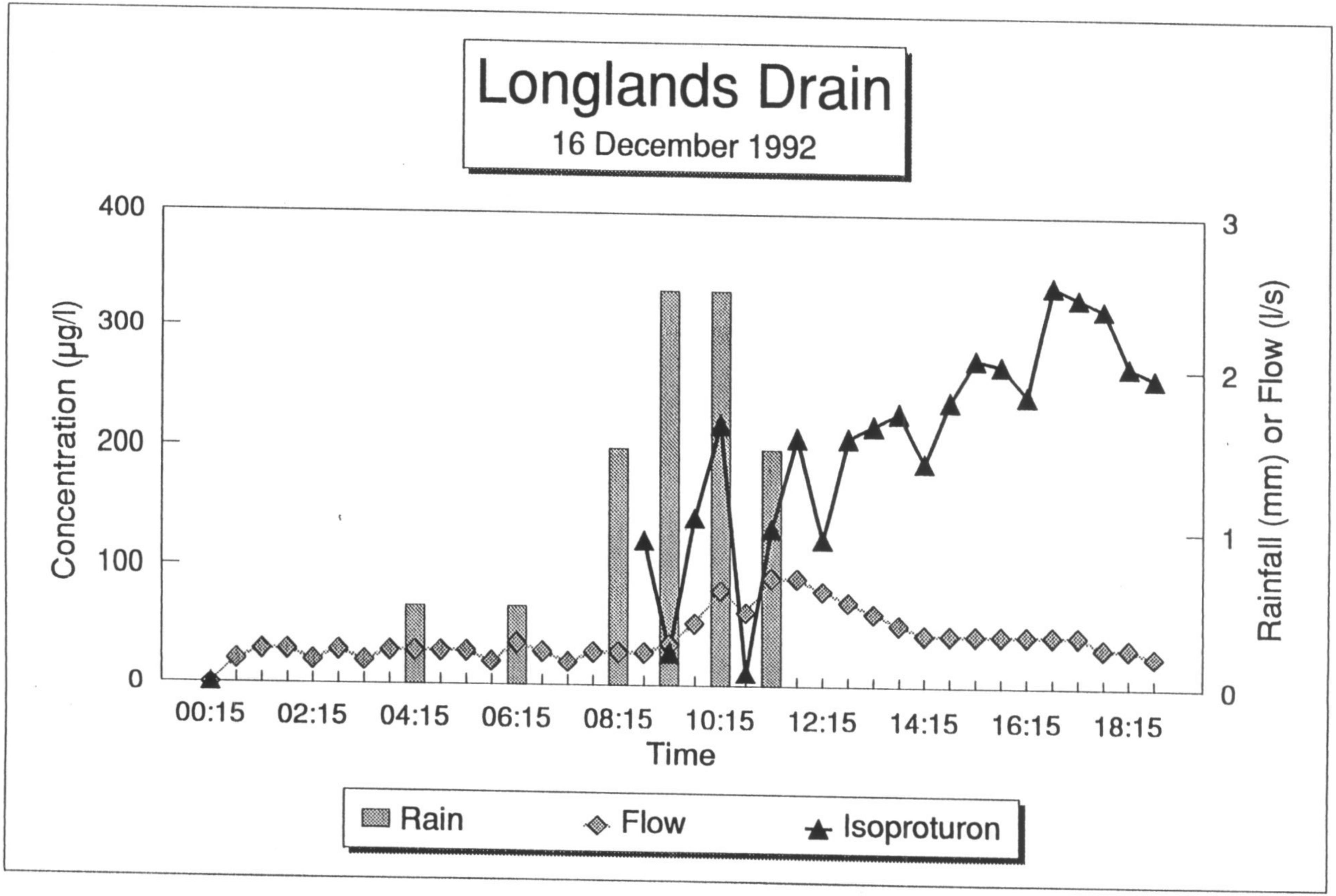
Isoproturon values, however, were very much higher than those for trifluralin and reflect the nearness of the rainfall event to its application. This event resulted in the highest concentration measured during the Rosemaund study (340 µg/l). The pattern of isoproturon concentrations during the event is shown in figure IH5. The pattern was different to those seen previously at Rosemaund. The values were at their lowest at the beginning of the event and then rose considerably during the event, to reach a maximum after the hydrograph had passed. The routine sampling data showed that high concentrations persisted through to early January 1993.

Particulate Pesticide Transport

Trifluralin has a relatively high potential to sorb to soils (K_{OC}), thus it is necessary to try to assess the significance of particulate transport for this herbicide. As was described previously, samples were taken from Longlands drain for three rainfall events following trifluralin application using the standard autosampler methods described in previous the Report of years 1 to 3. 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 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.

Table IH1 gives details of the concentrations and mass loads carried in the water samples taken from Longlands drain. Both the highest concentrations of trifluralin and of sediment were found in the first event of 11 Nov. 1992. However, the highest of the three pesticide values for this event was from the first sample in which the vast majority (92% by weight) of the pesticide 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. In only two events did the particulate load of pesticide exceed that in the water phase. The third event

Fig [illegible]


Longlands Drain
16 December 1992
Concentration (µg/l)
400
300
200
100
0
Rainfall (mm) or Flow (l/s)
3
2
1
0
00:15
02:15
04:15
06:15
08:15
10:15
12:15
14:15
16:15
18:15
Time
Rain
Flow
Isoproturon

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 the discussion of individual events above, the highly sorbed nature of this pesticide does not seem to alter the way in which it responds to rainfall as compared with the less sorbed pesticides studied previously. Since this highly sorbed chemical seems to have behaved in a similar manner as the less sorbed pesticides discussed earlier, then it maybe 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, sufficient resources were not available for a more extensive study of pesticides of this type.

Table IH1 Details of trifluralin concentrations and suspended sediment loads in three rainfall events collected from Longlands Drain, SO 5688 4849

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	0.00	0.37	0.36

Mobile Sediments

The concentrations of trifluralin in mobile surface sediments in the stream during rainfall events are given in Table IH2. 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. This limited data suggests that the fine particles are responsible for the bulk of the particulate pesticide transport and these are not deposited on the stream bed during or after events. It is of interest whether these concentrations in the sediment are of any environmental concern.

Table IH2 Trifluralin concentrations measured in the mobile bed sediments during rainfall events.

Date	Site	Concentration (μg/g)
24 Nov 92	Main Gauging Site	0.020
25 Nov 92	Upper Gauging Site	0.140
25 Nov 92	Upper Gauging Site	0.079
30 Nov 92	Upper Gauging Site	0.053
30 Nov 92	Upper Gauging Site	0.074

Overland Flow

Trifluralin concentrations were also measured in water samples collected by the overland flow traps following a number of rainfall events, these results are given in Table IH3. 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 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 rainfall have the maximum likelihood of producing high pesticide concentrations in overland flowing water.

Table IH3 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	0.15	0.43	1.74
27 Dec 92	0.99	0.91	2.0	0.61
20 Jan 93	0.80	1.55	-	-

5.5 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS - CHLORPYRIFOS/FENPROPIMORPH EXPERIMENT - SPRING 1993

5.5.1 Introduction

This was the final experiment conducted as part of the Rosemaund Pesticide Run-Off Study, and it continued the research started in 1992 on adsorptive pesticides. These are not expected to be so prone to leaching as, for example, the water-soluble herbicides.

The organophosphate insecticide chlorpyrifos has a reasonably high Koc value of 6100, with low water solubility (1.1 mg/l) and a long soil half-life (30-120 days). Chlorpyrifos is highly toxic to crustacea, so it was decided to monitor the toxicity of stream water using the *Gammarus pulex* in situ bioassay. The morpholine fungicide fenpropimorph is slightly less adsorptive than chlorpyrifos (Koc = 4400) and more water soluble (4.3 mg/l), and is moderately persistent in soil (DT50 = 15-93 days). It is much less toxic to crustacea than chlorpyrifos, so any effects seen with the *Gammarus* bioassay would only be attributable to the organophosphate.

The chlorpyrifos was applied as Dursban 4 (480 g/l EC) to the same 4.58 ha of Foxbridge and Longlands winter wheat that had received trifluralin and deltamethrin in late 1992. Chlorpyrifos was applied at a rate of 0.72 kg a.i./ha on 19 March 1993. Fenpropimorph was applied as Corbel (750 g/l EC) to the same area of Foxbridge and Longlands as the chlorpyrifos, on the same day, at a rate of 0.75 kg a.i./ha.

5.5.2 MAFF/BRE

5.5.2.1 Methods

Sample collection was conducted in the same manner as for trifluralin and deltamethrin earlier in the season. The soil sampling method was as trifluralin and deltamethrin, but samples were taken on two occasions. Samples were only analysed for chlorpyrifos.

Water analysis

The 1 l water samples were double-extracted with hexane in exactly the same manner as for trifluralin and deltamethrin described earlier, so the results given below are for 'total' residues, not just the dissolved fraction.

The analytical technique for chlorpyrifos was the same as that for trifluralin and deltamethrin; gas chromatography with electron capture detection. To enhance the separation of compounds, an adjusted chromatographic programme was employed. This did not interfere with the determination of trifluralin or deltamethrin, and as a result, reduced the analysis period. The conditions are given below:

Gas Chromatographic conditions used for the Analysis of Chlorpyrifos by GC-ECD

Initial oven temperature	50°C	hold for 0 minute
temperature ramp A	10° per min	
final temperature	300°C	hold for 15 minutes
Injector temperature	track oven temperature	
Detector Temperature	325°C	

The chlorpyrifos results have not been corrected for extraction efficiency, which was determined to be 87% +/- 12% (n=4) from replicate extractions and analyses of Rosemaund stream water spiked at 2 μg l^{-1}. Blank levels were below the detection limit of the technique.

Fenpropimorph was analysed by GC-MS operating in single ion mode. The instrument was a Hewlett Packard 5890 GC with a 5971A mass selective detector. The ion used for quantification was 128, determined by running the fenpropimorph calibration standard in full scan mode. The chromatographic conditions are listed below:

Gas Chromatographic Conditions used for the Analysis of Fenpropimorph by GC-MS

Initial oven temperature	55°C	hold for 1 minute
temperature ramp A	8°C min^{-1} to 200°C	hold for 2 minutes
temperature ramp B	25°C min^{-1} to 300°C	hold for 2 minutes
injector temperature	150°C	
MSD temperature	285°C	
Quantification ion	128	

Quantification was achieved by using an external standard supplied by Promochem Ltd, UK and the method was calibrated using the internal calibration software supplied by the Hewlett Packard chemstation system.

The fenpropimorph results have not been corrected for extraction efficiency, which was determined to be 82% +/- 9% (n=4) from replicate extractions and analyses of Rosemaund stream water spiked at 2 μg l^{-1}. Blank levels were below the detection limit.

Gammarus bioassays

These were conducted with the amphipod crustacean *Gammarus pulex* in exactly the same manner as during the carbofuran experiment described in the Report for years 3 to 5 (3rd project report). Animals were held in the stream at Site 1 in individual cages from 12 March (before chlorpyrifos was applied) to 21 April 1993, and mortality and feeding rate were recorded at weekly intervals.

Soil analysis

Chlorpyrifos

A sample of soil (40 g) was shaken for 2 hours with 100 ml of a 9:1 acetone-water mixture (v/v) and then centrifuged. An aliquot (50 ml ≡ 20 g soil) was filtered, collected and evaporated to the aqueous phase. After dilution with 20 ml water the aqueous phase was shaken with 25 ml dichloromethane. The lower organic layer was filtered through anhydrous sodium sulphate; a second extraction with 25 ml dichloromethane was carried out and the sodium sulphate was rinsed with a further 15 ml of dichloromethane. The three dichloromethane extracts were combined and evaporated to dryness. The residue was dissolved in 5 ml of 1:1 toluene-2,2,4-trimethylpentane for quantification by gas chromatography. Equipment and conditions used: Hewlett Packard 5890 GC fitted with flame photometric detector in phosphorus mode with HP 7673 autosampler; 2.5% Apiezon L on Gas Chrom Q (100-200 mesh) packed column; injector temperature 225 °C; column temperature 130 °C for 1 minute, then at 25 °C per minute to 200 °C, at 3 °C per minute to 210 °C, at 50 °C per minute to 270 °C, hold for 6 minutes; detector temperature 250 °C. The detection limit established was 0.003 ppm wet weight soil.

Soil moisture contents were determined as for trifluralin.

5.5.2.2 Results and Discussion

Water

Manual samples

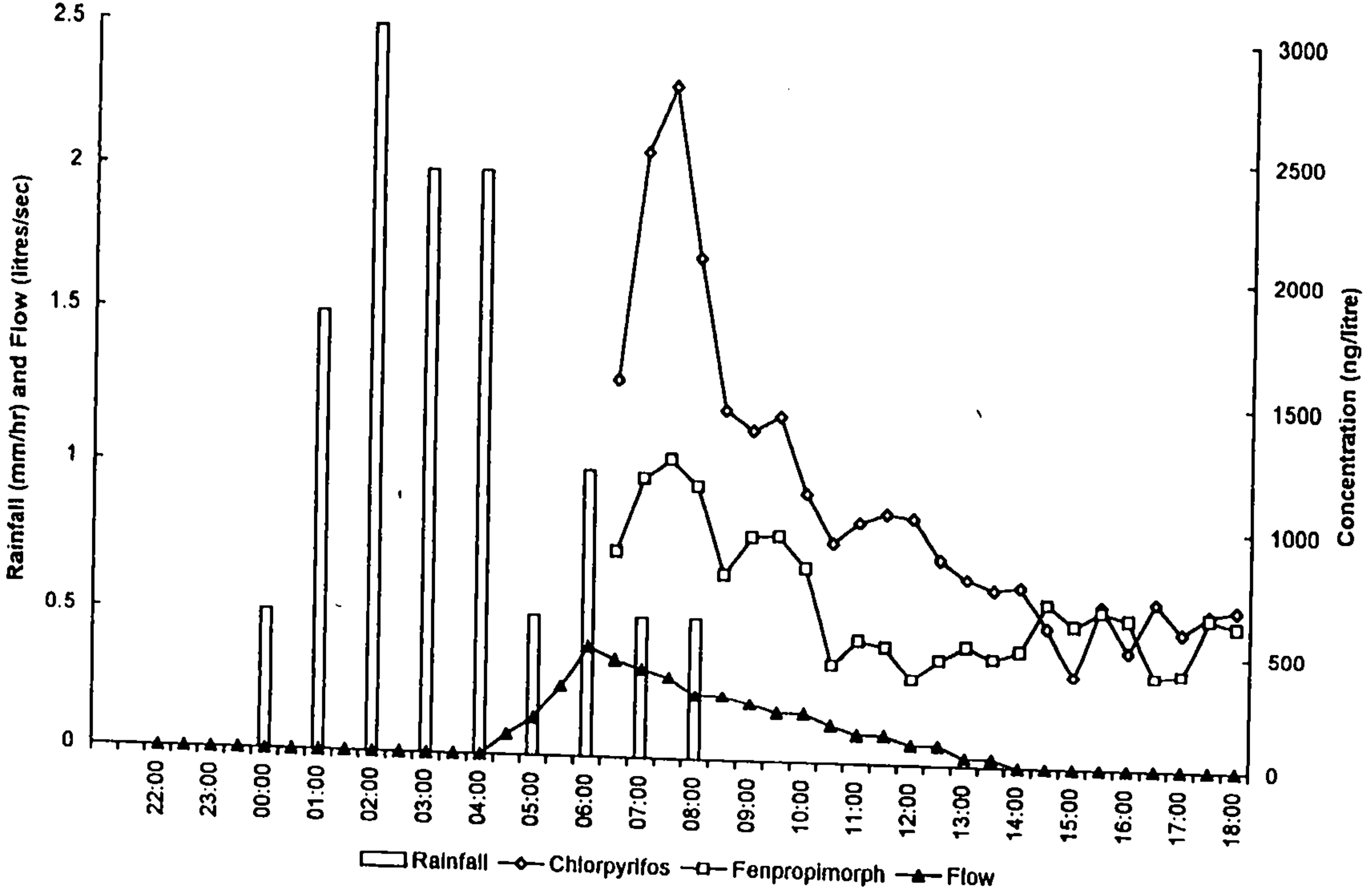
The relatively sparse available data are presented in Table W14 (Appendix 7). Both chlorpyrifos and fenpropimorph concentrations in drains and stream were effectively zero (0-2 ng/l) on 10/3/93 before spraying commenced. However, the samples taken on 8/4/93 and 13/4/93 cannot be considered genuine between-event samples because rainfall events of 11, 12 and 8.5 mm had occurred on 7/4/93, 9/4/93 and 11/4/93 respectively. Chlorpyrifos concentrations in the stream (Site 1), ditch (Site 2) and drains (Sites 3-5) were 60-115, 14-30 and 15-289 ng/l respectively. Equivalent values for fenpropimorph were 40-56, 18-55 and 22-169 ng/l.

Rainfall event on 7 April 1993 (Table W15, Appendix 7)

Between the spray date (19/3/93) and this event, a total of 31 mm of rain had fallen, but none of the individual bursts of rainfall (largest = 8.0 mm on 31/3/93) was big enough to trigger the autosamplers. The analytical data from this 11 mm event are shown in Figure W18. Both chlorpyrifos and fenpropimorph concentrations in the Site 3 field drain (there are no Site 1 stream data) peaked within 1 $^1/_2$ h of the peak hydrograph, at 2784 and 1250 ng/l respectively. Concentrations then tailed off rather slowly, reaching approximately 600 ng/l after 12 h in both cases.

Later, while extracting the samples with hexane in the laboratory, it was noticed that several of the extracts had an unusual smell of hydrocarbons, and it was speculated that this might be residues of tar oil which is used at Rosemaund on hops. However, subsequent analysis at Burnham-on-Crouch showed conclusively that the smell did not originate from tar oil, but probably from weathered kerosene. The main components of kerosene are various napthalenes, and although full quantification was not conducted , it was established that napthalene concentrations were not above the low µg/l range and were thus not acutely toxic

Fig. W18 Rosemaund Site 3: Chlorpyrifos/Fenpropimorph Experiment 7 4 93.



to aquatic life. It is possible that the kerosene originated from the wood between Foxbridge & Longlands and Slade Hopyard where contractors were at that time felling trees and using kerosene-powered equipment.

Rainfall event on 9 April 1993 (Table W16, Appendix 7)

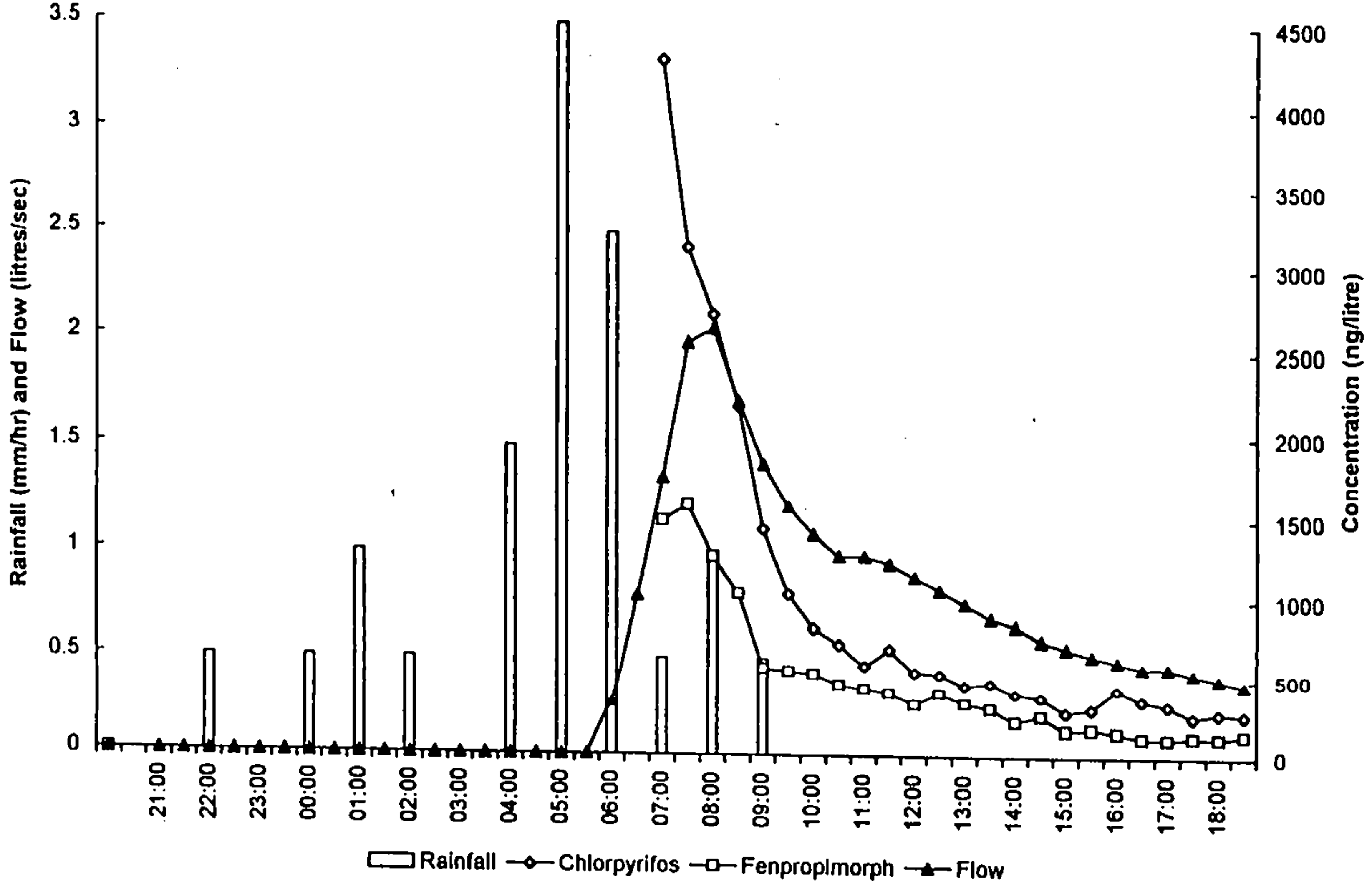
The analytical data from this 12 mm event are presented graphically in Figure W21. Peak chlorpyrifos and fenpropimorph concentrations (4287 and 1578 ng/l respectively) in the Site 3 drain were coincident with the peak of the hydrograph, and thereafter tailed off fairly rapidly, both reaching approximately 200 ng/l after 12 h.

Gammarus pulex feeding bioassay

This was deployed at Site 1, ~100 metres downstream from the Site 3 drain whose discharge was being monitored for chlorpyrifos and fenpropimorph. Between 12 March and 7 April (when the Site 3 sampler triggered at 06.30) the background mortalities of *Gammarus* ranged between 0-6%. Between the period 7th to the 14th of April there was 36% mortality. However, a further 47% animals were scored as moribund. In most cases these animals were returned to the laboratory for use in an acetyl choline esterase assay. The few moribund animals left at site probably died shortly after because in each case in the following period they were found to have died and were considerably decomposed. During the period 14th-21st April there were 27 remaining animals, 16 of which were only introduced on the 14th of April. Out of the new animals introduced 3 of 13 (23%) died in the subsequent period. Of the original animals (those in the field since the 12th of March) 7 out of 11 (69%) died during the subsequent period with 4 of these being scored as moribund at the start of this period. To summarise the mortality data, it would appear that if we count moribund animals as dead, 83% mortality occurred during the period 7th-14th of April co-incident with the two rainfall events. Feeding rate was extremely low (practically non-existent) indicating that even surviving animals were affected.

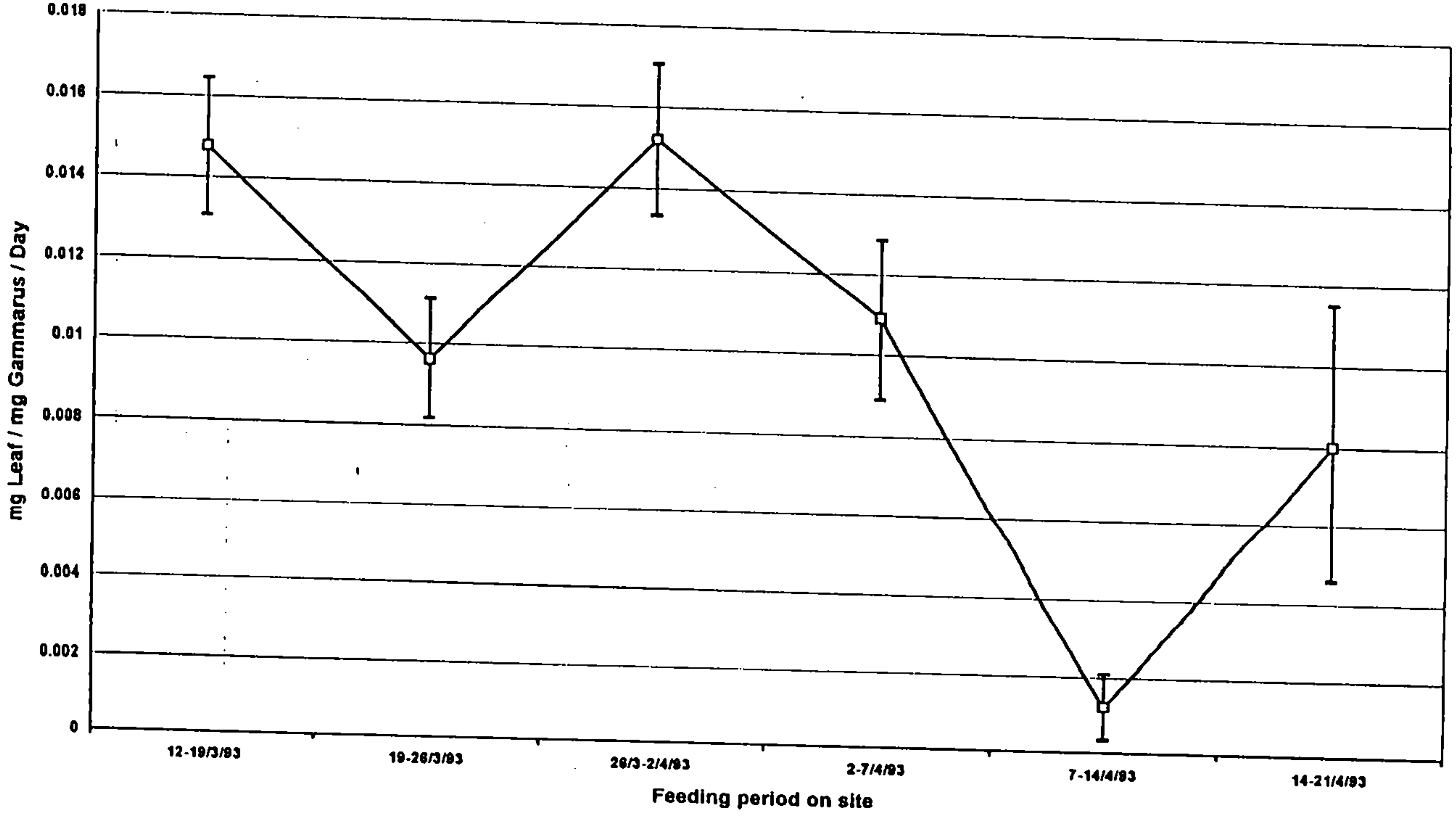
With reference to Figure W22 it can be seen that feeding rate dropped to a very low level during the period covering the runoff events. This value has resulted from the large mortality

Fig. W21 Rosemaund Site 3: Chlorpyrifos/Fenpropimorph Experiment 9 4 93.



TABLEW16.XLS

Fig. W22 GAMMARUS FEEDING DATA ROSEMAUND (SPRING 1993) (sediment covered leaves not included)



of organisms which occurred at this time. However, Figure W23 shows a re-evaluation of these data in which the feeding rate of surviving organisms is separated from that of those animals which died or were badly affected by the runoff events. Despite the small number of surviving animals it can be seen that their feeding rate is depressed if the actual amount of leaf material consumed is compared to the values recorded in Figure W22. The lower feeding rate values which occurred in the second week of the study (19-26/3/93) are probably due to the low temperatures (less than 8°C over five of the seven days) which occurred during this period. The decline in feeding rate in week 4 (2-7/4/93) cannot be explained in terms of low water temperature and it would appear likely that the rainfall occurring in the period from the 4-7th of April resulted in runoff of chlorpyrifos before increase in stream height resulted in the autosampler triggering.

There seems little doubt that chlorpyrifos was responsible for the observed effects. Fenpropimorph is considerably less toxic to crustacea (eg 48h EC50 to *Daphnia pulex* = 2.4 mg/l) than the organophosphate chlorpyrifos which acts by blocking the essential synapse enzyme, acetyl choline esterase. Published toxicity data on several *Gammarus* species show that the 24h LC50s for this group lie between 760 and 5600 ng/l. Unfortunately, chemical monitoring data are not available from Site 1 for the period in question, but past experience shows that residues at this stream site are diluted by a factor of 5-10 with respect to the Site 3 drain. This suggests that the peak chlorpyrifos concentrations at Site 1 in the 7/4/93 and 9/4/93 events may have been in the range 278-557 and 429-857 ng/l respectively. This is probably sufficient to explain the incidence of *Gammarus* mortality (36%), moribundity (47%), and low feeding rate which was observed between 7 and 14 April 1993.

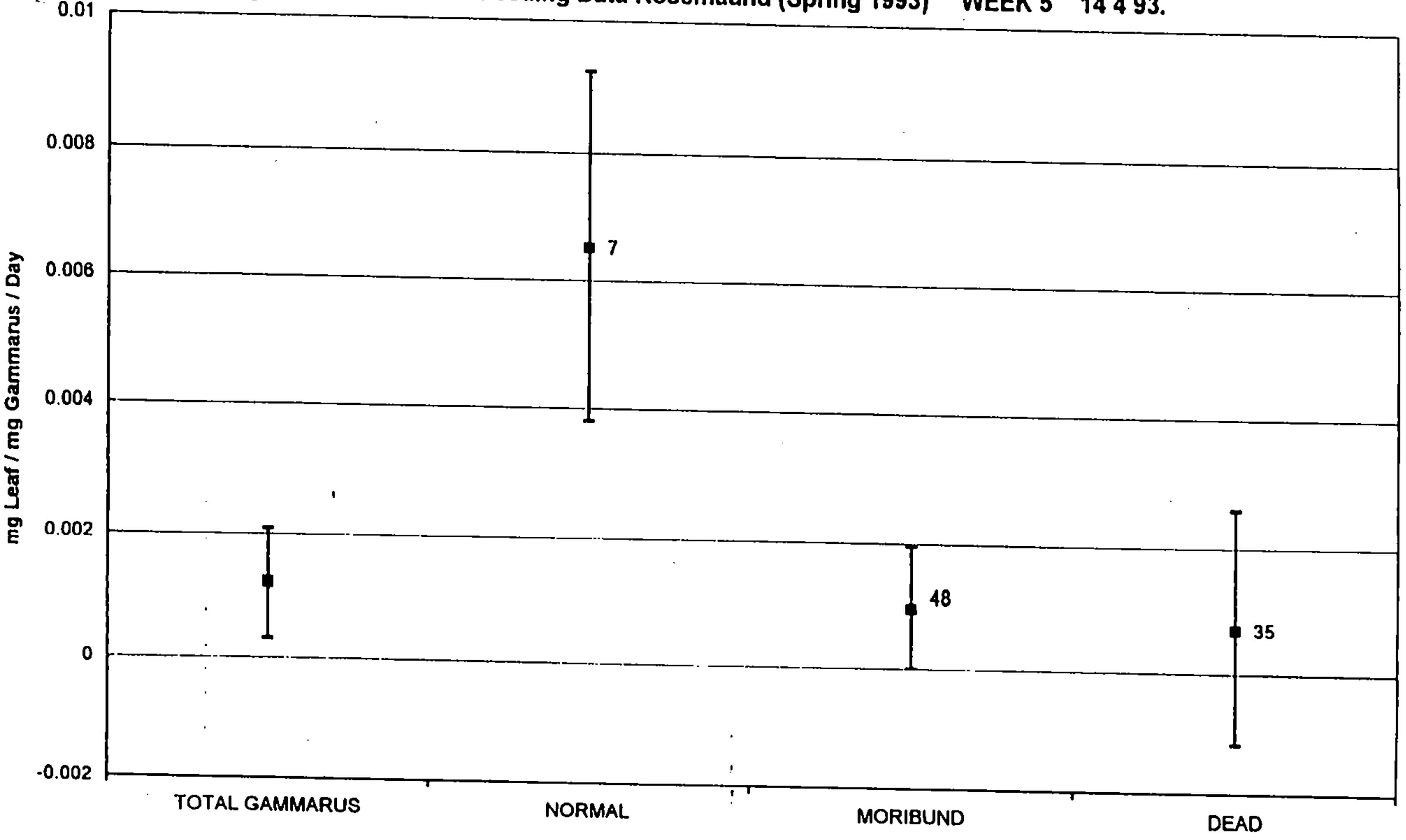
Soil

Chlorpyrifos

Background samples were taken on 3 March and were less than the detection limit of 0.003 ppm.

The concentrations measured in individual samples and the derived average concentrations over 1 metre are given in Tables B7 and B8 in Appendix 8. Although samples were taken on only two visits the results can give an indication of the persistence of chlorpyrifos in the Rosemaund soils.

Fig. W23 Gammarus Feeding Data Rosemaund (Spring 1993) WEEK 5 14 4 93.



From the average concentrations the rate constant is 3.6×10^{-4} hour^{-1}, corresponding to a half life of 80 days. On both visits the highest levels were measured in the Compton series.

5.5.2.3 Conclusions

Although the available data for chlorpyrifos and fenpropimorph only concern the Site 3 field drain, it is clear that these two pesticides are able to translocate in a similar way to trifluralin and deltamethrin. In other words, the data confirm that high adsorptivity and low solubility are not a barrier to the transfer of pesticides into headwater streams via field drains providing that by-pass flow is a dominant factor in the hydrological regime.

The bioassays show that the translocated deltamethrin is so strongly bound to particulates that it is not able to exert noticeable toxic effects on sediment-dwelling *Chironomus* larvae. On the other hand, chlorpyrifos is less strongly bound to soil particles than deltamethrin, and it was probably responsible for the lethal and sub-lethal effects observed in the *Gammarus* bioassays. This is the second observation of biological effects resulting from pesticide runoff at Rosemaund, the first having been made during the carbofuran experiments in 1992. It again calls into question the pesticide risk assessment system which hitherto, due to lack of suitable models, has been unable to predict the environmental concentrations which may appear in streams as a result of leaching and by-pass flow. It is hoped that the advent of validated models such as SoilFug (DiGuardo *et al.*, 1994b) will help to avoid biologically significant pesticide runoff in the future.

5.5.3 IH/NRA - Spring 1993

5.5.3.1 Methods

During the spring experiment only drain and stream samples were collected. Analysis was carried out for chlorpyrifos, fenpropimorph and, for one event, isoproturon, at the Institute of Hydrology.

Extraction for chlorpyrifos was by the same method employed for trifluralin. The extract was analysed by GC using a PTE-5 QTM column. The column temperature, initially at 65°C, was ramped to 177°C at 4°C/min and then 200°C at 15°C/min, where it was held for 2 minutes. The carrier gas was helium at a rate of 23 ml/min at 60°C and detection was by ECD. External standards gave a detection limit of 0.05 µg/l.

5.5.3.2 Results and Discussion

Event of 7 April 1993

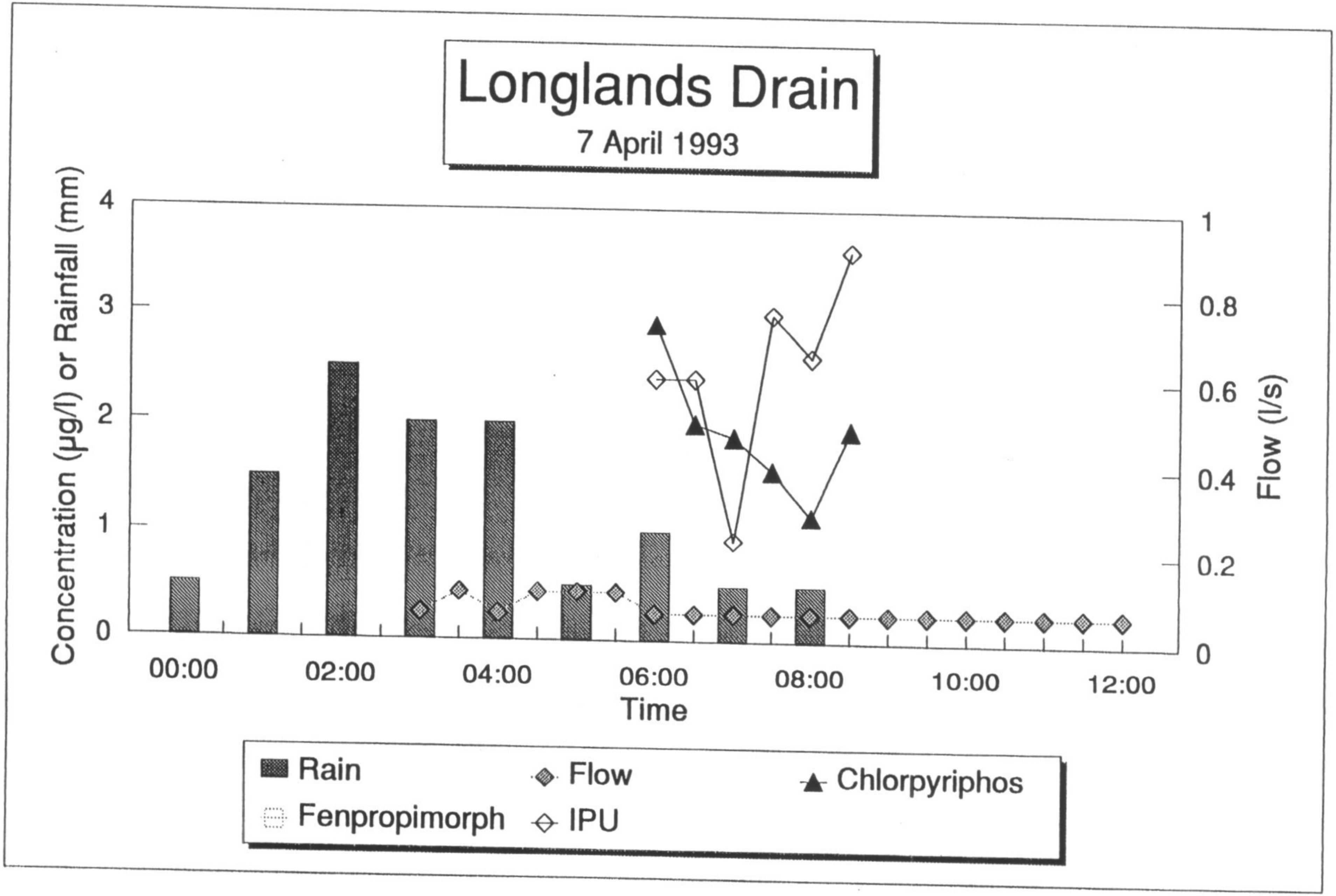
A rainfall event of 11 mm occurred between midnight and 0800 on 7 April 1993 causing a rise in flow rate from Longlands Drain sufficient to trigger the sampler at 0600 on the same day. Due to a sampler malfunction only the first 6 samples were collected, covering a period of 3 hours. The details of this event are given in Table A9. Appendix 9. The sampler at the main gauging site was not triggered.

The rainfall event produced only a very small increase in recorded drain flow. Concentrations of both isoproturon and chlorpyrifos were similar, the maximum values were 3.0 µg/l and 2.9 µg/l respectively. Figure IH6 shows the pattern of rainfall and the resulting stream response in terms of both flow and measured pesticide concentrations. From the few samples available, the chlorpyrifos concentration showed a different pattern to those for isoproturon. Chlorpyrifos concentrations decline through the event while isoproturon concentrations increased. However, there are probably too few samples to draw any inferences from this behaviour.

Event of 9 April 1993

Between midnight and 0900 on 9 April 1993, 10.5 mm of rain fell on the catchment causing the autosampler at the Main Gauging Site to trigger at 0600 the same day. A series of 24 samples were taken at hourly intervals. The details of this event are given in Table A10. Appendix 9. The sampler at Longlands Drain was not triggered.

Fig 1.16


Longlands Drain
7 April 1993
Concentration (µg/l) or Rainfall (mm)
0
1
2
3
4
Flow (l/s)
0
0.2
0.4
0.6
0.8
1
00:00
02:00
04:00
06:00
08:00
10:00
12:00
Time
Rain
Fenpropimorph
Flow
IPU
Chlorpyriphos

The rainfall resulted in a significant stream flow, however, all the samples analysed shows concentrations below the detection limit (0.05 µg/l). Since no pesticide was found in the first 12 samples, in order to reduce analysis costs the analysis was halted at this point.

Event of 26 April 1993

A small, but fairly intense, rainfall event of 4.5 mm in the two hours from 1600 on 26 April 1993, caused the autosampler at the Main Gauging Site to trigger at 1800 on the same day. A series of 24 samples were taken at one hour intervals. The details of the event are given in Table A11. Appendix 9. Only the first 12 samples were analysed for the same reasons as given in the previous event. The sampler at Longlands Drain was not triggered

The rainfall event produced only a small response in stream flow and as in the previous event the concentration of chlorpyrifos were below the detection limit.

6 MODELLING

6.1 Purpose of modelling

The overall aims of the Rosemaund project have been described in Section 3. The particular 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; however there are differences in what types of prediction are needed and why. For the NRA/IoH the objective was to produce and validate a simple model to estimate pesticide runoff 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/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 put on quantitative estimates from such models.

6.2 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.

6.2.1 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 chemical 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.

6.2.3 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 6.1 shows the structure of the 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.

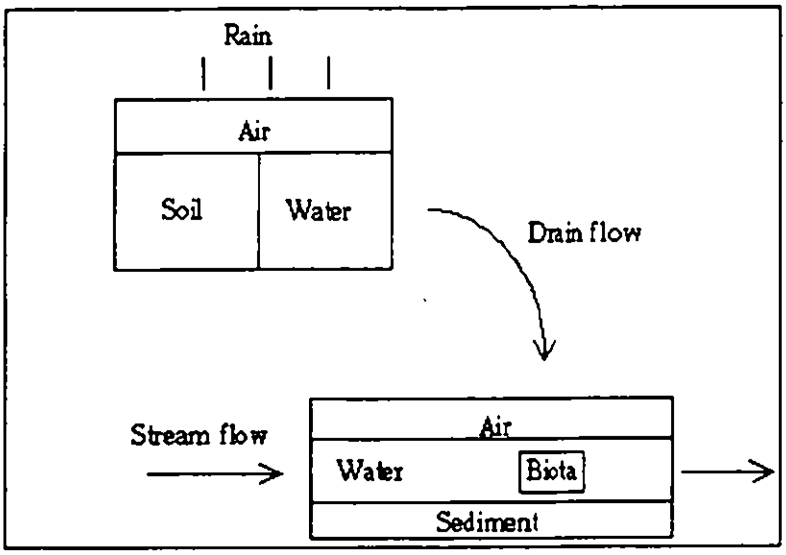


Figure 6.1. Structure of BRE model

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.

6.2.3 Soil Fug

This model was developed by Antonio di Guardo and co-workers at the University of Milan (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; runoff 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 though 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 runoff. The volume of runoff 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 removed by runoff leads to a concentration in the drainage water and hence to a concentration in the stream which is an average for the rainfall period.

6.2.4 IoH 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 Rosemaund Farm 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 6.2. 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 6.2, 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 absorbed pesticide in each box and calculates changes to these depending on a mass balance of inputs, outputs and internal sources and sinks.

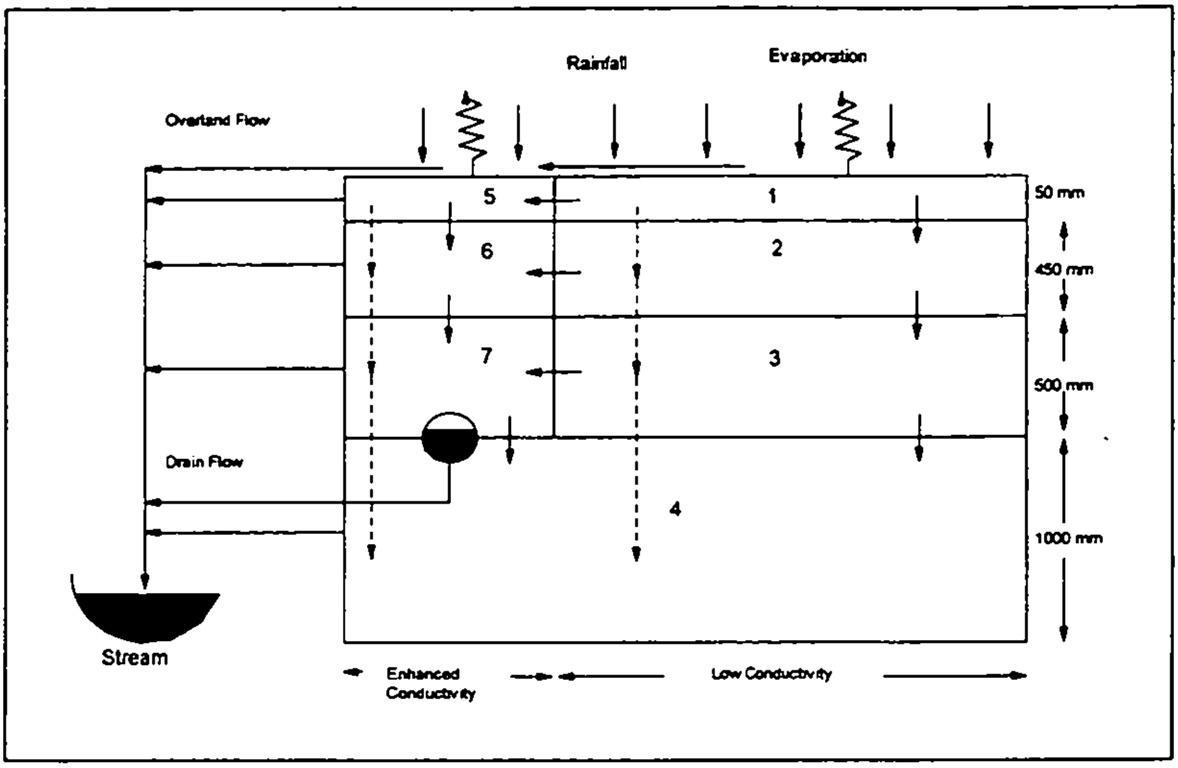


Figure 6.2 **Structure of IoH model showing division into compartments and water pathways.**

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 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, Fig 6.2) 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.

6.3 Results of model applications

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

6.3.1 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* (1991). 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 mg/l compared to model levels of 4.4 to 4.7 mg/l; for lindane the measured levels were 0.02 to 0.45 mg/l and the calculated levels were around 0.4 mg/l.

Levels predicted in the stream model were much closer to those measured than in the previous exercise for three of the four applications. Example plots showing the output from the model and the measured concentrations in the stream are shown in Figures 6.3-6.5. 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.

Figure 6.3 Isoproturon levels in stream

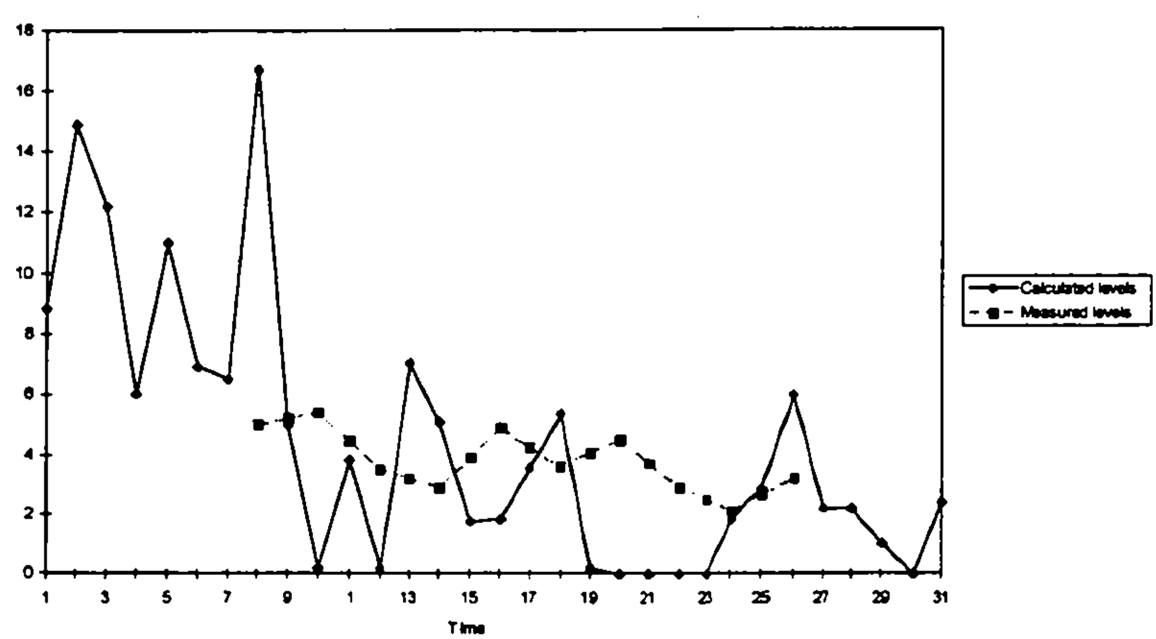


Figure 6.4 Lindane levels in stream

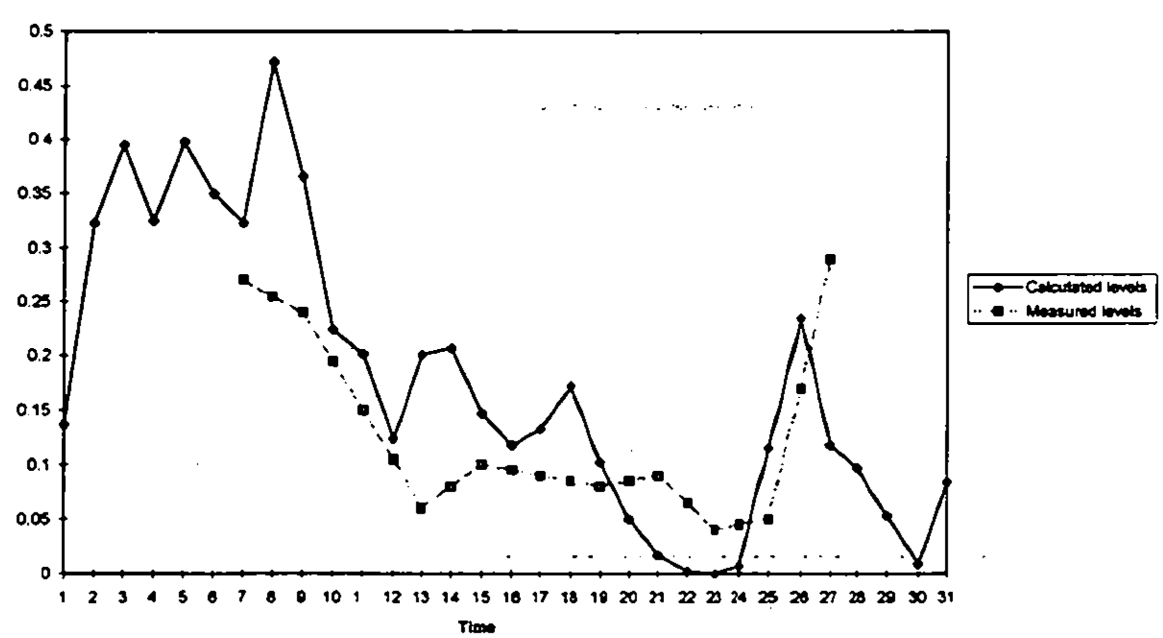
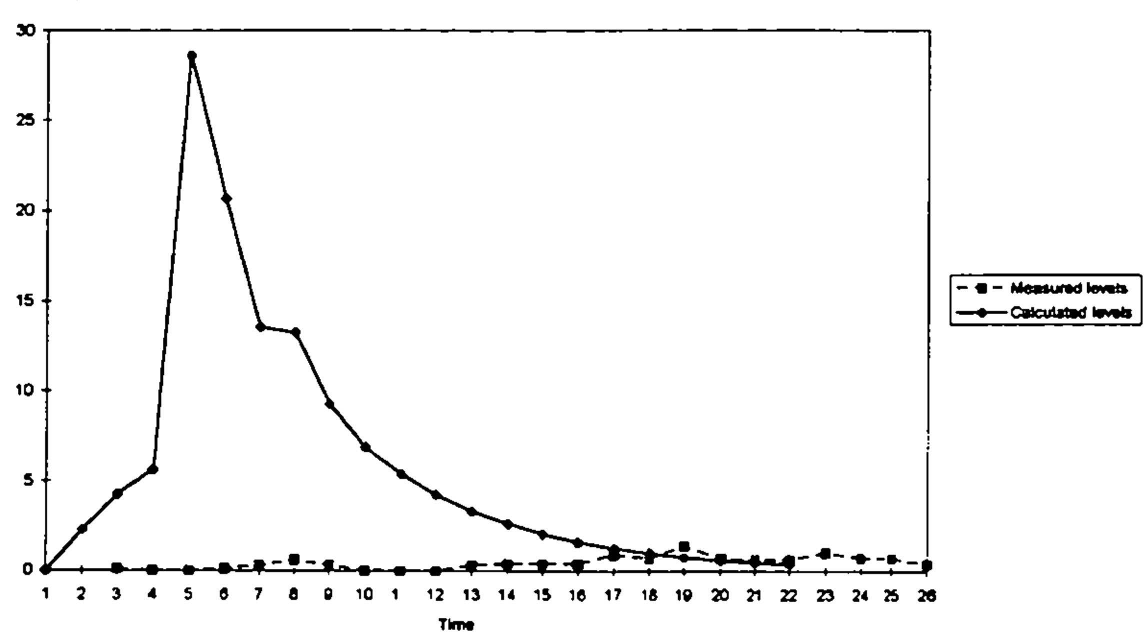


Figure 6.5 Mecoprop levels in stream



6.3.2 SoilFug model (Di Guardo *et al*, 1994b, reproduced in Appendix X)

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 64 predicted concentrations with corresponding measured levels. For comparison purposes 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 6.1 and 6.2.

For the 59 rainfall events monitored following the application of neutral or undissociated pesticides, 45 (76%) of the predicted average concentrations came within a factor of 10 of the measured average levels. Of the remaining 14 cases only 3 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.

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 pHs and hence would be expected to move more easily into water than the neutral compounds. A K_{oc} 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

Table 6.1 Results from SoilFug for neutral or undissociated pesticides

Chemical	Year	Site	Meas conc (µg/l)		Meas conc average (µg/l)	Model conc (µg/l)
			min	max		
Atrazine	91/92	0	0.06	1.79	0.6	6.09
			0.47	1.76	0.9	3.88
		1	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
		3	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
		5	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	1	0.07	26.78	10.4	7.99
			0.04	37.45	6.2	7.11
			0.01	2.35	0.46	2.31
			<0.01	0.02	0.006	1.29
		3	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
Dimethoate	90/91	0		<0.02	<0.02	0.42
				<0.02	<0.02	0.143
				<0.02	<0.02	0.103
		1	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

Table 6.1 (cont)

Chemical	Year	Site	Meas conc (µg/l)		Meas conc average	Model conc
			min	max	(µg/l)	(µg/l)
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	1.92	17.2	10.6	9.46
			0.1	2.62	0.96	5.76
			0.26	2.07	0.92	1.17
		5	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
		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	5	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 6.2 Results from SoilFug for phenoxy acid herbicides

Chemical	Year	Site	Meas conc (μg/l)		Meas conc average	Model conc
			min	max	(μg/l)	(μg/l)
Dichlorprop	89/90	1	<0.2	1	0.35	6.93
MCPA	90/91	1	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 6.1 and 6.2

Meas conc: measured maximum and minimum concentrations for the rain event
Meas conc average: flow weighted mean concentration during the rain event
Model conc: calculated mean concentration during the rain event
Sites: 0 = main stream; 1 = stream at top of catchment; 3,5 = drains

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.

6.3.3 IoH 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.

The properties of the various boxes in the model, eg 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 6.3 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 runoff patterns that have been observed. In Figure 6.6 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 6.7, 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 6.8, 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 6.9).

Table 6.3 Summary of the results of the simulation of pesticide concentrations at ADAS Rosemaund during a number of rainfall events.

Pesticide	Date of Event	Site No.	Obs. Mean[1] (µg/l)	Predicted Mean[1] (µg/l)	Error[4]	Obs. Max. (µg/l)	Predicted Max. (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	[2]0.85	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	[2]0.16	0.17	0.02	0.40	0.50	0.10	-[3]
	16/12/89	5	[2]0.57	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	[2]0.5	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	1	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.

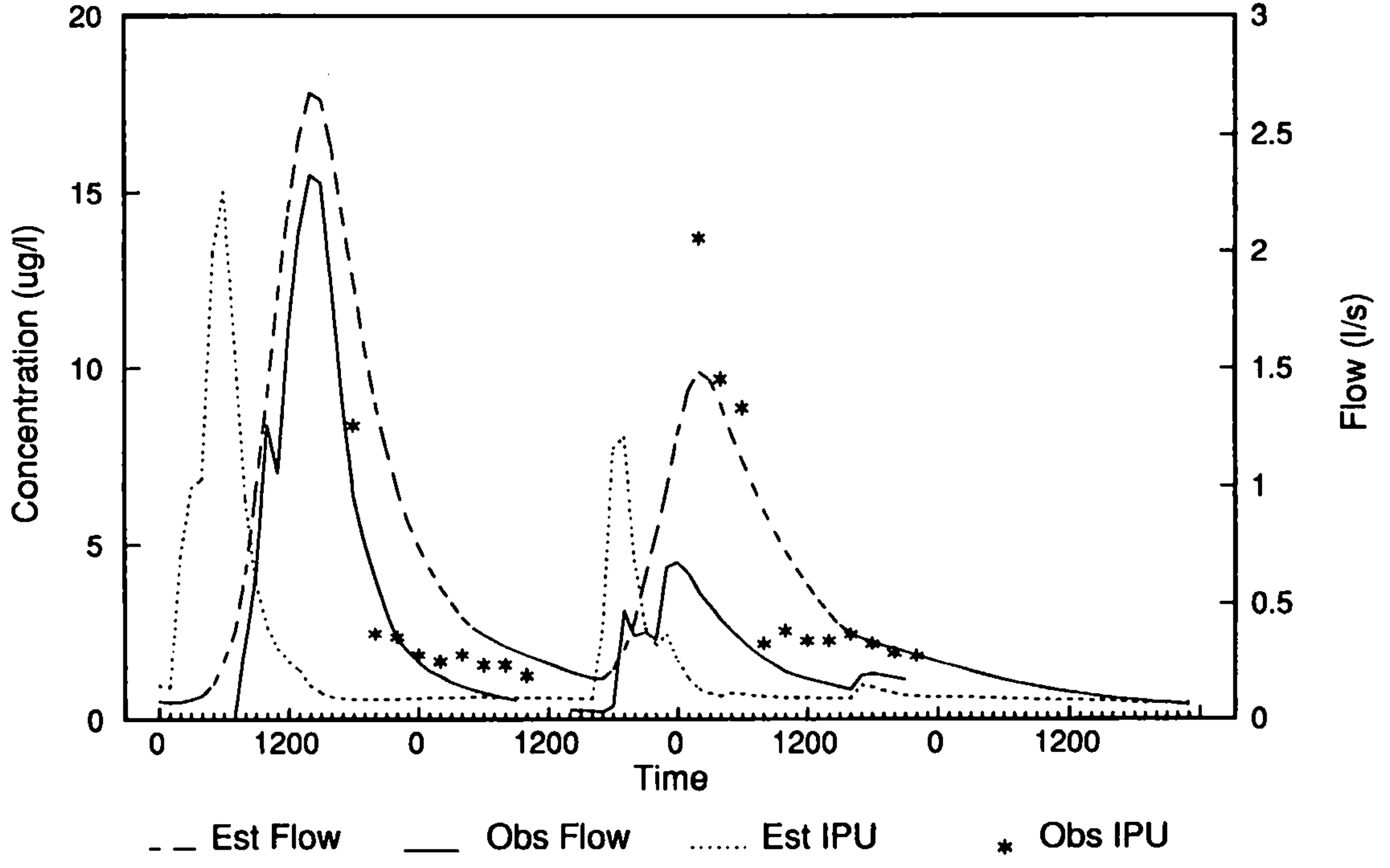
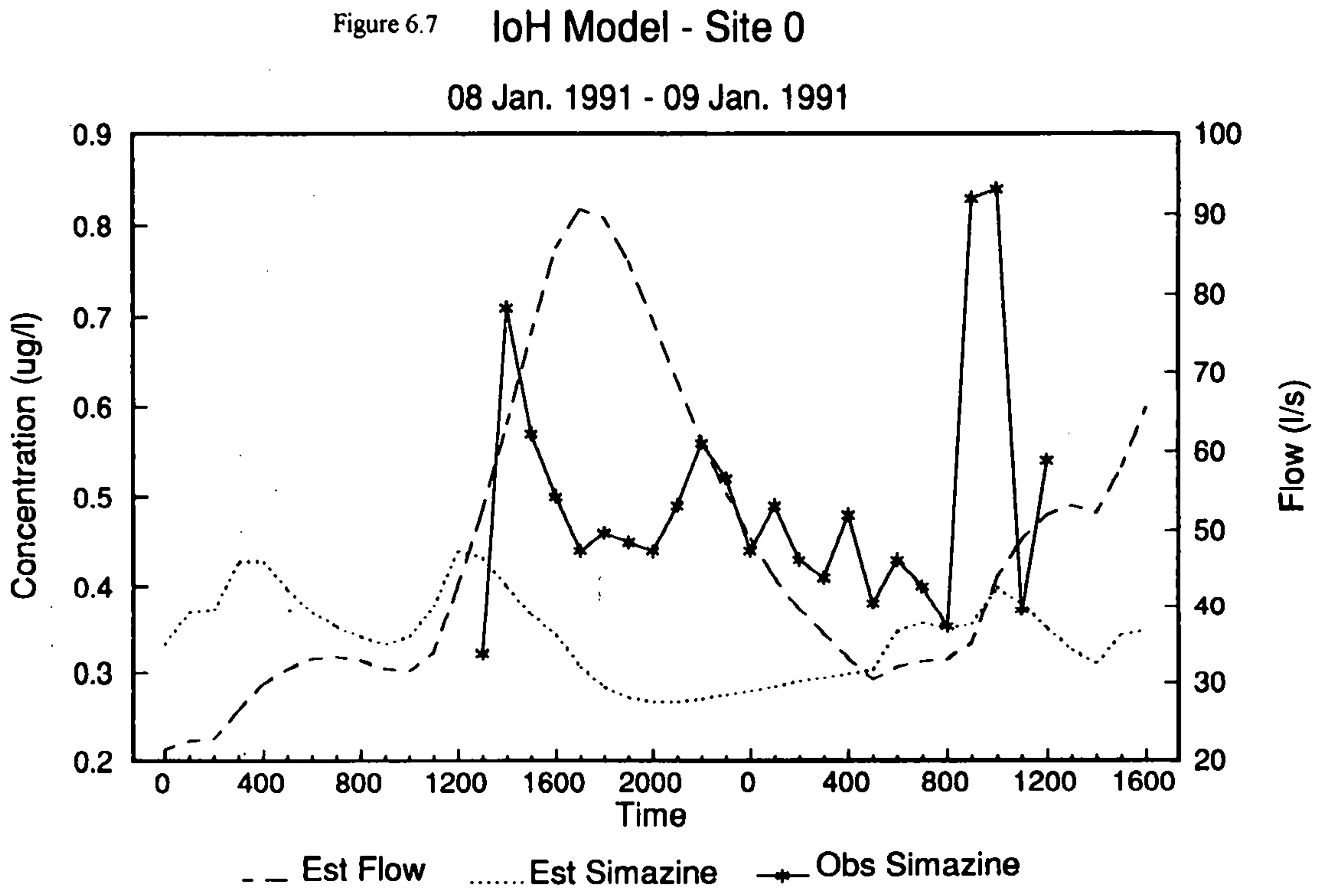


Figure 6.6 IoH Model - Site 3

08 Nov. 1989 - 11 Nov. 1989

Figure 6.7


IoH Model - Site 0
08 Jan. 1991 - 09 Jan. 1991
Concentration (ug/l)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
Flow (l/s)
100
90
80
70
60
50
40
30
20
0
400
800
1200
1600
2000
0
400
800
1200
1600
Time
Est Flow
Est Simazine
Obs Simazine

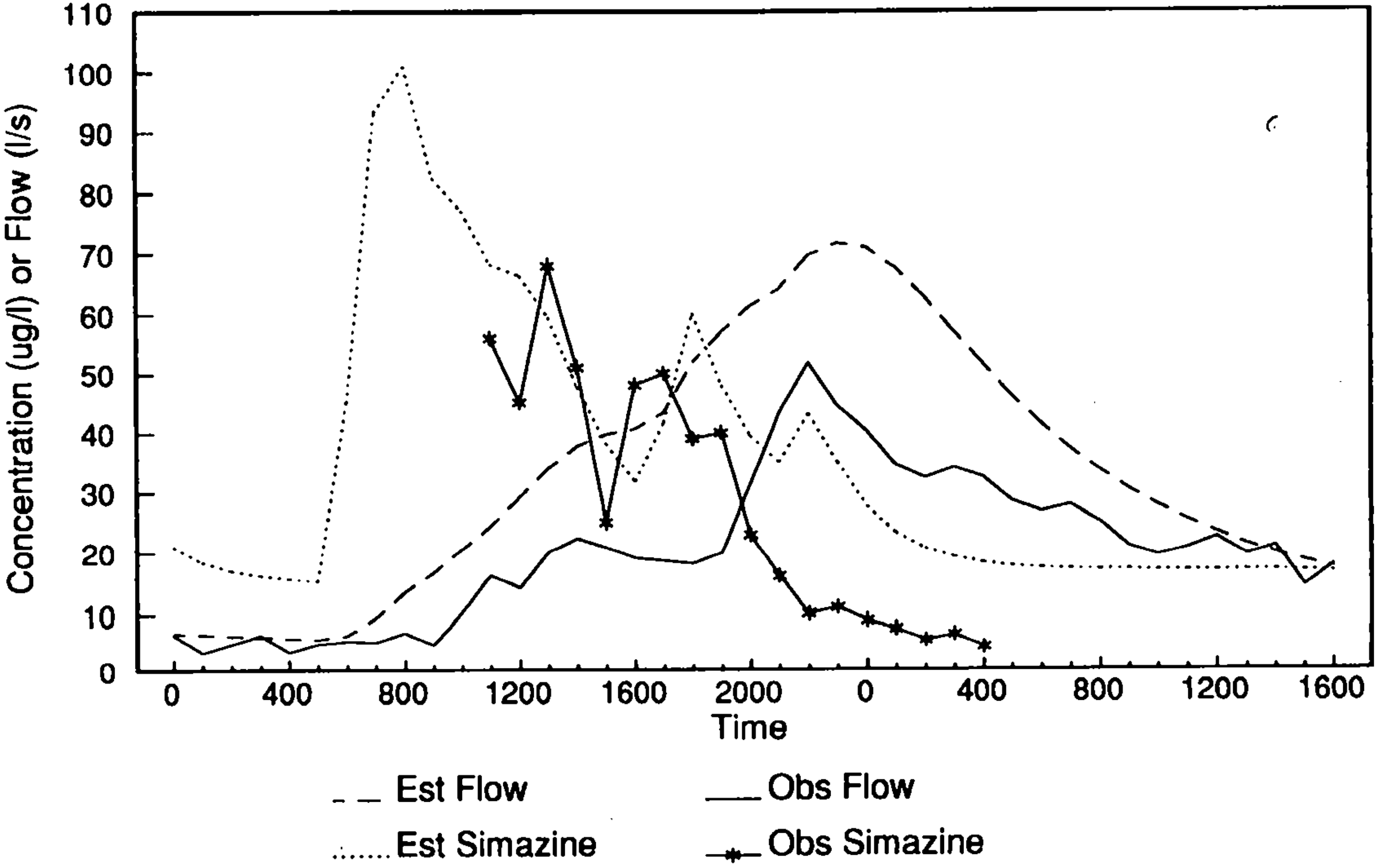
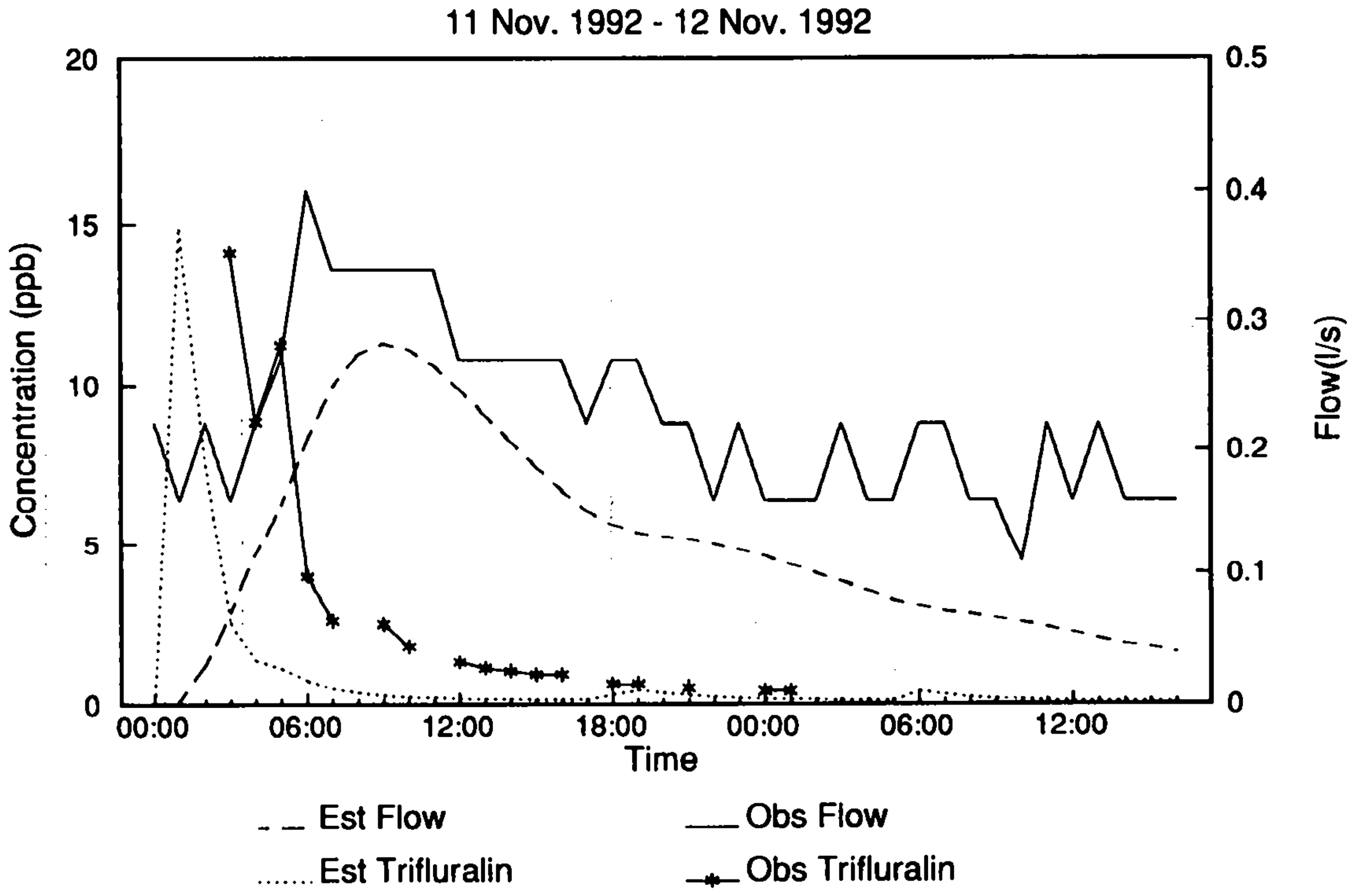


Figure 6.8 IoH Model - Site 0

24 Feb. 1990 - 25 Feb 1990

Figure 6.9 IoH Model - Site 5



6.4 Conclusions

The three different modelling approaches described here have been applied to the 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 use 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 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 program is much less user friendly than the SoilFug program.

The IoH model is much more detailed in its description of the field and therefore needs more data on this area. Estimates are needed for the minimum, maximum and field capacity water contents of the boxes in the model and for the parameters controlling water movement between them. This 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 IoH 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.

7. Summary discussion of experimental results

This phase of the project studied a group of highly sorbed chemicals (Kocs in the range 4400 - 72000) which would not be expected to be very mobile in the environment. The objectives were a) to see if these chemicals were transported to surface waters at measurable concentrations, b) whether they behaved in a similar manner to the less sorbed chemicals studied in previous years and c) if any biological effects could be detected. The chemicals studied were trifluralin, deltamethrin, chlorpyrifos and fenpropimorph.

The data described in section 5 clearly demonstrate that, under the conditions that prevailed at Rosemaund, all of these chemicals were able to reach the monitored surface waters. During rainfall events, higher pesticide concentrations were generally seen in the drains than the stream, reflecting the higher proportion of treated area draining to them. Peak concentrations in the drains were 14.1 µg/l (trifluralin), 2.9 µg/l (chlorpyrifos), 0.02 µg/l (deltamethrin) and 1.2 µg/l (fenpropimorph). Equivalent concentrations seen in the stream in the upper catchment were 0.9 µg/l (trifluralin) and 1.9 µg/l (deltamethrin); there were no stream data for chlorpyrifos and fenpropimorph. At the outflow from the catchment concentrations of all the pesticides were much lower and in the majority of the samples below detection limits. Only in the first event after application were concentrations significantly above detection limits with a maximum value of 0.37 µg/l (trifluralin). This demonstrates the dilution effect through the catchment as the contribution from water draining untreated land increases. The effect of dilution is one of the natural defences in river systems to pesticide concentrations exceeding drinking water limits in water abstracted for public water supply.

The values described above are certainly comparable with previous results obtained for more mobile pesticides studied in previous years (see reports 1-3). The most surprising chemical was deltamethrin which is applied at a rate of only 0.005 kg/ha as active ingredient and yet was still detectable, albeit at the lower end of concentrations compare
d to other pesticides studied. The way in which the pesticide concentrations in the surface waters varied through rainfall events can help explain the behaviour of these more sorbed chemicals. If the shapes of the chemographs are compared with those collected in the previous year, it can be seen that the pattern of behaviour was remarkably similar. The pesticide concentrations started at a peak value which occurred either before or coincident with the

hydrograph peak, the concentrations then tailed off quickly to return to background levels within 12 hours. Thus the mechanism of by-pass flow which was postulated to explain this behaviour for the mobile pesticides may be applied equally well to the more sorbed pesticides.

Sediments have been known to be mobilized and to discharge through drains into the stream during rainfall events. It was reasonable to suppose, therefore, that fine sediment, with pesticide sorbed to it, was being moved through macro-pores to the drains and was thus responsible for this similarity in behaviour with less highly sorbed chemicals. The limited measurements made of the particulate and dissolved concentrations of trifluralin at site 5 show that this was only partly true. Although the particulate pesticide load could be up to 50% of the total, in the initial few samples the dissolved load predominated. This is at least partly due to relative amounts of water and suspended sediments in the samples, maximμm suspended sediment loads reaching only around 3 mg/l.

The above analysis involved separation of the particulate and dissolved phase pesticide by filtration through a 0.45 μm filter. A recent paper (Worrall et al, 1994) has described the importance of dissolved organic carbon colloids (particles small enough to pass through 0.45 μm filters) in pesticide transport. Using soils from Rosemaund in mini-lysimeters, Worrall has shown that pesticides in solution may be sorbed onto the soil but can then be quickly desorbed onto organic colloids in solution. The result of this is to maintain higher concentrations in solution than could be expected by consideration of the pesticide partition coefficient. The implication for pesticide transport is that for highly sorbed chemicals, colloids may represent a significant loss pathway which would mimic those shown by more mobile, less sorbed chemicals. The question remains whether such bound pesticides are of environmental concern. These colloids may break down either naturally or by ingestion by aquatic faunna, so the pesticide may be released back into the environment. The bioassays carried out at Rosemaund give some indication in this area and are discussed later.

Overland flow was noted within Longlands field and high concentrations were measured in all four of the overland flow traps. It is thought that overland flow occurs only over small areas of the field and acts as a mechanism for redistributing water away from locally saturated areas to drier areas, perhaps caused by small scale variations in soil conductivity/rainfall acceptance potential. Although this may be a general mechanism for moving pesticide down slope it is unlikely that it will have discharged directly to the stream as there is significant vegetation on the stream banks. Overland flow might have been expected to result in a concentration of pesticide at the lower slopes and the valley bottom. This might explain the unusual soil residue data recorded for trifluralin over the period of the study. Samples taken from the Middleton and Compton series both showed an increase in soil residues following an initial decrease. These soils are found predominantly on the lower slopes (Middleton) and in the valley bottom (Compton). Although the number of samples taken was small, it is possible that this pattern of behaviour was caused by enrichment of the lower slopes with pesticide transported by overland flow from the upper parts of the field (Bromyard soil series).

The sediment bioassays carried out showed no significant differences between the growth rates of Chironomus riparius larvae held in control sediment and those held in stream bed sediments collected after the trifluralin and deltamethrin applications. This was to be expected with trifluralin which is not particularly toxic to arthropods but would not have been expected for deltamethrin had it been in the dissolved form. The implication here is that the deltamethrin is made unavailable by virtue of being bound tightly to the sediment.

A second bioassay was carried out after the spring applications of chlorpyrifos and fenpropimorph, using the feeding rate of Gammarus pulex as the measure of stress (see report number 3 and section 5 this report). In this case substantial mortality of the organisms was observed resulting from acutely toxic levels of chlorpyrifos. This result has significance because it shows that not only do sorbed, 'non-mobile', pesticides reach surface waters, but that they can do so at environmentally harmful levels. Whether this toxicity rests with the chemical in the truly dissolved phase or with that bound to colloids is not known in this case. Indeed the whole question of the toxicity of colloidally bound pesticide needs further investigation.

One of the main aims of the Rosemaund study has been to generate a data set which could be used for the testing of mathematical models of pesticide translocation. During the study three models have been tested against the Rosemaund data; two fugacity models and a combined water movement and pesticide model based on a conceptualization of the water flow in the catchment. There was generally a reasonable level of agreement between model simulations and measured values (see section x). Perhaps the model which showed most promise was the SoilFug model, which is designed to give estimates of exposure levels during individual rainfall events. Such a model has applicability for hazard assessment for both existing licensed products and at the pre-registration stage. SoilFug attempts only to estimate average concentrations in drainage water during rainfall events and this might partly account for its good predictions. SoilFug is also well packaged from the usability point of view as it operates in the WindowsTM environment. This combined with the relatively modest input data demands give this model the most immediate applicability. The remaining two models seek to describe the changes in pesticide concentration through a rainfall event, a much more onerous task. Consequently the input data requirements are more demanding and the level of knowledge required to run them is higher. These models are certainly more suited to site specific studies than as general screening models.

Although the models have been tested on a wide range of pesticides and at a number of scales within Rosemaund, further testing on data from other sites is required in order to establish additional confidence (or otherwise) in model performance. The modelling work carried out in this study has identified approaches which go a long way towards meeting the modelling aims identified at the start of the study, and have laid a foundation on which the use of models in registration and catchment planning can be based.

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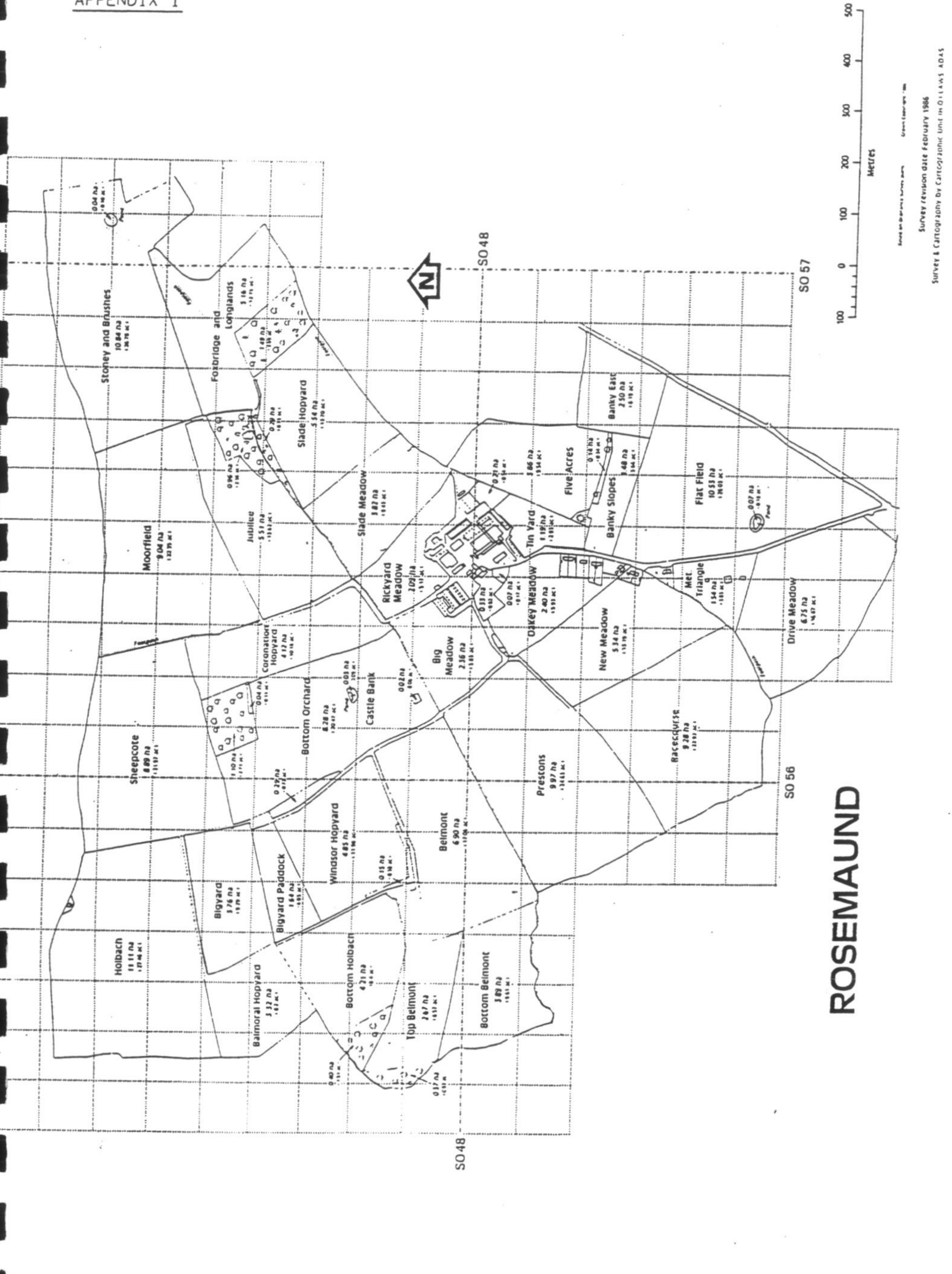
Also to be acknowledged is the assistance of Mr S Clews and Mr S Old of ADAS (Woodthorne) in the design and production of the front cover.

APPENDIX I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Foxbridge and Longlands
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Slade Hopyard
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Moorfield
9.04 ha
Jubilee
5.51 ha
Slade Meadow
3.82 ha
Rickyard Meadow
2.09 ha
Tin Yard
1.19 ha
Five Acres
Banky East
2.50 ha
Banky Slopes
3.48 ha
Flat Field
10.53 ha
Pond
Coronation Hopyard
4.12 ha
Bottom Orchard
8.28 ha
Castle Bank
Big Meadow
2.36 ha
Oakey Meadow
2.40 ha
New Meadow
5.34 ha
Met. Triangle
1.54 ha
Drive Meadow
6.75 ha
Sheepcote
8.89 ha
Racecourse
9.28 ha
Prestons
9.97 ha
Belmont
6.90 ha
Windsor Hopyard
4.85 ha
Bigyard Paddock
1.64 ha
Bigyard
3.76 ha
Holbach
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Balmoral Hopyard
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Bottom Holbach
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Top Belmont
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Footpath
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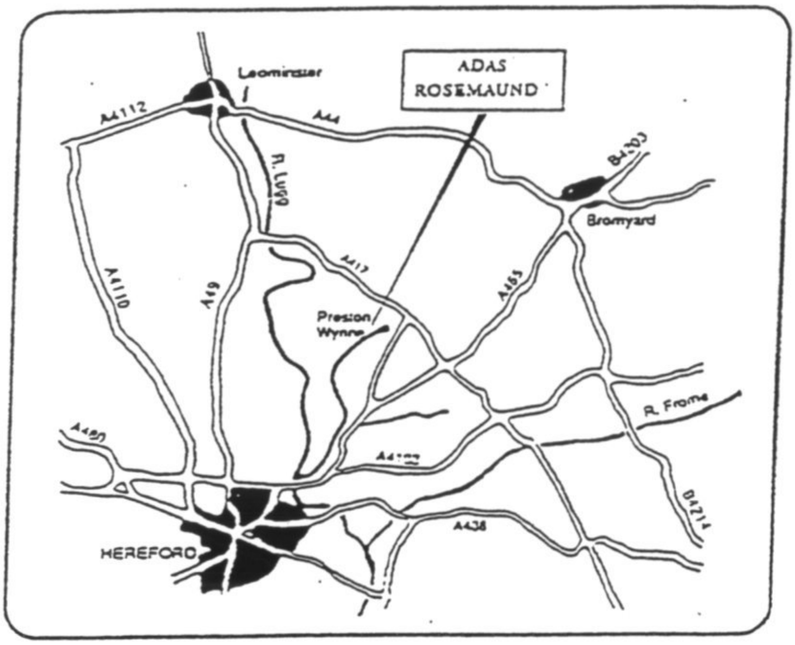
Metres
Survey revision date February 1986
Survey & Cartography by Cartographic Unit in ADAS

Location of Rosemaund Farm



Field boundaries and extent of catchment

APPENDIX II

WEATHER DATA SUMMARY FOR ADAS ROSEMAUND (1990-1992)

1990

	Rainfall (mm)		Sunshine (hrs)		Mean 10 cm Soil temp °C @ 0900 hrs GMT		No. of days rain (0.1 mm or more)	No. of ground frosts	No. of air frosts
	LTM	1990	LTM	1990	LTM	1990	1990	1990	1990
January	60.1	126.2	52.1	62.3	2.7	5.9	23	12	12
February	45.1	106.3	66.8	80.3	2.9	5.5	22	4	3
March	49.9	9.0	105.9	141.7	4.3	6.3	7	10	5
April	43.1	30.1	149.8	177.5	7.1	6.9	14	20	6
May	53.9	19.0	182.0	153.3	10.8	12.3	5	14	0
June	51.3	41.1	188.1	108.4	14.4	14.3	17	1	0
July	50.0	13.9	187.7	249.5	16.2	16.8	9	1	0
August	58.7	20.7	169.0	197.1	15.0	17.2	7	0	0
September	60.1	28.8	129.6	158.0	12.4	13.1	13	8	0
October	56.9	78.4	94.5	95.8	9.4	10.2	16	4	0
November	65.5	34.6	61.6	59.0	5.8	6.5	12	20	6
December	65.7	56.9	45.8	63.2	4.4	3.9	9	22	11

Summary: January and February very wet and mild; March warm and very dry; April average; May warm and dry; cool and dry June; July and August very hot and dry; dry September; October average; dry November and cold December.

LTM = Long-term mean since 1951.

1991

	Rainfall (mm)		Sunshine (hrs)		Mean 10 cm Soil temp °C @ 0900 hrs GMT		No. of days rain (0.1 mm or more)	No. of ground frosts	No. of air frosts
	LTM	1991	LTM	1991	LTM	1991	1991	1991	1991
January	61.0	88.7	52.6	67.8	2.73	2.60	18	26	14
February	44.4	24.5	66.5	55.3	2.86	1.81	13	23	19
March	50.9	78.6	105.1	82.4	4.35	6.15	15	14	4
April	43.3	48.1	148.7	118.9	7.09	7.45	10	16	4
May	52.2	3.7	180.5	138.1	10.84	11.63	7	8	0
June	52.2	78.8	185.3	103.0	14.39	12.84	26	7	1
July	51.0	79.6	187.7	187.5	16.21	16.38	11	0	0
August	57.3	15.5	169.7	189.0	15.04	16.21	7	2	0
September	59.5	49.2	130.3	156.6	12.45	13.93	12	5	0
October	55.9	42.3	73.6	66.7	9.40	9.34	18	7	1
November	65.3	60.0	61.1	47.9	5.77	5.92	9	18	7
December	64.0	17.4	45.2	27.2	4.35	3.9	5	16	13

LTM = Long-term mean since 1951

January wet; February dry with some snow; March wet; April average; May very dry and dull; June wet and dull; July wet; August very dry, September and October drier than average; November average; December dry and dull.

1992

	Rainfall (mm)		Sunshine (hrs)		Mean 10 cm Soil temp °C @ 0900 hrs GMT		No. of days rain (0.1 mm or more)	No. of ground frosts	No. of air frosts
	LTM	1992	LTM	1992	LTM	1992	1992	1992	1992
January	61.1	74.8	52.1	35.2	2.7	3.3	10	17	14
February	44.0	22.7	66.3	53.2	2.9	3.8	18	19	10
March	50.0	23.5	104.7	79.0	4.3	6.0	16	11	2
April	43.3	37.4	147.8	99.5	7.0	7.6	18	12	2
May	52.4	38.9	181.9	224.5	10.1	13.0	12	7	1
June	51.6	44.9	186.0	184.5	14.4	16.0	9	0	0
July	51.5	85.1	185.8	107.7	16.2	16.1	16	0	0
August	59.5	139.0	169.2	158.3	15.0	14.9	21	0	0
September	59.6	52.3	129.3	87.0	12.4	12.7	20	0	0
October	56.2	41.2	93.4	78.8	9.4	8.1	16	16	3
November	66.0	91.7	61.1	54.6	5.8	6.4	23	19	2
December	64.4	62.2	45.4	51.5	4.4	3.4	13	26	14

Summary: January wet, February and March dry and mild; dull in April; Warm May and June, July and August wet and dull; September to November wet and dull. December average.

LTM = Long-term mean since 1951.

1993

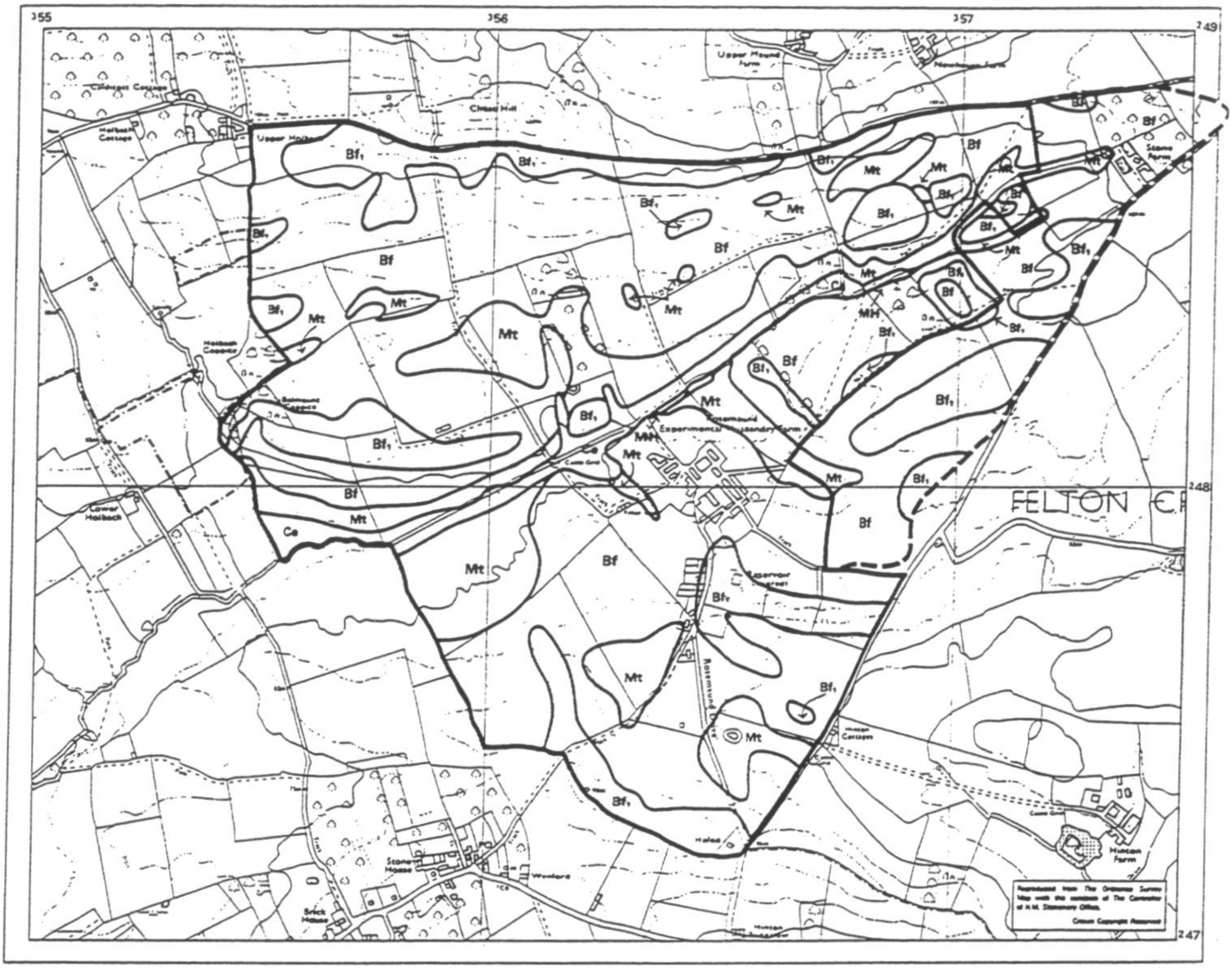
Month	Rainfall (mm)		Sunshine (hours)		Mean 10cm soil temp @0900 hrs GMT		No. of days rain (0.1mm or more)	No. of ground frosts	No. of air frosts
	LTM	1993	LTM	1993	LTM	1993	1993	1993	1993
January	61.3	68.5	51.4	21.9	2.7	4.4	22	20	6
February	43.1	3.5	65.8	46.3	2.9	4.6	2	17	6
March	49.2	14.9	104.2	84.6	4.3	5.0	7	20	8
April	43.6	56.6	146.2	77.6	7.0	8.5	18	-	3
May	52.6	61.9	179.5	78.8	10.2	11.0	20	17	0
June	51.6	43.9	185.8	177.3	14.4	15.1	11	6	0
July	51.5	52.3	185.7	181.4	16.2	15.6	10	1	0
August	58.6	21.8	169.1	164.3	15.0	14.2	9	2	0
September	60.0	79.4	128.2	84.8	12.3	11.9	15	8	0
October	57.1	96.6	93.5	98.4	9.3	7.8	14	14	6
November	65.9	61.8	60.6	39.7	5.7	5.0	14	18	12
December	64.9	85.5	45.6	54	4.3	4.3	24	21	6

Summary: January dull and mild. February dry and mild. March dry. April dull and mild. May dull. June and July average. August dry. September average. October wet and cold. November and December average.

APPENDIX III

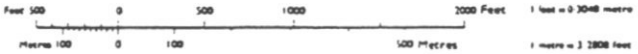
The Soils of Rosemaund Catchment, Worcester and Hereford

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



SSLRC

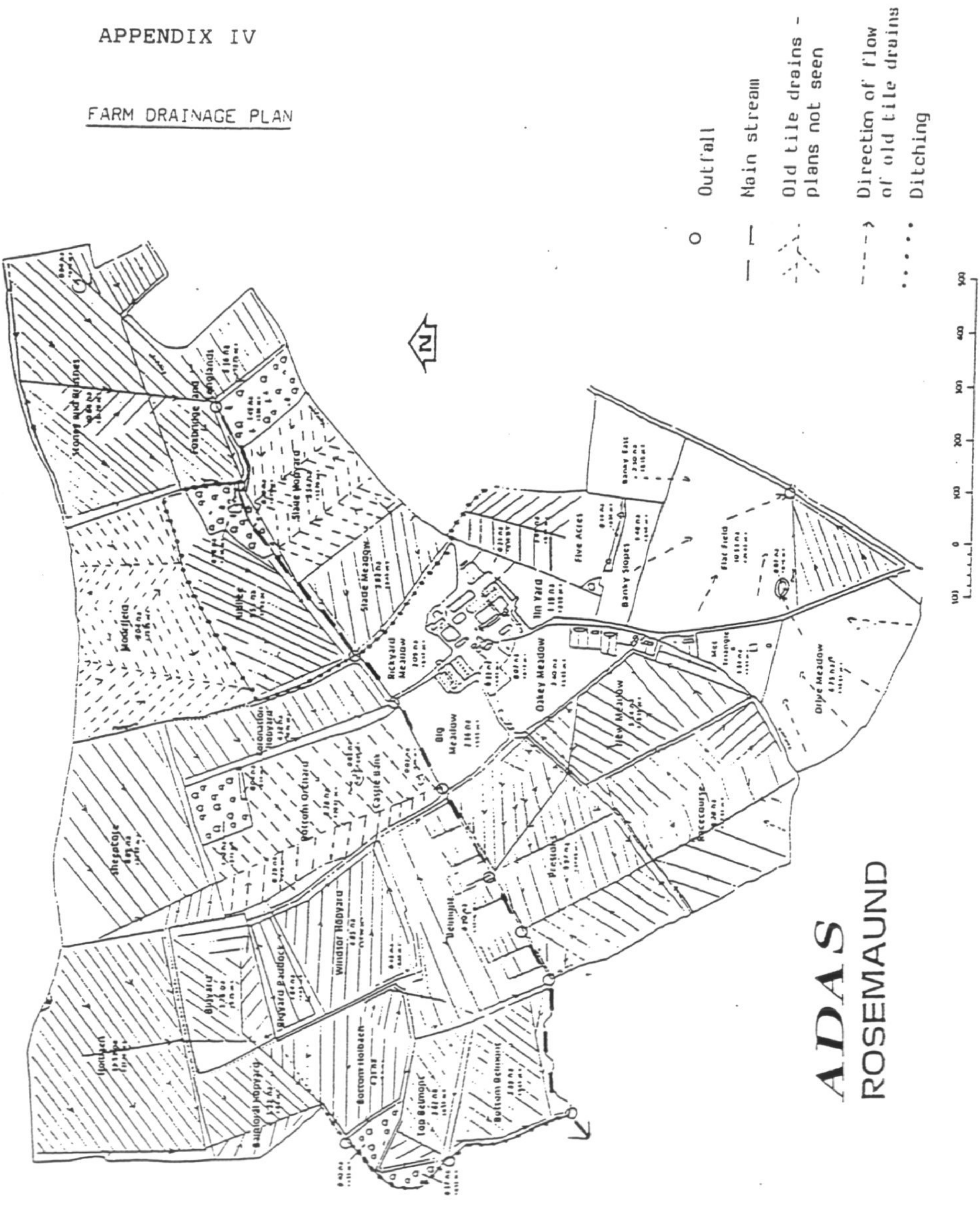
Symbol	Soil series	Topsoil characteristics	Subsoil characteristics	Soil water regime
Bf	Bromyard	Stoneless silty clay loam	Permeable stoneless reddish silty clay loam passing to soft blocky reddish and greenish grey siltstone and mudstone at about 55 cm depth	Slight seasonal waterlogging. Upper subsoil is wet for short periods during winter and early spring. Possibility of by-pass flow and surface runoff
Bf₁	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

APPENDIX IV

FARM DRAINAGE PLAN

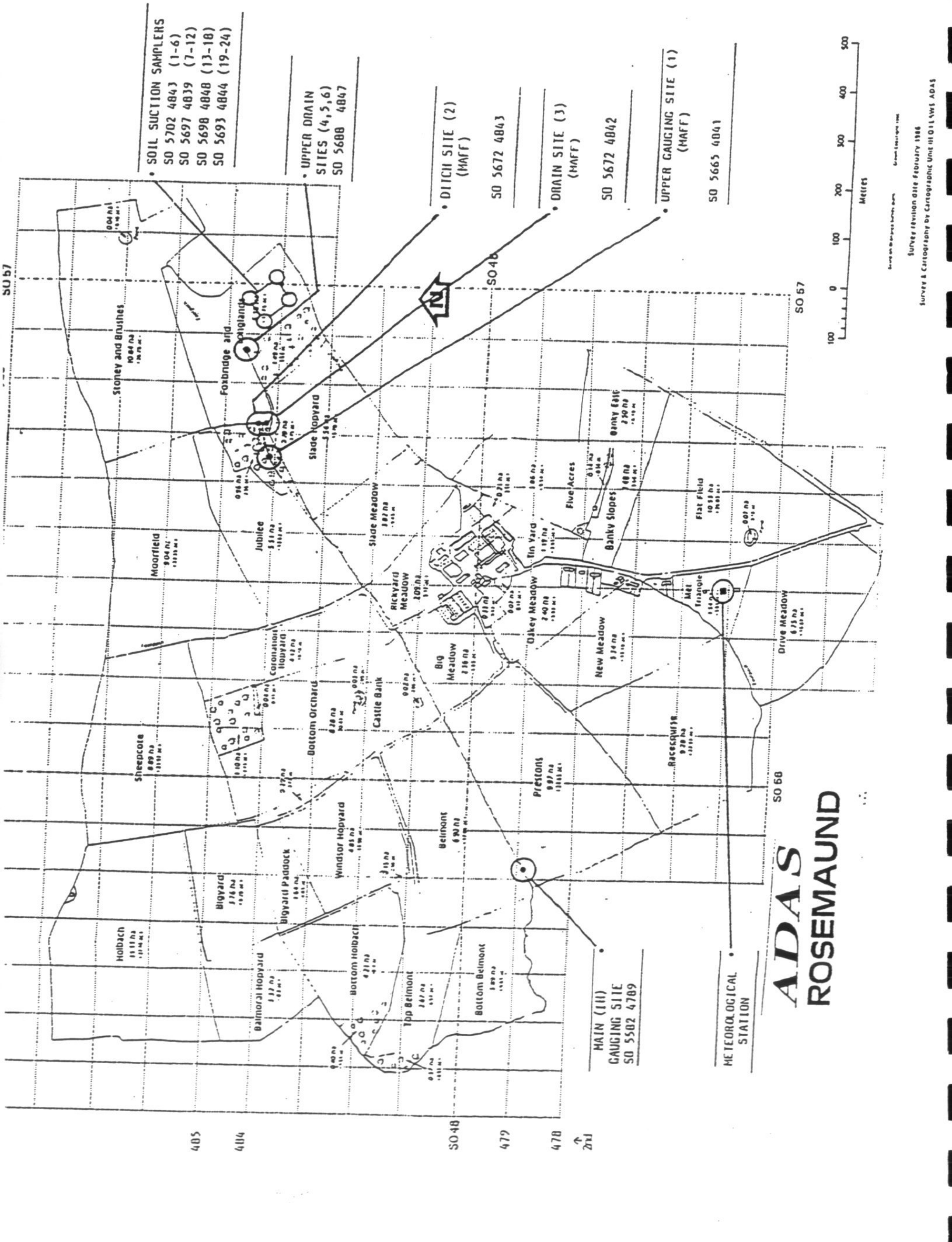


APPENDIX V
CROPPING HISTORY OF EACH FIELD 1985-1993

	Cropping Year								
Field	1985	1986	1987	1988	1989	1990	1991	1992	1993
Balmoral	FB	H	H	H	H	H	H	H	H
Banky East	L	L	WW	WB	SB/T	SB/T	WW	WB	WW
Banky Slopes	L	L	L	L	L	L	L	L	L
Belmont	P	WW	I	FM	SW	WO	I	WW	SB/SO
Big Meadow	I	I	L	L	L	FB	FB	FM	OSR
Big Yard	H	H	H	H	H	FM	BW	WW	L
Big Yard Paddock	I	FM	BS	WW	WO	T	BW	WW	Various
Bottom Belmont	L	WW	I	FM	WW	WO	IRG	FB	WO/WW/WB
Bottom Holback	SB	SB	SB	I	I	WW	WO	P	WW
Bottom Orchard	WW	WW	L	L	L	L	L	LS	O/DH
Castle Bank	WW	WW	L	L	L	L	L	L	L
Coronation	H	H	H	H	H	H	H	H	H
Drive Meadow	WW	P	WW	WB	OSR	WW	SB	WW	WW
Five Acres	WW	WW	P	WW	WW	WW	WW	WB	WW
Flat Field	OSR	WW	WW	P	WW	WB	OSR	WW/OSR	WW
Foxbridge & Longlands	I	I	WB/FM	I	I	WW	WB	BW	WW
Holbach	WW	WB	WB	OSR	WW	WB	WB/P	WW	WB
Jubilee	FB/H	I	I	WW	WB	OSR	WW	WO	WW
Met Triangle	PP	PP	PP	PP	PP	PP	PP	PP	PP
Moorfield	WW	WW	WB	WW	WB	OSR	WW	WW	WO
New Meadow	L	L	L	WW	L	L	L	L	L
Oakey Meadow	PP	PP	PP	PP	PP	PP	PP	PP	PP
Prestons	I	I	FM	WW	P	I	L	L	WW/L
Racecourse	I	FM	BW/SB/FB	SW	L	L	L	L	L
Richyard Meadow	L	L	L	L	L	L	L	L	L
Sheepcote	WB	WB	OSR	WW	SW/WW/WB	BW/P	WW/SW	WB	OSR
Slade Hopyard	L	L	L	WW	FM	WW	LS	WW	OSR
Slade Meadow	L	L	L	WB/SW	OSR	WW	WO	WW	OSR/BW
Stoney & Brushes	WB	OSR	WW	WB	P/BW	WW	WB	OSR	WW/BW
Tin Yard	PP	PP	PP	PP	PP	PP	PP	PP	PP
Top Belmont	L	SB	I	I	WW	L	FM	FB	FM
Windsor	H	H	H	H	H	H	H	H	H

Abbreviations:				
	BW	Winter beans	OSR	Oilseed rape
	BS	Spring beans	P	Peas
	DH	Dwarf hops	PP	Permanent pasture
	FB	Fodder beat	SB	Spring barley
	FM	Forage maize	SO	Spring oats
	H	Hops	SE	Spring wheat
	I	Italian ryegrass	T	Turnips
	L	Grass ley	WB	Winter barley
	LI	Linseed	WO	Winter oats
			WW	Winter wheat

Appendix VI


SOIL SUCTION SAMPLERS
SO 5702 4843 (1-6)
SO 5697 4839 (7-12)
SO 5698 4848 (13-18)
SO 5693 4844 (19-24)
UPPER DRAIN SITES (4,5,6)
SO 5688 4847
DITCH SITE (2) (MAFF)
SO 5672 4843
DRAIN SITE (3) (MAFF)
SO 5672 4842
UPPER GAUGING SITE (1) (MAFF)
SO 5665 4041
MAIN (III) GAUGING SITE
SO 5582 4789
METEOROLOGICAL STATION
ADAS
ROSEMAUND
N
SO 57
SO 48
SO 68
405
404
479
478
Metres
100
0
100
200
300
400
500
Survey revision date February 1986
Survey & Cartography by Cartographic Unit III O I LAWS ADAS
Stoney and Brushes
Foxbridge and
Moorfield
Jubilee
Slade Hopyard
Slade Meadow
Rickyard Meadow
Tin Yard
Five Acres
Banky End
Banky Slopes
Flat Field
Oakey Meadow
Met Triangle
Drive Meadow
New Meadow
Big Meadow
Coronation Hopyard
Bottom Orchard
Castle Bank
Sheepcote
Racecourse
Prestons
Belmont
Windsor Hopyard
Bigyard
Bigyard Paddock
Holbach
Bottom Holbach
Balmoral Hopyard
Top Belmont
Bottom Belmont

APPENDIX 7

Table W1. MANUAL WATER SAMPLES

Winter 1992/93 Trifluralin/Deltamethrin experiment

Date	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)	Trifluralin conc. (ng/l)	Deltamethrin conc. (ng/l)
13/10/92	1	3	2	2	2	2	1	0	-	-	-	-
8/11/92	44	0	38	0	7	0	22	0	194	0	-	-
12/11/92	64	0	27	0	85	0	10	0	193	0	63	0
25/11/92	-	-	29	0	73	4	27	1	215	0	30	1
27/11/92	44	1	9	0	34	3	13	0	371	0	21	0
9/12/92	32	0	25	0	45	0	132	0	39	0	13	0
16/12/92	345	250	674	832	106	105	1422	984	157	159	168	78
17/12/92	31	1	10	0	35	0	142	2	9	0	16	0
18/12/92	196	44	83	48	136	22	110	16	842	120	56	3
22/12/92	8	0	30	1	43	1	16	0	55	1	15	0
7/1/93	20	0	6	1	20	1	19	1	133	1	14	0
19/1/93	28	0	6	0	15	0	7	0	69	0	9	0
10/3/93	8	0	8	0	19	0	-	-	-	-	-	-
8/4/93	15	0	6	0	41	0	-	-	-	-	-	-
13/4/93	14	0	6	0	14	0	7	0	52	0	-	-

Table W2. Automatic Water Samples. Site 1

Deltamethrin/Trifluralin Experiment 11 11 92

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
11 11 92	00:00	1	0.54		
	00:30		0.42		
	01:00	2.5	0.54		
	01:30		0.67		
	02:00	5	0.67		
	02:30		0.67		
	03:00	0.5	0.97		
	03:30		2.47	2	150
	04:00	0.5	4.91	3	954
	04:30		4.64	3	924
	05:00	1	3.87	3	628
	05:30		3.87	4	939
	06:00	0	3.87	3	577
	06:30		3.87	2	693
	07:00	0	3.38	1	646
	07:30		3.14	2	665
	08:00	0	2.92	6	623
	08:30		2.92	1	497
	09:00	0	2.92	1	408
	09:30		2.69	0	440
	10:00	0	2.26	0	499
	10:30		2.06	0	480
	11:00	0	2.47	0	280
	11:30		2.06	0	382
	12:00	0	2.06	0	396
	12:30		2.06	0	350
	13:00	0	1.67	0	373
	13:30		1.67	0	408
	14:00	0	1.67	0	397
	14:30		1.67	0	434
	15:00	0	1.48	0	339

NB: The streamflow data was calculated by dividing the flow at the I H main site by a factor of 10.

Table W3. Automatic Water Samples. Site 3

Deltamethrin/Trifluralin Experiment 11 11 92

Date	Time	Rainfall mm/hr	Flow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
11 11 92	00:00	1	0.462		
	00:30		0.436		
	01:00	2.5	0.412		
	01:30		0.388		
	02:00	5	0.364		
	02:30		0.342		
	03:00	0.5	0.32		
	03:30		0.312	5	3010
	04:00	0.5	0.306	2	1528
	04:30		0.298	1	1506
	05:00	1	0.292	0	436
	05:30		0.284	1	393
	06:00	0	0.278	1	542
	06:30		0.272	1	386
	07:00	0	0.264	1	325
	07:30		0.258	1	242
	08:00	0	0.252	1	254
	08:30		0.246	1	243
	09:00	0	0.240	1	209
	09:30		0.234	1	154
	10:00	0	0.226	1	190
	10:30		0.220	1	166
	11:00	0	0.214	0	138
	11:30		0.208	1	143
	12:00	0	0.202	1	158
	12:30		0.196	1	112
	13:00	0	0.190	0	88
	13:30		0.186	1	126
	14:00	0	0.180	1	213
	14:30		0.174	-	-
	15:00	0	0.168	-	-

Table W4. Automatic Water Samples. Site 1

Deltamethrin/Trifluralin Experiment 15 11 92

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
14 11 92	19:00	0.5	0.68		
	19:30		0.68		
	20:00	0	0.68		
	20:30		0.68		
	21:00	0	0.68		
	21:30		0.68		
	22:00	0.5	0.68		
	22:30		0.68		
	23:00	1.5	0.68		
	23:30		0.68		
15 11 92	00:00	0.5	0.68		
	00:30		0.85		
	01:00	1	0.85	4	126
	01:30		1.03	2	178
	02:00	0	1.37	1	337
	02:30		2.05	0	384
	03:00	0	2.91	0	310
	03:30		3.76	0	307
	04:00	0	4.44	0	325
	04:30		4.10	0	376
	05:00	0	3.76	0	274
	05:30		3.42	0	247
	06:00	0	2.91	0	199
	06:30		2.74	0	185
	07:00	0	2.56	0	174
	07:30		2.56	0	196
	08:00	0	2.39	0	167
	08:30		2.39	0	115
	09:00	0	2.39	0	158
	09:30		2.39	0	156
	10:00	0	2.22	0	135
	10:30		2.22	0	123
	11:00	1	2.22	0	131
	11:30		2.22	0	153
	12:00	0	2.22	0	110
	12:30		2.22	0	97

Table W5. Automatic Water Samples. Site 3

Deltamethrin Experiment 15 11 92

Date	Time	Rainfall mm/hr	Flow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
14 11 92	19:00	0.5	0.57		
	19:30		0.57		
	20:00	0	0.57		
	20:30		0.57		
	21:00	0	0.56		
	21:30		0.56		
	22:00	0.5	0.56		
	22:30		0.56		
	23:00	1.5	0.55		
	23:30		0.55		
15 11 92	00:00	0.5	0.54		
	00:30		0.54		
	01:00	1	0.52	2	638
	01:30		0.5	1	438
	02:00	0	0.49	0	424
	02:30		0.49	0	341
	03:00	0	0.47	-	-
	03:30		0.46	-	-
	04:00	0	0.45	0	211
	04:30		0.45	0	198
	05:00	0	0.44	0	147
	05:30		0.43	0	114
	06:00	0	0.43	0	94
	06:30		0.42	0	93
	07:00	0	0.42	0	88
	07:30		0.41	0	86
	08:00	0	0.41	0	80
	08:30		0.4	0	83
	09:00	0	0.4	0	75
	09:30		0.39	0	96
	10:00	0	0.39	0	71
	10:30		0.38	0	66
	11:00	1	0.38	0	58
	11:30		0.37	0	59
	12:00	0	0.36	0	64
	12:30		0.36	0	51

Table W6. Automatic Water Samples. Site 1.
Deltamethrin/Trifluralin Experiment 26 11 92.

The Autosamplers were triggered manually at 12:00 on 26 11 92.

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
24 11 92	16:00	0	0.34		
	16:30		0.34		
	17:00	0	0.34		
	17:30		0.34		
	18:00	0.5	0.34		
	18:30		0.34		
	19:00	3.5	0.34		
	19:30		0.34		
	20:00	0.5	0.51		
	20:30		0.51		
	21:00	0	0.68		
	21:30		0.68		
	22:00	0	0.68		
	22:30		0.68		
	23:00	4.5	0.68		
	23:30		0.68		
25 11 92	00:00	1	0.85		
	00:30		1.54		
	01:00	0	2.39		
	01:30		3.59		
	02:00	0	4.96		
	02:30		5.30		
	03:00	0	4.79		
	03:30		4.44		
	04:00	0	4.10		
	04:30		3.93		
	05:00	0	3.59		
	05:30		3.25		
	06:00	0	3.08		
	06:30		2.91		
	07:00	0.5	2.74		
	07:30		2.56		
	08:00	2	2.56		
	08:30		2.39		
	09:00	0	2.74		
	09:30		3.08		
	10:00	0	3.25		
	10:30		3.42		
	11:00	0	3.59		
	11:30		3.59		
	12:00	1	3.59		
	12:30		3.76		
	13:00	1.5	3.76		
	13:30		3.76		
	14:00	0.5	3.76		
	14:30		3.93		
	15:00	1.5	5.81		
	15:30		8.89		

Table 6. Continued.

	16:00	2.5	12.82		
	16:30		21.54		
	17:00	3	36.75		
	17:30		38.12		
	18:00	2.5	39.66		
	18:30		41.03		
	19:00	1	38.63		
	19:30		35.38		
	20:00	0.5	32.31		
	20:30		29.40		
	21:00	0.5	26.67		
	21:30		24.27		
	22:00	0	22.39		
	22:30		21.20		
	23:00	0.5	20.00		
	23:30		18.80		
26 11 92	00:00	0	17.61		
	00:30		16.58		
	01:00	0	15.56		
	01:30		14.53		
	02:00	0	13.68		
	02:30		12.65		
	03:00	0	12.14		
	03:30		11.97		
	04:00	0	11.79		
	04:30		11.62		
	05:00	1.5	11.45		
	05:30		11.28		
	06:00	0.5	11.11		
	06:30		10.77		
	07:00	0	10.43		
	07:30		10.26		
	08:00	0	9.91		
	08:30		9.57		
	09:00	0	9.40		
	09:30		9.06		
	10:00	0	8.89		
	10:30		8.55		
	11:00	0	8.38		
	11:30		8.03		
	12:00	0	7.86	17	134
	12:30		7.52	2	75
	13:00	0	7.35	3	73
	13:30		7.18	3	71
	14:00	0.5	6.84	1	58
	14:30		6.67	4	67
	15:00	0	6.50	-	-
	15:30		6.32	-	-
	16:00	0	6.32	2	98
	16:30		6.15	4	94
	17:00	0	5.98	5	86
	17:30		5.98	0	53
	18:00	0	5.81	3	77
	18:30		5.64	0	70
	19:00	0	5.47	2	60

Table 6. Continued.

19:30		5.30	1	62
20:00	0	5.30	-	-
20:30		5.13	-	-
21:00	0	5.13	-	-
21:30		4.96	-	-
22:00	0	4.79	-	-
22:30		4.79	-	-
23:00	0	4.62	-	-
23:30		4.62	-	-

Table W7. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin Experiment 26 11 92

The Autosamplers were triggered manually at 12:00 on 26 11 92

Date	Time	Rainfall mm/hr	Deltamethrin ng/litre	Trifluralin ng/litre
24 11 92	16:00	0		
	16:30			
	17:00	0		
	17:30			
	18:00	0.5		
	18:30			
	19:00	3.5		
	19:30			
	20:00	0.5		
	20:30			
	21:00	0		
	21:30			
	22:00	0		
	22:30			
	23:00	4.5		
	23:30			
25 11 92	00:00	1		
	00:30			
	01:00	0		
	01:30			
	02:00	0		
	02:30			
	03:00	0		
	03:30			
	04:00	0		
	04:30			
	05:00	0		
	05:30			
	06:00	0		
	06:30			
	07:00	0.5		
	07:30			
	08:00	2		
	08:30			
	09:00	0		
	09:30			
	10:00	0		
	10:30			
	11:00	0		
	11:30			
	12:00	1		
	12:30			
	13:00	1.5		
	13:30			
	14:00	0.5		
	14:30			
	15:00	1.5		

Table 7. Continued.

	15:30			
	16:00	2.5		
	16:30			
	17:00			
	17:30			
	18:00	2.5		
	18:30			
	19:00			
	19:30			
	20:00	0.5		
	20:30			
	21:00	0.5		
	21:30			
	22:00	0		
	22:30			
	23:00	0.5		
	23:30			
26 11 92	00:00	0		
	00:30			
	01:00	0		
	01:30			
	02:00	0		
	02:30			
	03:00	0		
	03:30			
	04:00	0		
	04:30			
	05:00	1.5		
	05:30			
	06:00	0.5		
	06:30			
	07:00	0		
	07:30			
	08:00	0		
	08:30			
	09:00	0		
	09:30			
	10:00	0		
	10:30			
	11:00	0		
	11:30			
	12:00	0	2	72
	12:30		2	76
	13:00	0	2	64
	13:30		1	74
	14:00	0.5	2	66
	14:30		2	65
	15:00	0	2	106
	15:30		2	109
	16:00	0	1	83
	16:30		2	80
	17:00		1	55
	17:30		2	82
	18:00		1	60
	18:30		1	46

Table 7. Continued.

19:00	1	58
19:30	1	60
20:00	1	54
20:30	2	65
21:00	1	57
21:30	1	59
22:00	2	56
22:30	2	56
23:00	1	44
23:30	1	55

NB: There were no flow data for this event.

Table W8. Automatic Water Samples. Site 1.

Deltamethrin/Trifluralin Experiment 16 12 92

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
16 12 92	00:00	0	1.20		
	00:30		1.20		
	01:00	0	1.20		
	01:30		1.20		
	02:00	0	1.20		
	02:30		1.20		
	03:00	0.5	1.20		
	03:30		1.20		
	04:00	0	1.20		
	04:30		1.20		
	05:00	0.5	1.20		
	05:30		1.20		
	06:00	0	1.20		
	06:30		1.71		
	07:00	1.5	2.74		
	07:30		3.76		
	08:00	2.5	4.79	8	23
	08:30		6.15	1	22
	09:00	2.5	6.84	1	31
	09:30		6.32	1	19
	10:00	1.5	5.64	1	13
	10:30		5.30	1	13
	11:00	0	5.13	1	24
	11:30		4.96	2	28
	12:00	0	4.62	1	25
	12:30		4.44	1	27
	13:00	0	4.27	1	34
	13:30		4.10	1	57
	14:00	0	3.93	2	78
	14:30		3.76	1	42
	15:00	0	3.76	1	40
	15:30		3.59	1	26
	16:00	0	3.59	1	34
	16:30		3.42	1	33
	17:00	0	3.42	1	27
	17:30		3.42	1	16
	18:00	0	3.25	1	37
	18:30		3.25	2	27
	19:00	0	3.25	1	31
	19:30		3.08	1	24

Table W9. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin Experiment 16 12 92

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
16 12 92	00:00	0			
	00:30				
	01:00	0			
	01:30				
	02:00	0			
	02:30				
	03:00	0.5			
	03:30				
	04:00	0			
	04:30				
	05:00	0.5			
	05:30				
	06:00	0			
	06:30				
	07:00	1.5			
	07:30				
	08:00	2.5		-	-
	08:30			-	-
	09:00	2.5		-	-
	09:30			-	-
	10:00	1.5		-	-
	10:30			-	-
	11:00	0		-	-
	11:30			-	-
	12:00	0		-	-
	12:30			-	-
	13:00	0		-	-
	13:30			-	-
	14:00	0		-	-
	14:30			-	-
	15:00	0		-	-
	15:30			-	-
	16:00	0	0.410	-	-
	16:30		0.400	-	-
	17:00	0	0.390	-	-
	17:30		0.380	-	-
	18:00	0	0.370	-	-
	18:30		0.362	-	-
	19:00	0	0.352	-	-
	19:30		0.344	-	-

NB: There were no flow data until 16.00.

Table W10. Automatic Water Samples. Site 1.

Deltamethrin/Trifluralin Experiment 18 12 92

Date	Time	Rainfall mm/hr	Streamflow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
18 12 92	00:00	0	2.22		
	00:30		2.39		
	01:00	1	3.08		
	01:30		3.93		
	02:00	1	4.79	1872	1040
	02:30		5.64	584	448
	03:00	2.5	9.40	86	150
	03:30		16.41	174	429
	04:00	2.5	30.43	70	103
	04:30		50.43	47	151
	05:00	2.5	76.92	60	126
	05:30		85.47	77	150
	06:00	2.5	85.47	123	223
	06:30		79.83	74	141
	07:00	3	79.15	41	140
	07:30		78.46	28	108
	08:00	1.5	77.26	80	131
	08:30		71.11	135	88
	09:00	1.5	65.47	33	105
	09:30		60.00	36	99
	10:00	1.5	54.87	88	77
	10:30		49.91	53	62
	11:00	0	45.3	53	66
	11:30		41.54	50	70
	12:00	0.5	38.97	34	77
	12:30		36.41	38	91
	13:00	0	34.02	44	88
	13:30		31.62	24	73

Table W11. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin Experiment 18 12 92

Date	Time	Rainfall mm/hr	Flow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre
18 12 92	00:00	0	0.95		
	00:30		4.24		
	01:00	1	10.73		
	01:30		16.25		
	02:00	1	15.82	19	389
	02:30		15.40	5	158
	03:00	2.5	14.98	4	76
	03:30		14.57	3	64
	04:00	2.5	14.17	2	57
	04:30		13.78	2	45
	05:00	2.5	13.10	2	46
	05:30		12.04	1	41
	06:00	2.5	11.04	0	35
	06:30		10.09	0	32
	07:00	3	9.19	1	31
	07:30		8.34	0	29
	08:00	1.5	7.54	0	26
	08:30		6.78	0	27
	09:00	1.5	6.17	0	23
	09:30		5.75	0	30
	10:00	1.5	5.35	0	25
	10:30		4.96	0	20
	11:00	0	4.59	0	27
	11:30		4.24	0	21
	12:00	0.5	3.91	0	25
	12:30		3.59	0	22
	13:00	0	3.28	0	22
	13:30		3.00	0	19

Table W12. Automatic Water Samples. Site 1.

Deltamethrin/Trifluralin Experiment 5.1.93

Date	Time	mm/hr Rainfall	litres/sec Streamflow	ng/litre Deltamethrin	ng/litre Trifluralin
05 01 93	00:00	0	1.03		
	00:30		1.03		
	01:00	0	1.03		
	01:30		1.03		
	02:00	0	1.03		
	02:30		1.03		
	03:00	0	1.03		
	03:30		1.03		
	04:00	0	1.03		
	04:30		1.03		
	05:00	0.5	1.03		
	05:30		1.03		
	06:00	0.5	1.03		
	06:30		1.20		
	07:00	0.5	1.20		
	07:30		1.37		
	08:00	0	1.37		
	08:30		1.54		
	09:00	0	1.54		
	09:30		1.71		
	10:00	0	1.88		
	10:30		1.88		
	11:00	0	2.05		
	11:30		2.05		
	12:00	0	2.05		
	12:30		2.05		
	13:00	0	2.05		
	13:30		2.05		
	14:00	0	2.05		
	14:30		2.05		
	15:00	0	2.05		
	15:30		2.05		
	16:00	0	2.05		
	16:30		2.05		
	17:00	1	1.88		
	17:30		1.88		
	18:00	1	1.88		
	18:30		1.88		
	19:00	1	1.88		
	19:30		1.88		
	20:00	0.5	1.88	2	66
	20:30		1.88	1	48
	21:00	0.5	2.22	2	95
	21:30		2.74	3	83
	22:00	0.5	3.25	4	92
	22:30		3.76	4	78
	23:00	0	4.10	2	60
	23:30		4.44	2	67

Table W12. Continued

00:00	0	4.79	0	57
00:30		4.79	3	65
01:00	0	4.96	0	42
01:30		5.13	3	51
02:00	0	4.96	0	55
02:30		4.96	0	46
03:00	0	4.96	0	34
03:30		4.79	0	43
04:00	0	4.79	0	30
04:30		4.79	0	36
05:00	0	4.62	4	39
05:30		4.44	2	35
06:00	0	4.44	0	39
06:30		4.27	11	30
07:00	0	4.27	1	26
07:30		4.10	2	8

Table W13. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin Experiment 5.1.93

Date	Time	mm/hr Rainfall	litres/sec Flow	ng/litre eltamethri	ng/litre Trifluralin
05 01 93	00:00	0	0.022		
	00:30		0.022		
	01:00	0	0.022		
	01:30		0.022		
	02:00	0	0.022		
	02:30		0.022		
	03:00	0	0.022		
	03:30		0.022		
	04:00	0	0.022		
	04:30		0.022		
	05:00	0.5	0.022		
	05:30		0.022		
	06:00	0.5	0.022		
	06:30		0.022		
	07:00	0.5	0.022		
	07:30		0.022		
	08:00	0	0.022		
	08:30		0.022		
	09:00	0	0.022		
	09:30		0.022		
	10:00	0	0.022		
	10:30		0.022		
	11:00	0	0.022		
	11:30		0.022		
	12:00	0	0.022		
	12:30		0.022		
	13:00	0	0.022		
	13:30		0.022		
	14:00	0	0.022		
	14:30		0.022		
	15:00	0	0.022		
	15:30		0.022		
	16:00	0	0.022		
	16:30		0.022		
	17:00	1	0.022		
	17:30		0.022		
	18:00	1	0.022		
	18:30		0.022		
	19:00	1	0.024		
	19:30		0.024		
	20:00	0.5	0.024	0	177
	20:30		0.024	1	141
	21:00	0.5	0.024	1	98
	21:30		0.024	1	128
	22:00	0.5	0.024	0	117
	22:30		0.024	1	107
	23:00	0	0.024	1	88
	23:30		0.024	1	91
	00:00	0	0.024	0	64

Table W13. Continued

00:30		0.024	0	69
01:00	0	0.024	0	61
01:30		0.026	1	66
02:00	0	0.026	1	63
02:30		0.026	0	52
03:00	0	0.026	0	57
03:30		0.026	1	52
04:00	0	0.026	1	58
04:30		0.026	1	49
05:00	0	0.026	0	44
05:30		0.026	0	53
06:00	0	0.034	0	44
06:30		0.044	0	46
07:00	0	0.056	0	47
07:30		0.072	0	36

Table W14. MANUAL WATER SAMPLES.

Spring 1993 Chlorpyriphos/fenpropimorph experiment.

Date	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)	Chlorpyriphos conc. (ng/l)	Fenpropimorph conc. (ng/l)
10 03 93	0	2	0	1	0	0	0	-	0	-	0	-
08 04 93	115	56	30	18	289	169	-	-	-	-	-	-
13 04 93	60	40	14	55	47	27	15	22	136	78	-	-

Table W15. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin/Chloripyrifos/Fenpropimorph Experiment 7.4.93

Date	Time	mm/hr Rainfall	litres/sec Flow	ng/litre Deltamethrin	ng/litre Trifluralin	ng/litre Chlorpyrifos	ng/litre Fenpropimorph
06 04 93	22:00	0	0.00				
	22:30		0.00				
	23:00	0	0.00				
	23:30		0.00				
	00:00	0.5	0.00				
	00:30		0.00				
	01:00	1.5	0.00				
	01:30		0.00				
	02:00	2.5	0.00				
	02:30		0.00				
	03:00	2	0.00				
	03:30		0.00				
	04:00	2	0.00				
	04:30		0.07				
	05:00	0.5	0.13				
	05:30		0.26				
	06:00	1	0.40				
	06:30		0.36	0	40	1564	868
	07:00	0.5	0.33	0	74	2496	1172
	07:30		0.30	1	101	2784	1250
	08:00	0.5	0.23	8	72	2056	1146
	08:30		0.23	12	95	1452	788
	09:00	0	0.20	10	88	1373	940
	09:30		0.17	9	80	1432	946
	10:00	0	0.17	7	74	1128	822
	10:30		0.13	6	53	926	437
	11:00	0	0.10	4	60	1011	534
	11:30		0.10	4	64	1049	512
	12:00	0	0.07	5	77	1034	377
	12:30		0.07	3	60	870	468
	13:00	0	0.03	4	74	792	523
	13:30		0.03	#N/A	#N/A	750	476
	14:00	0	0.00	4	54	762	511
	14:30		0.00	3	51	605	695
	15:00	0	0.00	3	114	404	612
	15:30		0.00	2	56	693	670
	16:00	0	0.00	2	40	518	640
	16:30		0.00	1	27	710	406
	17:00	0	0.00	1	51	595	418
	17:30		0.00	0	44	664	652
	18:00	0	0.00	0	46	685	622

Table W16. Automatic Water Samples. Site 3.

Deltamethrin/Trifluralin/Chlorpyrifos/Fenpropimorph Experiment 9.4.93

Date	Time	Rainfall mm/hr	Flow litres/sec	Deltamethrin ng/litre	Trifluralin ng/litre	Chlorpyrifos ng/litre	Fenpropimorph ng/litre
08 04 93	21:00	0	0.000				
	21:30		0.000				
	22:00	0.5	0.000				
	22:30		0.000				
	23:00	0	0.000				
	23:30		0.000				
	00:00	0.5	0.000				
	00:30		0.000				
	01:00	1	0.000				
	01:30		0.000				
	02:00	0.5	0.000				
	02:30		0.000				
	03:00	0	0.000				
	03:30		0.000				
	04:00	1.5	0.000				
	04:30		0.000				
	05:00	3.5	0.000				
	05:30		0.000				
	06:00	2.5	0.264				
	06:30		0.792				
	07:00	0.5	1.353	10	109	4287	1482
	07:30		1.980	6	93	3125	1578
	08:00	1	2.046	2	109	2714	1268
	08:30		1.716	0	92	2176	1033
	09:00	0.5	1.419	0	73	1433	584
	09:30		1.221	0	68	1031	562
	10:00	0	1.089	0	56	826	547
	10:30		0.990	0	52	731	471
	11:00	0	0.990	0	47	605	441
	11:30		0.957	0	49	709	408
	12:00	0	0.891	0	38	561	326
	12:30		0.825	0	39	548	405
	13:00	0	0.759	0	36	465	331
	13:30		0.693	0	40	484	297
	14:00	0	0.660	0	29	403	215
	14:30		0.594	0	27	376	250
	15:00	0	0.561	0	25	276	162
	15:30		0.528	0	26	300	171
	16:00	0	0.495	0	31	432	150
	16:30		0.462	0	27	354	120
	17:00	0	0.462	0	24	322	115
	17:30		0.429	0	20	249	126
	18:00	0	0.396	0	20	273	120
	18:30		0.363	0	31	262	140

Appendix 8

Trifluralin

Soil levels in Foxbridge and Longlands following application in Winter 1992.

For the first three soil types (Bromyard shallow, Bromyard and Middleton), three different sites were sampled over three depth increments; the three samples for each depth were pooled before analysis to give one value for each depth and soil type. Values for the Compton series were obtained from one sample at each depth. The mean concentration over the full 1 metre sample depth is also given.

Table B1: Sampling visit 1. 12 November 1992

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	22.9	0.092	0.064
Bromyard S	25-50	17.6	0.042	
Bromyard S	50-100	14.9	0.061	
Bromyard	0-25	24.2	0.123	0.046
Bromyard	25-50	23.6	0.011	
Bromyard	50-100	19.7	0.025	
Middleton	0-25	26.6	0.313	0.087
Middleton	25-50	24.3	0.016	
Middleton	50-100	19.1	0.010	
Compton	0-25	33.3	0.090	0.054
Compton	25-50	23.2	0.005	
Compton	50-100	21.2	0.060	

Mean of full depth concentrations 0.063±0.018 ppm

Table B2: Sampling visit 2. 26 November 1992

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	24.3	0.069	0.022
Bromyard S	25-50	20.4	0.015	
Bromyard S	50-100	12.9	<0.003	
Bromyard	0-25	27.8	0.131	0.042
Bromyard	25-50	19.4	0.023	
Bromyard	50-100	18.2	0.007	
Middleton	0-25	27.4	0.078	0.021
Middleton	25-50	24.6	0.003	
Middleton	50-100	20.2	<0.003	
Compton	0-25	31.3	0.042	0.012
Compton	25-50	27.5	<0.003	
Compton	50-100	21.9	<0.003	

Mean of full depth concentrations 0.024±0.013 ppm

Table B3: Sampling visit 3. 14 December 1992

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	24.6	0.131	0.034
Bromyard S	25-50	19.6	0.003	
Bromyard S	50-100	13.7	<0.003	
Bromyard	0-25	26.5	0.130	0.038
Bromyard	25-50	23.7	0.007	
Bromyard	50-100	15.5	0.008	
Middleton	0-25	29.5	0.021	0.010
Middleton	25-50	27.0	0.011	
Middleton	50-100	20.3	0.004	
Compton	0-25	34.3	0.079	0.022
Compton	25-50	29.2	0.006	
Compton	50-100	21.1	<0.003	

Mean of full depth concentrations 0.026±0.013 ppm

Table B4: Sampling visit 4. 7 January 1993

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	24.4	0.117	0.066
Bromyard S	25-50	23.1	0.038	
Bromyard S	50-100	16.8	0.054	
Bromyard	0-25	28.0	0.116	0.049
Bromyard	25-50	23.1	0.045	
Bromyard	50-100	14.7	0.018	
Middleton	0-25	30.9	0.059	0.020
Middleton	25-50	28.3	0.010	
Middleton	50-100	25.3	0.005	
Compton	0-25	32.2	0.023	0.014
Compton	25-50	26.9	0.008	
Compton	50-100	22.6	0.012	

Mean of full depth concentrations 0.037±0.025 ppm

Table B5: Sampling visit 5. 10 February 1993

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	23.3	0.060	0.020
Bromyard S	25-50	19.5	0.011	
Bromyard S	50-100	13.3	0.004	
Bromyard	0-25	28.2	0.088	0.027
Bromyard	25-50	22.4	0.008	
Bromyard	50-100	17.0	0.006	
Middleton	0-25	29.0	0.112	0.041
Middleton	25-50	24.0	0.015	
Middleton	50-100	20.7	0.019	
Compton	0-25	32.0	0.103	0.027
Compton	25-50	30.4	<0.003	
Compton	50-100	21.6	<0.003	

Mean of full depth concentrations 0.029±0.009 ppm

Table B6: Sampling visit 6. 2 March 1993

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	22.4	0.106	0.043
Bromyard S	25-50	20.7	0.023	
Bromyard S	50-100	16.9	0.022	
Bromyard	0-25	27.1	0.068	0.025
Bromyard	25-50	23.4	0.007	
Bromyard	50-100	18.7	0.013	
Middleton	0-25	26.7	0.166	0.062
Middleton	25-50	24.4	0.018	
Middleton	50-100	20.3	0.031	
Compton	0-25	30.3	0.165	0.065
Compton	25-50	30.5	0.015	
Compton	50-100	21.8	0.040	

Mean of full depth concentrations 0.049±0.019 ppm

Results of Chlorpyrifos analysis

Soil levels in Foxbridge and Longlands following application in Spring 1993

For the first three soil types (Bromyard shallow, Bromyard and Middleton), three different sites were sampled over three depth increments; the three samples for each depth were pooled before analysis to give one value for each depth and soil type. Values for the Compton series were obtained from one sample at each depth. The mean concentration over the full 1 metre sample depth is also given.

Table B7: Sampling visit 1. 24 March 1993

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	20.4	0.086	0.053
Bromyard S	25-50	19.3	0.012	
Bromyard S	50-100	17.3	0.057	
Bromyard	0-25	21.9	0.170	0.058
Bromyard	25-50	19.3	0.039	
Bromyard	50-100	16.9	0.011	
Middleton	0-25	25.5	0.127	0.059
Middleton	25-50	24.4	0.038	
Middleton	50-100	19.3	0.035	
Compton	0-25	29.5	0.366	0.139
Compton	25-50	27.0	0.104	
Compton	50-100	19.2	0.042	

Mean of full depth concentrations 0.077±0.041 ppm

Table B8: Sampling visit 2. 22 April 1993

Soil type	Depth (cm)	Moisture content (%)	Conc (ppm wet weight)	Conc over 1m (ppm)
Bromyard S	0-25	18.8	0.146	0.046
Bromyard S	25-50	18.9	0.017	
Bromyard S	50-100	14.6	0.011	
Bromyard	0-25	22.7	0.136	0.058
Bromyard	25-50	23.9	0.022	
Bromyard	50-100	18.7	0.037	
Middleton	0-25	23.8	0.026	0.036
Middleton	25-50	21.5	0.021	
Middleton	50-100	17.8	0.048	
Compton	0-25	24.5	0.068	0.098
Compton	25-50	21.3	0.040	
Compton	50-100	21.4	0.142	

Mean of full depth concentrations 0.060±0.027 ppm

Appendix 9

Table A1. Routine Samples Spring 1992 to Spring 1993
Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Simazine (µg/l)	Atrazine (µg/l)	Isoproturon (µg/l)	Trifluralin (µg/l)	Chlorpyriphos (µg/l)
10-Nov-92				1.02	
25-Nov-92				1.73	
30-Nov-92				1.09	
08-Dec-92			3.0		
22-Dec-92	0.08	0.21	77.0	LT 0.08	
06-Jan-93			112.0		
16-Mar-93	0.10	0.68	3.7		LT 0.05
14-Apr-93	0.07	0.21	7.0		0.06
27-Apr-93	0.10	0.71	5.5		0.08
12-May-93					LT 0.06

Table A2. Routine Samples Spring 1992 to Spring 1993

Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Simazine (µg/l)	Atrazine (µg/l)	Isoproturon (µg/l)	Aldicarb (µg/l)	Carbofuran (µg/l)	Trifluralin (µg/l)	Chlorpyriphos (µg/l)
07-Jul-92	1.63	3.00	21.00	LT 0.2	LT 0.1		
21-Jul-92	2.10		7.50	LT 0.2	LT 0.1		
05-Aug-92	1.16		21.00	LT 0.2	LT 0.1		
18-Aug-92	1.04		10.60	LT 0.2	LT 0.1		
01-Sep-92				LT 0.2	LT 0.1		
29-Sep-92			8.80	LT 0.2	LT 0.1		
13-Oct-92	0.40	1.02	8.80	LT 0.2			
29-Oct-92	0.31	0.58	4.10	LT 0.2			
10-Nov-92			5.80			LT 0.08	
25-Nov-92						LT 0.08	
30-Nov-92						0.17	
08-Dec-92			3.70				
22-Dec-92	1.20	0.30	5.10			LT 0.08	
06-Jan-93			13.40				
16-Mar-93	0.35	0.60	2.60				LT 0.05
30-Mar-93	0.30	0.54	2.90				LT 0.05
14-Apr-93	1.30	0.23	1.35				LT 0.05
27-Apr-93	0.59	1.63					LT 0.04
12-May-93							LT 0.05
25-May-93			4.00				LT 0.05
08-Jun-93			5.50				LT 0.05

Table A3. Autumn 1992 Event: 11 November 1992

Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Trifluralin (µg/l)
	23:50	1.0	0.16	
11-Nov-92	00:20		0.22	
	00:50	2.5	0.16	
	01:20		0.22	
	01:50	5.0	0.16	
	02:20		0.22	
	02:50	0.5	0.27	
	03:20		0.40	
	03:50	0.5	0.34	14.12
	04:20		0.34	8.86
	04:50	1.0	0.34	11.25
	05:20		0.34	3.90
	05:50	0.0	0.34	2.60
	06:20		0.27	
	06:50	0.0	0.27	2.50
	07:20		0.27	1.80
	07:50	0.0	0.27	
	08:20		0.27	1.30
	08:50	0.0	0.22	1.10
	09:20		0.27	1.00
	09:50	0.0	0.27	0.90
	10:20		0.22	0.90
	10:50	0.0	0.22	
	11:20		0.16	0.60
	11:50	0.0	0.22	0.60
	12:20		0.16	
	12:50	0.0	0.16	0.50
	13:20		0.16	
	13:50	0.0	0.22	
	14:20		0.16	0.40
	14:50	0.0	0.16	0.40

Table A4. Autumn 1992 Event: 11 November 1992

Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time (mm)	Rain (l/s)	Flow (l/s)	Trifluralin (µg/l)
	00:00	1.0		
11-Nov-92	01:00	2.5	7.96	
	02:00	5.0	9.06	
	03:00	0.5	10.61	0.13
	04:00	0.5	36.58	0.10
	05:00	1.0	48.27	0.13
	06:00	0.0	43.02	LT 0.08
	07:00	0.0	40.52	LT 0.08
	08:00	0.0	36.00	LT 0.08
	09:00	0.0	32.46	0.24
	10:00	0.0	29.31	0.37
	11:00	0.0	26.56	0.16
	12:00	0.0	24.42	LT 0.08
	13:00	0.0	22.89	LT 0.08
	14:00	0.0	20.86	LT 0.08
	15:00	0.0	19.88	LT 0.08
	16:00	0.0	19.88	LT 0.08
	17:00	0.0	17.97	LT 0.08
	18:00	0.5	16.56	LT 0.08
	19:00	0.5	16.11	LT 0.08
	20:00	0.0	16.11	LT 0.08
	21:00	0.0	15.21	LT 0.08
	22:00	0.0	16.11	LT 0.08
	23:00	0.0	13.89	LT 0.08

Table A5. Autumn 1992 Event: 15 November 1992

Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Trifluralin (µg/l)
14-Nov-92	21:50	0.5	0.22	
	22:20		0.22	
	22:50	1.5	0.22	
	23:20		0.27	
	23:50	0.5	0.22	
	00:20		0.27	
15-Nov-92	00:50	1.0	0.34	2.20
	01:20		0.34	1.35
	01:50	0.0	0.34	0.89
	02:20		0.40	1.49
	02:50	0.0	0.47	1.33
	03:20		0.47	1.05
	03:50	0.0	0.47	0.83
	04:20		0.40	0.69
	04:50	0.0	0.40	0.59
	05:20		0.40	0.57
	05:50	0.0	0.40	0.42
	06:20		0.40	0.37
	06:50	0.0	0.34	0.40
	07:20		0.34	0.34
	07:50	0.0	0.34	0.33
	08:20		0.34	0.29
	08:50	0.0	0.34	0.27
	09:20		0.40	0.20
	09:50	0.0	0.40	0.29

10:20		0.34	0.24
10:50	1.0	0.34	0.20
11:20		0.34	0.23
11:50	0.0	0.34	0.18
12:20		0.34	0.25
12:50	0.0	0.34	0.62
13:20		0.34	2.20
13:50	0.0	0.34	0.18

Table A6. Autumn 1992 Event: 15 November 1992

Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Trifluralin (µg/l)
14-Nov-92	16:00	0.0	13.0	
	17:00	0.0	13.0	
	18:00	0.0	13.0	
	19:00	0.5	13.0	
	20:00	0.0	13.0	
	21:00	0.0	13.0	
	22:00	0.5	13.0	
	23:00	1.5	13.0	
15-Nov-92	00:00	0.5	13.0	
	01:00	1.0	14.8	
	02:00	0.0	22.4	
	03:00	0.0	24.4	0.08
	04:00	0.0	24.4	0.08
	05:00	0.0	24.4	0.08
	06:00	0.0	24.4	LT 0.08
	07:00	0.0	24.4	LT 0.08
	08:00	0.0	20.4	LT 0.08
	09:00	0.0	20.4	LT 0.08
	10:00	0.0	20.4	LT 0.08
	11:00	1.0	18.4	LT 0.08
	12:00	0.0	18.4	LT 0.08
	13:00	0.0	18.4	LT 0.08
	14:00	0.0	18.4	LT 0.08
	15:00	0.0	16.6	LT 0.08
	16:00	0.0	16.6	LT 0.08

	17:00	0.0	16.6	LT 0.08
	18:00	0.0	16.6	LT 0.08
	19:00	0.0	16.6	LT 0.08
	20:00		16.6	LT 0.08
	21:00		16.6	LT 0.08
	22:00		16.6	LT 0.08
	23:00		16.6	LT 0.08
	00:00		16.6	LT 0.08
	01:00		16.6	LT 0.08

Table A7. Autumn 1992 Event: 25 November 1992

Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Trifluralin (µg/l)
25-Nov-92	12:00	1.0	0.92	
	12:30		0.92	
	13:00	1.5	1.09	
	13:30		0.92	
	14:00	0.5	1.17	
	14:30		1.43	
	15:00	1.5	1.71	
	15:30		1.80	
	16:00	2.5	1.90	
	16:30		2.49	
	17:00	3.0	3.90	
	17:30		5.32	
	18:00	2.5	6.07	
	18:30		6.20	
	19:00	1.0	6.20	
	19:30		5.94	
	20:00	0.5	5.08	
	20:30		4.48	
	21:00	0.5	3.68	
	21:30		3.23	
	22:00	0.0	2.91	
	22:30		2.60	
	23:00	0.5	2.29	
	23:30		1.99	
26-Nov-92	00:00	0.0	1.90	
	00:30		1.71	
	01:00	0.0	1.62	

01:30		1.52	
02:00	0.0	1.62	
02:30		1.26	
03:00	0.0	1.17	
03:30		1.09	
04:00	0.0	1.17	
04:30		1.09	
05:00	1.5	1.09	
05:30		1.26	
06:00	0.5	1.26	
06:30		1.26	
07:00	0.0	1.17	
07:30		1.17	
08:00	0.0	1.17	
08:30		1.09	
09:00	0.0	1.00	
09:30		1.00	
10:00	0.0	1.00	
10:30		1.00	
11:00	0.0	1.09	
11:30		0.84	
12:00	0.0	0.84	0.35
12:30		0.92	0.31
13:00	0.0	0.84	0.38
13:30		0.76	0.38
14:00	0.5	0.76	0.34
14:30		0.84	0.26
15:00	0.0	0.84	0.27
15:30		0.76	0.44
16:00	0.0	0.84	0.52
16:30		0.69	1.01
17:00	0.0	0.69	0.85

17:30		0.76	0.81
18:00	0.0	0.69	0.74
18:30		0.61	0.21
19:00	0.0	0.61	0.24
19:30		0.61	0.23
20:00	0.0	0.61	0.20
20:30		0.61	0.20
21:00	0.0	0.61	0.16
21:30		0.61	0.16
22:00	0.0	0.61	0.18
22:30		0.54	0.16
23:00	0.0	0.50	0.18
23:30		0.50	0.15

Table A8. Autumn 1992 Event: 16 December 1992

Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Trifluralin (µg/l)	Isoproturon (µg/l)
16-Dec-92	00:15		0.16		
	00:45	0.0	0.22		
	01:15		0.22		
	01:45	0.0	0.16		
	02:15		0.22		
	02:45	0.0	0.16		
	03:15		0.22		
	03:45	0.5	0.22		
	04:15		0.22		
	04:45	0.0	0.22		
	05:15		0.16		
	05:45	0.5	0.27		
	06:15		0.22		
	06:45	0.0	0.16		
	07:15		0.22		
	07:45	1.5	0.22		
	08:15		0.22	LT 0.32	123.00
	08:45	2.5	0.27	0.22	30.00
	09:15		0.40	0.15	143.00
	09:45	2.5	0.61	0.08	220.00
	10:15		0.47	0.11	12.20
	10:45	1.5	0.69	LT 0.08	134.00
	11:15		0.69	0.08	210.00
	11:45	0.0	0.61	0.12	125.00
	12:15		0.54	0.09	210.00
	12:45	0.0	0.47	0.08	220.00

13:15		0.40	0.11	230.00
13:45	0.0	0.34	0.23	190.00
14:15		0.34	0.21	240.00
14:45	0.0	0.34	0.17	275.00
15:15		0.34	0.19	270.00
15:45	0.0	0.34	0.20	245.00
16:15		0.34	0.14	340.00
16:45	0.0	0.34	0.17	330.00
17:15		0.27	0.17	320.00
17:45	0.0	0.27	0.17	270.00
18:15		0.22	0.19	260.00

Table A9. Spring 1993 Event: 07 April 1993

Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Chlorpyriphos (µg/l)	Isoproturon (µg/l)
07-Apr-93	00:00	0.5			
	01:00	1.5			
	02:00	2.5			
	03:00	2.0	0.06		
	04:00	2.0	0.06		
	05:00	0.5	0.11		
	06:00	1.0	0.06	2.90	2.40
	06:30		0.06	2.00	2.40
	07:00	0.5	0.06	1.88	0.92
	07:00		0.06	1.57	3.00
	08:00	0.5	0.06	1.16	2.60
	08:30		0.06	1.95	3.60

Table A10. Spring 1993 Event: 09 April 1993

Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Chlorpyriphos (µg/l)
09-Apr-93	00:00	0.50	4.2	
	01:00	1.00	5.1	
	02:00	0.50	6.1	
	03:00	0.00	6.5	
	04:00	1.50	4.9	
	05:00	3.50	4.8	
	06:00	2.50	15.5	LT 0.05
	07:00	0.50	33.4	LT 0.05
	08:00	1.00	47.8	LT 0.05
	09:00	0.50	38.2	LT 0.05
	10:00	0.00	31.5	LT 0.05
	11:00	0.00	29.8	LT 0.05
	12:00	0.00	28.0	LT 0.05
	13:00	0.00	24.2	LT 0.05
	14:00	0.00	21.6	LT 0.05
	15:00	0.00	20.1	LT 0.05
	16:00	0.00	20.1	LT 0.05
	17:00	0.00	17.6	LT 0.05
	18:00	0.00	17.6	
	19:00	0.00	14:8	
	20:00	0.00	12.2	
	21:00	0.00	12.2	
	22:00	0.00	12.6	
	23:00	0.00	11.8	

Table A11. Spring 1993 Event: 26 April 1993

Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Chlorpyriphos (µg/l)
26-Apr-93	12:00	0.0	6.7	
	13:00	0.0	6.7	
	14:00	0.0	6.4	
	15:00	0.5	6.1	
	16:00	4.0	6.7	
	17:00	0.0	9.5	
	18:00	0.0	14.9	LT 0.05
	19:00	0.0	8.6	LT 0.05
	20:00	0.0	6.7	LT 0.05
	21:00	0.0	6.4	LT 0.05
	22:00	0.0	6.7	LT 0.05
	23:00	0.0	6.1	LT 0.05
27-Apr-93	00:00	0.0	5.7	LT 0.05
	01:00	0.0	6.4	LT 0.05
	02:00	0.0	5.4	LT 0.05
	03:00	0.0	6.4	LT 0.05
	04:00	0.0	5.7	LT 0.05
	05:00	0.0	5.7	LT 0.05

Evaluation of Fate and Exposure Models*

Appendix X

Simulation of Pesticide Runoff at Rosemaund Farm (UK) Using the SoilFug Model**

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* For the preface of this series see ESPR No. 2/1994, p. 93

Abstract

A validation exercise of the SoilFug model using field runoff data from Rosemaund Farm (UK) is described. A comparison has been made of modelled and measured concentrations of several pesticides in surface water and soil during and after specific rain events following application. The field experiments were designed to obtain data on rainfall, outflows of water, pesticide application rates and concentrations in soil and water. The results were satisfactory for the undissociated pesticides (atrazine, carbofuran, dimethoate, isoproturon, lindane, simazine and trifluralin), whose concentrations in water were mostly predicted within an order of magnitude of measured data. The results for the dissociated pesticides (dichlorprop, MCPA, mecoprop) were less satisfactory, giving generally much higher predicted concentrations in water. The use of the SoilFug model is suggested for the calculation of predicted environmental concentrations (PECs) in water, since it generally produces acceptable results from a relatively small set of input data, most of which is generally available.

1 Introduction

Pesticides may contaminate surface water and cause effects on non target organisms (ecotoxicological damage) or have the potential to contaminate water for drinking purposes.

Generally the environmental residues data available are few and are often very site and situation specific (i.e. there are difficulties in generalising the results). In any case, such data are only available after a product has entered general use.

There is therefore a need for computerized models of pesticide runoff which can be applied predictively to products for which few environmental data are yet available. These could assume great importance for regulatory purposes where the predicted exposures of aquatic life which result from leaching and run-off are poorly modelled at present.

Modelling efforts are however generally too simplistic (predicting average distributions in model worlds) or too complex (huge amount of input data required). Often the environmental data for testing and/or calibration of the models are not available or applicable.

The SoilFug model, (Di Guardo et al. 1994) follows a middle path because, while simple in terms of data requirements and ease of use (user-friendly Windows™ program), it attempts to predict average pesticide concentrations in streamwater following particular rainfall events in given scenarios. It also facilitates the comparison of chemicals having different properties. The purpose of this paper is to report a validation exercise with this model using field data from Rosemaund Farm, UK.

2 Materials and Methods

2.1 Study Site

The study catchment lies mainly within the boundaries of Agricultural Development and Advisory Service (ADAS) Rosemaund, 15 km north east of Hereford, UK, near the England/Wales border.

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 km² with an altitude range of 76 m to 115 m and correspondingly gentle slopes. The soils are from two series, the Bromyard and the Middleton and have been mapped and analyzed by the Soil Survey and Land Research Centre (Hodgeson 1989). The Bromyard series predominates and is found on the slope areas of the catchment. The wetter Middleton series tends to occur on flatter ground and towards the lower end of the slopes. The soil texture is silt clay loam in the top 60 cm changing to silt loams below this depth, the largest clay fraction being between 25 and 60 cm below the surface. The soil is subject to considerable cracking following periods of low rainfall during the summer months. The organic matter content of the surface 25 cm

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cultivated layer under long term arable cropping is within the range of 1 – 3 per cent with little organic matter present below 35 cm. The geology is made up of effectively impermeable siltstones and mudstones which lie between 1 m and 3 m below the surface.

Under-drained soils of this type, where by-pass flow is an important component of the hydrological regime, probably constitute a reasonable worst case for pesticide transfer to surface waters, and are representative of about 28 % of agricultural soils in the UK (HOLLIS 1993, personal communication). The land within Rosemaund Farm *(→ Fig. 1)* 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 catchment rainfall is 664 mm. The catchment is drained by a single stream that continues to flow in all but the driest years. Most of the fields have been 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.

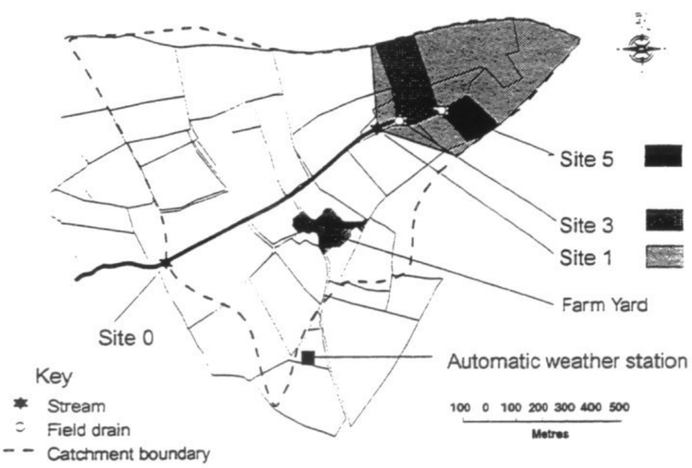


Fig. 1: Location of the sampling sites within the Rosemaund catchment. Shading indicates areas draining to corresponding sampling sites. Site 0 drains the entire area within the catchment boundary

2.2 Environmental Data

Soil data

The soils within ADAS Rosemaund have been mapped and described by the Soil Survey of England and Wales. There are four soil series present, Bromyard normal phase, Bromyard Shallow phase, Middleton and Compton. The Bromyard normal phase series predominates and details of its physical characteristics are given in **Table 1**; details of the complete survey are available elsewhere (CARTER and BEARD 1992).

The soil water regime present in one field within the farm was monitored through several seasons principally using arrays of mercury manometer tensiometers and neutron probe access tubes. These instruments were distributed as a profile along a drainage element i.e. from mid drain across the drain to the next mid drain position. Details of the instrumentation and experiments carried out are given elsewhere (HACK 1992). Combination of water content measurements from the neutron probe and matrix potentials from the tensiometers allowed the construction of water release curves for different depths. These data were used for deriving the volumes used in the model compartments (see below).

Table 1: Physical characteristics of the soil at Rosemaund Farm

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	$CaCO_3$ Equiv.	pH in water (1:2.5)
0 – 30	9	60	31	0.10	6.3
30 – 48	10	58	32	0.00	6.8
48 – 67	5	52	43	0.01	6.7
67 – 83	4	50	46	0.06	6.7

Stream flow

Within the catchment four monitoring sites were instrumented (sites 0,1,3, and 5; *Fig. 1.*). At each site flowrate was measured continuously, using standard V-shaped or rectangular notch weirs. Details of the methods used for flow measurement and water sampling are given elsewhere (MATTHIESSEN et al. 1992). Rainfall data were obtained from an Automatic Weather Station, (STRANGEWAYS 1972), as hourly totals (see *Fig. 1* for location).

Water samples

Water samples were taken from sites 0,1,3, and 5 as indicated in Fig. 1. 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 one of two types of automatic water samplers, a suction sampler and a peristaltic pump sampler. Both samplers collected drain or stream water 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 which started the sampler when the stream rose to a specified level was employed. The latter has proved more reliable. Water samples were generally collected within 24 hours and stored in the dark at below 4 °C for a maximum of 10 days prior to extraction and analysis.

Soil samples

Soil samples were taken from the fields onto which the pesticides had been applied at randomly chosen points on the intersects of a 25 m grid superimposed on the fields. They 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 analyzed. The frequency of the 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 bulked to give a mean soil pesticide concentration in the top 1 m of the soil.

2.3 Chemicals

The selected physico-chemical properties of the investigated pesticides are reported in Table 2.

The data were generally selected from the literature, with the exception of the halflife of isoproturon, the value for which was derived from a half life extrapolation of soil concentration data from Rosemaund Farm (WILLIAMS et al. 1991). Measured Koc values from the literature were employed for the simulation (the Log Kow and the corresponding Koc calculated by means of Karickhoff's equation (KARICKHOFF 1981) are reported for comparison). A value of Koc = 20 was employed for some simulations of the phenoxy acid herbicides (dichlorprop, mecoprop, MCPA), as suggested by WAUCHOPE et al. (1992). Since no data were available for the mineral/water partition coefficient, a typically low value was assumed (Kmin = 0.01).

Soil analysis

Some of the chemicals were measured in soil, in the top one metre. A summary of the soil analytical methods is shown in Table 3.

Table 2: Selected physico-chemical properties for the investigated pesticides. The numbers in brackets refer to the literature cited

Chemical	Molecular Weight	Water Solubility (mg/L)	Vapour Pressure (Pa)	Log Kow	Koc (est)*	Koc (measured)	$t_{1/2}$ (d)
isoproturon	206.3	55 (1)	3.3E-6 (1)	2.25 (1)	73	129 (2)	20 (3)
lindane	290.85	6.5 (4)	3E-3 (4)	3.8 (4)	2587	1100 (5)	266 (6)
simazine	201.7	5 (1)	8.1E-7 (1)	1.96 (1)	37.4	130 (5)	60 (5)
mecoprop	214.6	620 (1)	3.1E-4 (7)	2.3 (2) 0.1 (pH 7) (1)	81.8 0.52	79.4 (7) 20 (5)	7 (8)
MCPA	200.6	825 (1)	2E-4 (9)	2.7 (neutral) -1 (diss.) (2)	204 0.041	20 (5)	7 (8)
dichlorprop	235.07	350 (9)	< 1E-5 (5)			20 (5)	10 (5)
atrazine	215.7	30 (1)	4E-5 (4)	2.34 (1)	89.8	122 (10)	60 (5)
carbofuran	221.25	351 (5)	1.5E-3 (4)	1.6 (4)	16	22 (5)	50 (5)
dimethoate	229.2	25000 (1)	1E-3 (1)	0.8 (4)	3.9	20 (5)	7 (5)
trifluralin	335.38	0.5 (4)	0.006 (4)	5.07 (1)	48380	8000 (5)	60 (5)

Notes: Kow = octanol/water partition coefficient; Koc = soil organic carbon adsorption coefficient; $t_{1/2}$ = half life in soil

* = "est" is referred to the Koc estimated by means of the Karickhoff's equation Koc = Kow · 0.41 (KARICKHOFF 1981)
(1) = WORTHING and HANCE (1991); (2) JOICE (1990); (3) Fitted from Rosemaund Field Data; (4) SUNTIO et al. (1988)
(5) WAUCHOPE et al. (1992); (6) JURY et al. (1984); (7) BROOKE and MATTHIESSEN (1991);
(8) HOWARD et al. (1991); (9) KIDD and JAMES (1991); (10) HOWARD (1991)

Table 3: Soil analytical methods used at Rosemaund

Chemical	Extraction	Clean Up/Derivatization	Quantification Method (Final Solvent)
isoproturon	acetone/water	hexane wash, extraction into dichloromethane	HPLC, UV detector (methanol/water)
simazine	water/methanol	acidified hexane wash, extracted into dichloromethane	GC, NP detector (ethyl acetate)
mecoprop	acidified, dichloromethane	reaction with BrPFT, ectraction into iso-octane	GC, EC detector (iso-octane)
MCPA	acidified, dichloromethane	reaction with BrPFT, extraction into iso-octane	GC, EC detector (iso-octane)

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

Water analysis

The water samples for chemical analysis were taken during rainfall events following pesticide application and less frequently between events. The analyses were performed according to the summary of Table 4.

Table 4: Water analytical methods used at Rosemaund

Chemical	Extraction	Quantification	Detection Limit (µg/l)	Extraction Efficiency (%)
isoproturon	dichloromethane	RP-HPLC	0.01	95
lindane	hexane	GC-ECD	0.001	102
simazine	dichloromethane	GC-MS	0.1	80
mecoprop	C_{18}SPE	HPLC	0.2	82
MCPA	C_{18}SPE	HPLC	0.02	78
dichlorprop	C_{18}SPE	HPLC	0.2	81
atrazine	C_{18}SPE	GC-MS	0.01	71
carbofuran	dichloromethane	GC-NPD	0.01	91
dimethoate	dichloromethane	GC-NPD	0.02	91
trifluralin	dichloromethane	HPLC	0.08	77

Notes: HPLC = high pressure liquid chromatography
GC = gas liquid chromatography
ECD = electron capture detector
MS = mass spectrometer
NPD = nitrogen phosphorus detector
C_{18}SPE = C_{18} solid phase extraction cartridges

2.4 Model Description

The SoilFug model is essentially an unsteady-state but equilibrium event model. This is because it takes into account the disappearance of the chemical according to different phenomena (degradation, volatilization, runoff), but then derives the partition among the different phases of the soil according to a Level I fugacity calculation (MACKAY 1979; MACKAY and PATERSON 1981) in specific periods of time, i.e. the rain events. Full description of the model is given in DI GUARDO et al. (1994). Briefly, the model considers four different compartments in the soil: soil air, soil water, organic matter and mineral matter. For each of these compartments a capacity (Z) can be calculated and therefore, the fugacity can be calculated, once the volume and the chemical input are known. From the fugacity, amounts and concentrations in each compartment can be deduced. The model calculates soil and outflowing water concentrations at each rain event, which is defined as the period of time starting with the rainfall and ending when the water outflowing from the basin returns to the normal background conditions. The soil and water concentrations are therefore a sort of average concentration of the whole event. The concept of a rain event greatly simplifies the modelling exercise, since few calculations are necessary. In contrast, most unsteady-state models perform day-by-day simulation, requiring large amounts of data. In the case of a rain event, the SoilFug model needs only rainfall and outflow data. The model does not precisely calculate a water balance and therefore is not appropriate for the estimation of infiltration of water and consequent leaching. The soil is regarded as one layer and its depth must be determined when evaluating the properties of the soil.
The SoilFug model has been developed and validated by comparing its results with two field experiments conducted in Northern Italy. The basins were two flat areas (300 and 1700 ha) hydraulically isolated (i.e. they did not receive water from the outside, except, of course, from rainfall) and according to their soil properties, the average depth of the soil was set to 30 cm, resulting from the average infiltration of the water before reaching the surface canals and then the outflow. For the simulation conducted comparing predictions with Rosemaund farm data, the average depth of the soil was set to 50 cm, which is considered the average travel length of the water before reaching the drains. This depth may appear excessive, but it must be regarded as the maximum available distance allowed to the water before leaving the pesticide-containing soil.
The other input data of the model are the physico-chemical properties of the chemicals (molecular weight, water solubility, vapour pressure, Koc, mineral/water partition coefficient, when available), the degradation half-life in soil, some soil characteristics, (temperature, air and water fraction in soil at field capacity, organic carbon content), rainfall/outflows data (number of rain events, rainfall and outflow amounts for each rain event, duration of the rain events and duration of the period between rain events) and data concerning the treated areas and the application rates.

Each simulation has a "before rain event" and a "during rain event" period. In the first, only degradation and volatilization are calculated (as no water is outflowing) and in the second, runoff is also taken into account as a disappearance phenomenon. At the end of each "during rain event" period a fugacity calculation is performed and the concentrations in each soil compartment are deduced. Multiple areas may be treated at different times, since the model performs single sets of calculations for each of them. A total outflowing water concentration for the catchment in question is then obtained and the result is displayed in tabular or chart format.

The soil is considered at field capacity in the "between rain event" periods, a condition necessary to keep the model simple. This is generally valid for winter conditions in Northern Europe (as in these simulations). In the "during rain event" periods the air and water fraction are calculated according to the saturation of the porosity caused by the incoming water.

Table 5 shows the derivation of the selected organic carbon content used in the simulation. It is a weighted average of the data available for topsoil and upper subsoil. The single value is necessary for the reasons outlined above. This may lead to an underestimation of the sorptive potential of the upper layer, but greatly simplifies the calculation.

The volumes of soil air and soil water are calculated from the product of the air and water volume fractions in the soil at field capacity and the soil volume. The water volume fraction was estimated from the water retention curves assuming field capacity represented by a matrix potential of – 100 cm of water (Marshall and Holmes 1988). The air volume fraction was taken as the total porosity (matrix potential 0 cm of water) minus the water volume fraction. Water release curves were available at 10 and 30 cm and the volume fractions used in the model were taken as a simple average of the volume fractions estimated from the two curves (→ *Table 6*).

Table 5: Selected organic carbon content of Rosemaund Soil

Layer	Depth (cm)	Organic Carbon (%)	
		Actual	W. A.
Topsoil	0 – 30	1.66	
			1.36
Upper Subsoil	30 – 48	0.91	

Notes: W. A. = Weighted Average: obtained using a weight of 0.6 for Topsoil and 0.4 for Upper Subsoil

Table 6: Selected porosity for the simulation

Depth (cm)	Porosity (%)				
	Total	Water		Air	
		Actual	Avg.	Actual	Avg.
10 cm	47	35		12	
			38.5		8.5
30 cm	47	42		5	

3 Results and Discussion

The model was run, according to the environmental scenario outlined above for the chemicals listed in Table 2. The different pesticides were applied on the areas described previously at different application rates. Sites, areas, rates, rain events, measured (minimum/maximum and average values) and modelled concentrations are reported in Table 7 (neutral or undissociated pesticides) and Table 8 (phenoxy acid pesticides). The results are grouped with respect to application of a given pesticide to a site. In certain cases the applications were repeated once or twice on the same site. Tables 7 and 8 report only the modelled concentrations for which measured data were available. Full data are reported by Bird et al. (1991), Brooke and Matthiessen (1991), Hack (1992), Matthiessen et al. (1992), Matthiessen et al. (1993), Williams et al. (1991 a) and Williams et al. (1991 b).

Some general observations can be made on the 59 events reported in Table 7, for the neutral or undissociated pesticides. Good overall agreement between observed (measured) and simulated (modelled) data is shown. The goal of the modelling exercise being to predict observed values to within a factor of 10 it can be noted that 45 cases satisfy this condition (76 %). In 14 cases predictions and observations differ by more than a factor of ten (24 %), and only 3 differ by more than a factor of 100. The overall tendency of the model is to overpredict the measured average values, predictions being generally within a factor of 3 of maximum concentrations. This characteristic can be considered a positive feature, because it can be assumed to be a worst-case scenario for a given chemical and is therefore protective of the environment, but not excessively overprotective when used in risk predictions. The average values calculated by the model tend to become "instantaneous" concentrations when the duration of the rain events is shortened to 1 or 2 days. In these situations, the variability related to the partitioning between the chemical in soil and the incoming water increases, leading to larger errors. Only in 5 cases has the model underpredicted the measured results, in three of them with a difference of a factor of two or three. However, all the underpredictions were within an order of magnitude of the observations.

The picture obtained from the analysis of the data in Table 8 (phenoxy acid herbicide simulations) is slightly different from that which emerged from Table 7. Only one modelled value is close to the measured one, while the others are between one and two orders of magnitude higher than the measured data. These results are quite surprising, since the physico-chemical properties of these chemicals (high solubility, low soil adsorption in the dissociated form) may lead one to expect higher concentrations in surface water. The Koc chosen for the simulations (Koc = 20) was that proposed by Wauchope et al (1992) for chemicals present in dissociated, anionic form at environmental pH. This is the case for the phenoxy acid herbicides, whose low pKa predicts the almost complete dissociation of the chemicals. However, the modelling of these chemicals by the fugacity approach is not appropriate, since no appreciable vapour pressure could be properly defined for the dissociated form and therefore neither can the value of Henry's Law constant.

Some measured and modelled concentrations of the investigated pesticides in soil are shown in Fig. 2.

The comparison of measured and modelled soil concentrations confirms the general tendency of the SoilFug model to overpredict the observed values, usually by a factor of two or three. An exception is the case of mecoprop (Site 1 87/88) where the modelled concentration is about four times the measured one. It must be remembered that the measured soil concentrations are an average of samples in the upper one metre of soil, while the model predictions concern the top half meter. Some graphic examples of the modelling exercise for drain and streamwater are reported in Fig. 3 and 4. Fig. 3 shows the measured and modelled concentrations of lindane, applied upstream of Site 3 in the 1989 – 90 experiment. Considering the relatively high soil adsorption of lindane, disappearance is presumed mainly to be due to degradation phenomena, rather than volatilization or runoff/leaching. The fit between measured and modelled concentrations for the first three events is excellent. The last event (at time = 140 days) shows an overprediction by the model. This may be explained by the fact that the apparent Kd for the soil seems to increase with time, as shown by Walker (1987) for a number of herbicides.

Table 7: Results of the application of the model to some pesticide runoff data from Rosemaund Farm (neutral or undissociated pesticides)

Chemical	Site	Year	2nd Appl. at day	3rd Appl. at day	Modelled area (ha)	Treated area (ha)	Rate (kg/ha)	Days from 1st Appl.	Rain Event Amount (mm)	Rain Event Runoff (mm)	Meas. Conc. min/max (µg/l)	Meas. Conc. avg. (µg/l)	Mod. Conc. (µg/l)
atrazine	0	91/92	–	–	151	5.2	2.8	20	5.5	0.1	0.06 / 1.79	0.6	6.09
			158	–		2.4	2.4	178	18	1	0.47 / 1.76	0.9	3.88
atrazine	1	91/92	–	–	35.5	5	2.8	46	72.5	14.3	0.01 / 5.67	2	17.8
			–	–				59	9	8.2	< 0.01 /13.3	1.9	15.6
			–	–				138	19	0.4	0.02 / 0.23	0.11	6.18
								181	10	0.3	< 0.01 / 0.13	0.06	3.79
atrazine	3	91/92	–	–	5.3	2.14	2.8	46	72.5	24.1	0.38 /51.3	10.6	50.8
			–	–				59	9	0.1	1.02 / 7.07	5.7	44.5
								138	19	0.2	0.09 / 0.65	0.45	17.7
								181	10	0.04	0.03 / 1.73	1.60	10.8
atrazine	5	91/92	–	–	2	2	2.8	39	4	0.3	20.25 /56.5	35.7	142
								43	67	25	3.2 /81.4	15.9	129
								138	16.5	0.1	8.7 /16.2	11.2	46.7
carbofuran	1	91/92	–	–	35.5	1	3	41	72.5	14.3	0.07 /26.78	10.4	7.99
								54	9	6.2	0.04 /37.45	6.2	7.11
								133	19	0.4	0.01 / 2.35	0.46	2.31
								178	10	0.3	< 0.01 / 0.02	0.008	1.29
carbofuran	3	91/92	–	–	5.3	1	3	41	72.5	24.1	12.24 /264	25.7	53.1
								54	9	0.1	6.13 /58.39	37.2	47.1
								133	19	0.2	< 0.01 / 9.87	1.0	15.4
								178	10	0.04	< 0.01 / 0.18	0.09	8.61
dimethoate	0	90/91			151	10	0.34	28	17.5	0.7	<0.02	< 0.02	0.42
								37	9.5	1	<0.02	< 0.02	0.143
								40	20	2	<0.02	< 0.02	0.103
	1	90/91			35.5	16	0.34	26	17.5	0.3	0.28 / 3.05	1.2	2.86
dimethoate								40	20	1.5	< 0.05 / 0.16	0.03	0.69
isoproturon	0	90/91	31	43	151	13.8/23.4/5.2	1/0.5/2.13	75	17.5	0.7	0.05 / 1.76	0.49	3.33
								86	9.5	1	0.02 / 5.19	0.36	2.28
								89	20	2	< 0.02 / 6.7	0.60	2.04

Table 7, continued

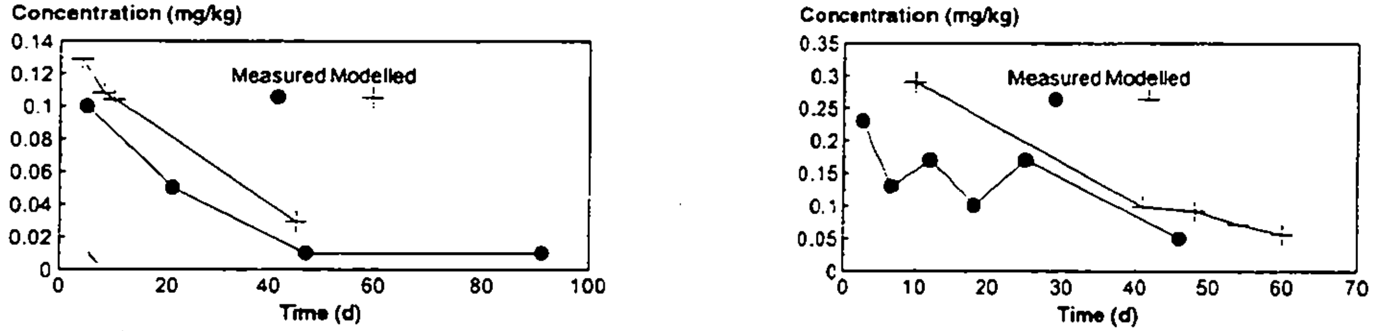
								Rain Event					
Chemical	Site	Year	2nd Appl. at day	3rd Appl. at day	Modelled area (ha)	Treated area (ha)	Rate (kg/ha)	Days from 1st Appl.	Amount (mm)	Runoff (mm)	Meas. Conc. min/max (μg/l)	Meas. Conc. avg. (μg/l)	Mod. Conc. (μg/l)
isoproturon	1	89/90	18	–	35.5	6/10	1/0.375	45	54	5.4	2.1 / 5.4	3.3	5.78
isoproturon	1	90/91	39	–	35.5	10.8/5.2	1/2.13	72	17.5	0.3	1.92 /17.2	10.6	9.46
								86	20	1.5	0.1 / 2.62	0.96	5.76
								132	11.5	1.5	0.26 / 2.07	0.92	1.17
isoproturon	3	89/90	–	–	5.34	2.14	1	8	28.5	1.5	1.2 / 8.4	4.3	22.9
								10	10.5	0.6	1.8 /13.7	6.7	21.6
			18			3.2	0.375	45	54	7.2	1.1 / 8.8	3.2	12.9
isoproturon	5	90/91	–	–	2	2	2.1	47	20	0.6	0.09 / 0.38	0.14	31.2
								91	11.5	2.9	0.02 / 2.7	1.4	6.81
								113	13.5	3.0	1.41 / 2.46	1.7	3.03
lindane	0	89/90	–	–	151	6	0.56	49	56	5.6	< 0.001/ 0.75	0.16	0.20
lindane	1	89/90	–	–	35.5	6	0.56	43	54	5.4	0.04 / 0.29	0.012	0.864
								138	9.0	0.26	0.004/ 0.03	0.011	0.668
lindane	3	89/90	–	–	5.3	2.14	0.56	6	28.5	1.5	0.04 / 4.46	1.2	2.28
								8	10.5	0.6	0.06 / 4.14	1.2	2.27
								43	54	7.2	0.016/ 0.45	0.14	2.06
								138	9	0.2	0.001/ 0.027	0.013	1.6
lindane	5	89/90	–	–	2	2	0.56	8	28.5	2.4	0.03 / 1.74	0.85	5.61
								49	56	5.6	< 0.01 / 2.55	0.57	5.03
simazine	0	88/89	70	–	151	5/3.2	1.15/1.7	79	13.5	1.6	4.4 /68	22.4	3.57
								85	11	1.0	4.5 /13.9	8.2	3.33
simazine	0	90/91	–	–	151	5.4	1.15	33	17.5	0.7	1.01 / 4.12	1.67	2.10
								44	9.5	1	0.46 / 1.49	0.9	1.85
								47	20	2	0.32 / 0.84	0.5	1.77
								107	54.5	11.2	0.1 / 0.36	0.26	0.88
			110	–	3.2	3.2	0.5	113	13.5	3	0.65 /15.3	3.30	1.58
simazine	1	88/89	–	–	35.5	5	1.15	79	13.5	1.9	< 0.1 / 1.8	0.5	4.87
trifluralin	5	92/93			2	2	1.1	5	11.5	1	0.38 /14.12	3.1	1.49
								9	9	0.85	0.18 / 2.2	0.63	1.43
								18	34.5	12	0.15 / 1.0	0.36	1.26

Notes: Meas. conc. = measured concentrations; Mod. Conc. = modelled concentrations; min/max = minimum and maximum of measured samples available for that rain event; avg. = average of all the samples available for that rain event (arithmetic mean)

Table 8: Results of the application of the model to some pesticide runoff data for Rosemaund Farm (phenoxy acid herbicides)

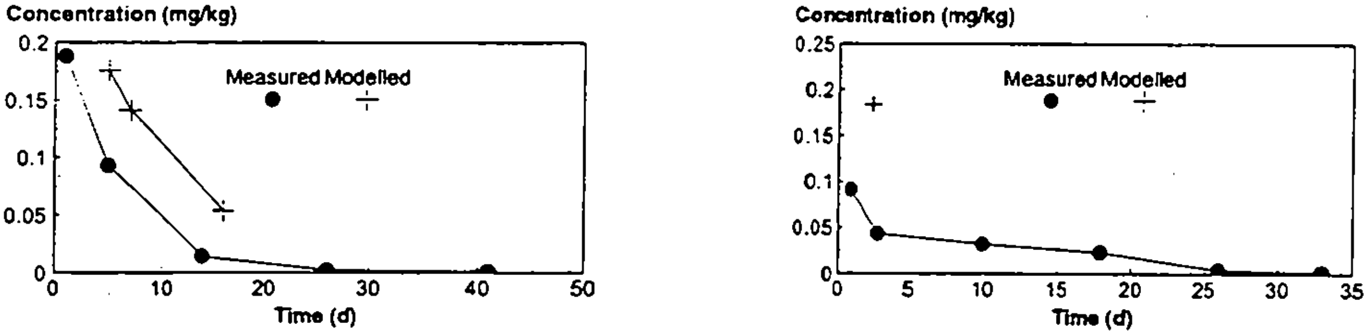
									Rain Event				
Chemical	Site	Year	2nd Appl. at day	3rd Appl. at day	Modelled area (ha)	Treated area (ha)	Rate (kg/ha)	Days from 1st Appl.	Amount (mm)	Runoff (mm)	Meas. Conc. min/max (µg/l)	Meas. conc. (µg/l)	Mod. Conc. (µg/l)
dichlorprop	1	89/90	–	–	35.5	16	2.6	55	12	0.2	< 0.2 / 1	0.35	6.93
MCPA	1	90/91	–	–	35.5	16	1.68	5	15.5	0.22	0.28 /12.44	1.90	131
								7	28	1	0.34 / 2.23	1.20	104
								16	13.5	1.3	0.27 /12.68	1.90	42.1
MCPA	3	90/91	–	–	5.3	5.3	1.68	5	15.5	1.6	0.38 /18.8	5.40	291
mecoprop	1	87/88	–	–	35.5	5.5	2	3	25	5.2	< 0.2 /11.7	4.2	60.5
mecoprop	1	89/90	–	–	35.5	16	0.65	55	12	0.2	< 0.2 / 1.4	0.30	0.343

Notes: Meas. conc. = measured concentrations; Mod. Conc. = modelled concentrations; min/max = minimum and maximum of measured samples available for that rain event; avg. = average of all the samples available for that rain event (arithmetic mean)



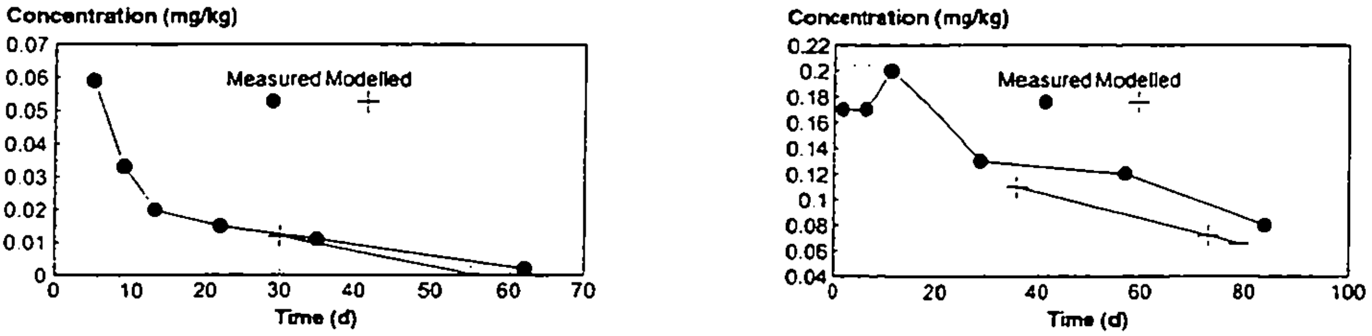
isoproturon 89/90; a.r.=1 kg/ha

isoproturon 90/91; a.r.=2.1 kg/ha



MCPA 90/91; a.r.=1.68 kg/ha

mecoprop 87/88; a.r.=2 kg/ha



mecoprop 89/90; a.r.=0.65 kg/ha

simazine 88/89; a.r.=1.15 kg/ha

Fig. 2: Concentrations of some pesticides in soil from a field upstream of Site 1. Only modelled concentrations are reported for which rain event data were available. a.r. = application rate

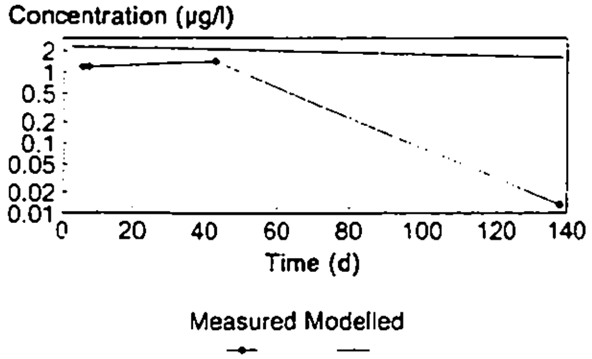


Fig. 3: Concentration of lindane in field drain water. Simulation at Site 3 (1989 – 90)

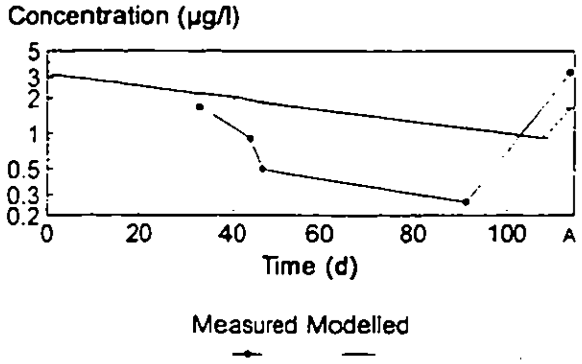


Fig. 4: Concentration of simazine in stream water. Simulation at Site 0 (1990 – 91). A = second application

A similar situation is shown in Fig. 4, where the simazine simulation for the stream at Site 0 in 1990 – 91 is presented. In this case a second application took place about 110 days after the first. The higher measured concentration at 110 days can be explained by the rainfall which occurred the day after the application in an area made almost impermeable by high level of operational "traffic". In this situation, it is reasonable to assume that the amount of soil available for partitioning was considerably reduced.

Some general observations can be made concerning evaluation of the results:

1. The model generally overpredicts the concentrations in water within an order of magnitude of accuracy (as explained above). It should, however, be remembered that no initial loss of chemical is taken into account. The loss may derive from drift during the application of the chemical or from volatilisation from the surface of the soil immediately after the application, when the chemical has not reached equilibrium with the soil.
Another cause of overprediction may be the uneven flow path of water through the soil, which prevents the pesticide coming into contact with the whole soil mass. One of the assumptions of the model is the complete mixing of the chemical with the soil phases and then an instantaneous equilibrium. Uneven mixing can be caused by preferential or by-pass flow, due to cracks or to the presence of macropores. It should also be remembered that not all the chemical in the top layer of the soil is available for mixing (LEONARD 1990); a factor between 0.05 and 0.2 has been suggested in order to take into account the so called "extraction ratio".
The assumption of the "average organic carbon content" in the soil (albeit a weighted average) may lead to an underestimation of sorption in the top layer, which in reality may bind the chemical to a greater extent, making it less available for subsequent partition with the percolating water.
Furthermore, the large available depth of soil (50 cm) assumed in the model may lead to an underestimation of the volatilization of certain chemicals, especially in the initial period after the application. Very soluble chemicals (like the weak acids) may be transported to a soil layer deeper than the surface one and therefore be less available for successive extraction of the water flowing through the soil, when considering a preferential flow path.

2. The sporadic underpredictions of the model seem more related to the specific circumstances of certain applications: for example, the case of underprediction of the simazine concentration in the simulation of Site 0 (1988 – 89) at about 80 days after the first application seems to be related to the second application. This was made to land compacted by vehicles (and therefore more impermeable) close to the sampling station, and therefore there was not enough time for dilution of the peak concentrations. The short time between treatment and rainfall may then have had the effect of reducing the amount of soil available for partition, as described earlier.

Other behaviours have to be investigated thoroughly, like the large overprediction of the concentrations of the phenoxy acids (mecoprop, dichlorprop, MCPA). Their physicochemical properties (high solubility, low Koc, low vapour pressure) show a great affinity for water, and this should result in high concentrations in the drains and stream; however the measured concentrations are at least two orders of magnitude lower than the modelled values. This could be explained assuming a higher Kd than that expected from such properties, involving perhaps different sorption mechanisms. To verify this hypothesis additional work has to be done, in particular the experimental measurement of Kd of these chemicals, since recent studies have shown that phenoxy acids may partition significantly to clays (YONG et al. 1992).

4 Conclusions

The SoilFug model has now been run in comparison with data on a total of 14 pesticides used in 3 catchments. Two catchments are in Northern Italy (DI GUARDO et al. 1994) and one is in England, but they have a number of similarities.

In particular, they all contain cracking clay soils prone to by-pass flow, and all are artificially drained. This type of agricultural situation is common in Europe and elsewhere, and can be considered as a reasonable worst case for the translocation of pesticides from soils to surface waters. While the predictions of the model are not very accurate for dissociated pesticides, they generally lie within an order of magnitude of observed mean values for the others which have been investigated. Furthermore, the model tends to overestimate somewhat the concentrations to be expected in drains and streams.

The above considerations suggest that SoilFug, if used with caution, can be employed to calculate predicted environmental concentrations (PECs) in water of some groups of new pesticides (particularly the more water-soluble molecules). For the reasons already discussed, such PEC values will tend to lie somewhat on the conservative side, but this is a desirable property in the early stages of any risk evaluation. At that point, simple models such as SoilFug are the most appropriate due to the relative lack of data, whereas more complex models become applicable at later stages. Pesticide companies and regulatory authorities are therefore invited to test and use SoilFug on a trial basis for preliminary risk evaluations.

Copies of the program diskette and documentation can be obtained from A. Di Guardo. The program requires an MS-DOS system (386 computer or above) and Windows 3.1.

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Appendix XI SE DIVISION ENVIRONMENTAL APPRAISAL UNIT ADHOC INVESTIGATION REPORT

Tech.Memo.No.: SE/EAE/95/1
Investigating Officer: P.Clabburn

Date of Survey: 10/11/94 Date reported: 3/1/95

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1. INTRODUCTION

Gammarus bioassays carried out in the Rosemaund stream during some pesticide applications have demonstrated a toxic effect. It was anticipated therefore that the impact of pesticide run-off on the macroinvertebrate fauna of the headwater stream of the Rosemaund catchment may also be evident. In order to test this theory a benthic macroinvertebrate survey of the stream was carried out by NRA staff of the SE Area Environmental Appraisal Unit. This report is based on the findings of this survey.

2. METHODS

Four macro-invertebrate samples were taken, using standard Institute of Freshwater Ecology methodology from close to the source of the stream in Foxbridge and Longlands field, above and below the STW discharge point adjacent to Big Meadow and at the downstream end of the farm, adjacent to Belmont and Prestons fields. (see Figure 1).

The samples were returned to the laboratory for analysis. Identification of macro-invertebrates was taken as far as possible, using the available keys. Due to the disproportionate amount of time taken sorting and picking the samples (because of large amounts of leaf litter and debris) certain groups such as Oligochaeta and Chironomidae were identified primarily to family level.

Since the stream rises in a field subject to pesticide applications, there was no suitable control site on the farm. The results were therefore compared with data from a similar site in the Lugg catchment gathered during the 1991 IFE headwaters study (The Faunal Richness of Headwater Streams: Stage 2 - Catchment Studies. Vol 2. Appendices. R&D Note 221), in which only pristine sites were included. This site was located on Newbridge Brook at Shoal's Bank (grid ref. SO 394494) and was selected on substrate characteristics, being the only headwater site in the Lugg catchment with a similar substrate to the Rosemaund sites.

3. LOCATIONS (see figures)

SITE	NGR	DESCRIPTION
1	SO 56854845	Stream close to source
2	SO 56204807	Upstream of Rosemaund STW
3	SO 56154808	Downstream of Rosemaund STW
4	SO 55784788	Stream close to point of exit from farm

4. RESULTS AND DISCUSSION

Using the BMWP scoring system as an indicator of biological quality, all four Rosemaund sites and the control site on Newbridge Brook were of poor biological quality, having BMWP scores in the range of 27 - 53. The full range of BMWP scores and the class descriptions to which they are allocated are given in table 1. No significant differences in scores occurred between any of the sites, including the control site on Newbridge Brook.
Assuming the control site was not affected by pesticide pollution, there was no evidence from the BMWP scores of any detrimental effects on the farm stream due to pesticide applications. Identification of taxa further than family level revealed a similar situation to the BMWP data. All sites were fairly similar, including the control. Within the Rosemaund stream changes in abundance do suggest that the farm's STW is having an impact; all but 3 taxa showed a decrease in abundance below the works. In most cases the decrease was of no consequence since the organisms were of a low abundance generally (e.g. _Baetis rhodani_, Hydracarina, _Laccobius spp_. and _Hemerdromia spp_.) and, as the BMWP score does not take account of abundance, only presence and absence, would not show up anyway. However the six most abundant taxa all showed a substantial if not significant decrease. These decreases were; _Polycelis spp_. 81%, _Glossiphonia complanata_ 79%, Oligochaeta ind. 76%, _Potamopyrgus jenkinsi_ 74%, Chironomidae 63% and _Pisidium spp_. 60%. These taxa all score poorly on the BMWP system and as such are fairly tolerant of organic enrichment. They are also likely to be relatively tolerant of pesticide pollution, especially from insecticides. _Gamarus pulex_, the species used in the bioassay experiments, was present at all but the uppermost Rosemaund site although only in low numbers. Pollution sensitive insect nymphs were rare or absent from all sites.

The predominant land uses around the control site are lowland agricultural grassland and woodland. Therefore, although the sites in the IFE study were chosen assuming they were in pristine condition, it is possible that pesticide applications to the control catchment could have occurred, albeit significantly less than at Rosemaund. Nevertheless, if a significant pesticide impact had occurred at Rosemaund then one would expect the BMWP scores for the Rosemaund sites to be lower than at Newbridge Brook.

Both the control site on the Newbridge Brook and the upper Rosemaund stream do dry up during the summer. There are therefore other physical influences affecting the biological quality of both streams which may override any impact due to pesticides.

5. CONCLUSIONS

1. The tributary of the Little Lugg running through Rosemaund Farm was of generally poor biological quality, being typical of a small, silty, stream impacted by drainage and general agricultural activity.

2. There was no evidence that the poor quality was due to pesticide applications, although, as the control was of similarly poor quality, this cannot be ruled out.

3. The farm STW does have a limited impact on the fauna of the stream, although there is no reason to believe that the effluent contains pesticides.

4. Comparisons with the site on Newbridge Brook should be viewed with caution due to its shortcomings as a control site.

TABLE 1: Macroinvertebrate Taxa Recorded

River: Tributary of Little Lugg (sites 1,2,3,4) & Newbridge Brook (control)
Date: 10/11/94 (sites 1,2,3,4) & 7/11/91 (control)

FAMILY	SCORE PER FAMILY	SITE NUMBERS 1	2	3	4	control
Nemouridae	7					+
Limnephilidae	7	2			1	+
Gammaridae	6		+	1	1	+
Dytiscidae	5	1	1	1	2	
Hydrophilidae	5	1	1		1	+
Tipulidae	5	2	1	1	1	+
Planariidae	5		2	1	1	
Baetidae	4			1		
Hydrobiidae	3		4	3		+
Lymnaeidae	3	1			1	
Sphaeriidae	3	3	2	2		+
Glossiphoniidae	3		2	1	1	
Erpobdellidae	3	1				
Chironomidae	2	2	3	3	3	+
Oligochaeta	1	3	3	2	2	+
Hydracarina	0	+	+	+	+	
Muscidae	0	+				
Ceratopogonidae	0	+		+	+	+
Empididae	0	+	+		+	
Psychodidae	0	+	+	+	+	+
Curculionidae	0	+				
Dolichopodidae	0	+				+
Stratiomyidae	0			+		
Hydra	0			+		
BMWP SCORE		34	38	38	42	39
NO. BMWP TAXA		9	10	10	10	9
A.S.P.T.		3.77	3.8	3.8	4.2	4.3
BMWP CLASS		4	4	4	4	4

Abundance Categories

1=1-9
2=10-99
3=100-999
etc

BMWP Score Ranges and Classes

Class 1	>165	Very Good Quality
Class 2	110 - 164	Good Quality
Class 3	54 - 109	Moderate quality
Class 4	27 - 53	Poor Quality
Class 5	<27	Very Poor Quality

TABLE 2: Macroinvertebrate Species Recorded

TAXON NAME	SITE NUMBERS 1	2	3	4	control
Hydra	0	0	3	0	0
Planariidae					
Polycelis spp.	0	16	3	5	0
Hydrobiidae					
Potamopyrgus jenkinsi (Smith)	0	1196	315	0	+
Lymnaeidae					
Lymnaea truncatula (Muller)	3	0	0	0	0
Lymnaea peregra (Muller)	0	0	0	9	0
Sphaeridae					
Pisidium spp.	959	48	19	0	+
Oligochaeta ind.	134	284	68	63	
Limnodrilus hoffmeisteri Claparede			+		0
Eisenella tetraeda (Savigny)	+				+
Tubifex tubifex (Muller)		+			+
Rhyacodrilus falciformis Bretscher					+
Stylodrilus spp.					+
Enchytraeus group					+
Haplotaxis gordioides (Hartmann)	+				0
Hirudinea					0
Erpobdella octoculata (L.)	3	0	0	0	
Glossiphonia complanata (L.)	0	19	4	7	
Hydracarina					0
Oribatei	5	3	2	1	
Gammariidae					
Gammarus pulex (L.)	0	1	1	4	+
Baetidae					0
Baetis rhodani (Pictet)	0	1	0	0	
Nemouridae					
Nemoura cambrica group	0	0	0	0	+
Dytiscidae ind.	1		3	7	
Colymbetinae					
Agabus paludosus (Fab.)		1			
Agabus spp.		1		11	
Hydroporinae					
Hygrotus spp.				1	
Hydrophilidae/Hydraenidae	1	1	0	1	
Elodes spp.					+
Laccobius spp.		1			
Curculionidae	2	0	0	2	
Limnichidae					
Limnichus pygmaeus (Sturm)	2	0	0	0	

TAXON NAME	SITE NUMBERS				
	1	2	3	4	control
Limnephilidae ind.	42	0	0		
Micropterna sequax McLachlan		0	0		+
Micropterna lateralis Stephens	+	0	0		
Stenophylax group		0	0	1	
Tipulidae ind.	24	1	1		
Tipula spp.		1			
Pseudolimnophila spp.				1	
Limnophila					+
Molophilus					+
Scleroprocta					+
Empididae			0	1	0
Hemerdromia spp.	1	1			
Muscidae	3				0
Dolichopodidae		0	0	0	+
Hydrophorus spp.	2				
Stratiomyidae	0	0		0	0
Nemotelus spp.			1		
Ceratopogonidae	2	0	3	2	0
Psychodidae			1		
Pericoma spp.	3	2		1	
Pericoma trivialis					+
Chelifera group	0	0	0	0	+
Chironomidae	21	336	124	368	+

Fig 1.

BIOLOGICAL SAMPLING SITES
AT ROSEMAUND FARM.