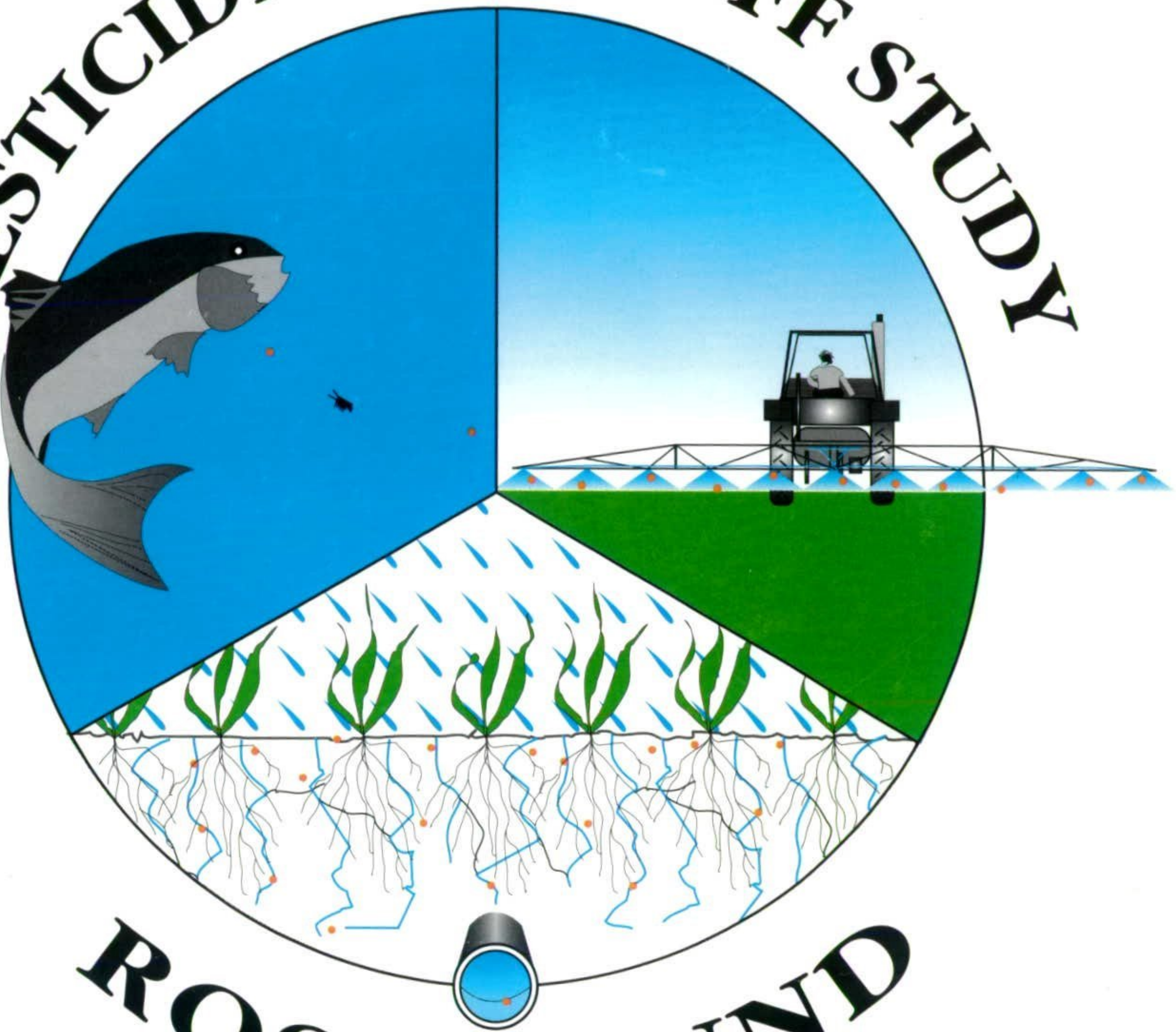
PESTICIDE RUN - OFF STUDY



ROSEMAUND

[redacted]

MAFF

ADAS
FOOD, FARMING, LAND & LEISURE

Institute of Hydrology

NRA

bre

SSLRC

THE UNIVERSITY
OF BIRMINGHAM

[redacted]

1991/039

PESTICIDE RUN-OFF STUDY
AT ADAS ROSEMAUND

Report of Years 2 to 4
Autumn 1989 to Spring 1991

Editor: C M Hack

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CONTENTS

Page No.

12. APPENDICES

1. EXECUTIVE SUMMARY

1.1 Rosemaund is an ADAS Research Centre in Herefordshire which encompasses an entire small water catchment that ultimately drains into the River Lugg. The catchment is largely surface-dominated i.e. water and agrochemicals applied to the fields will tend to migrate laterally into the stream rather than percolating down into the underlying groundwater.

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 dispersion of operationally-applied pesticides from the fields into the stream. The first report of this programme covered Years 1 to 3 (Autumn 1987-Spring 1990), while this report covers some additional data from August 1989 and full data from Autumn 1990 and Spring 1991. The report is intended both as a summary of progress and as a repository of the raw data.

1.3 The primary purpose of this work is to provide reliable data on the environmental concentrations of pesticides which can result from their normal agricultural use. The participants in this work are conscious that Rosemaund's catchment characteristics and cropping practices are such that pesticide concentrations appearing in the stream probably represent a reasonable 'worst-case'. The data are therefore likely to set an upper limit for the pesticidal contamination of UK surface waters.

1.4 The long-term aim of the programme is to use the field data to validate and improve computer models which can be employed to predict the environmental exposure which may result from the use of new pesticides, and to predict how catchment characteristics, weather and land use interact to affect downstream water quality.

1.5 The core of the work at Rosemaund continues to include monitoring of pesticide concentrations in soil, soil water, field drainage water and stream water. There has been particular emphasis on the dynamic situation during and after rainfall events, which the project has already established are associated with the highest pesticide concentrations in the stream. The main datasets referred to in this report cover lindane and isoproturon applications in Autumn 1989, isoproturon and dimethoate applications in Autumn 1990, and MCPA and oxydemeton-methyl applications in Spring 1991. All these pesticides were applied to one or both of the fields at the top end of the catchment, but some data are also reported for simazine and atrazine that were applied to other fields. The applications of mecoprop and diclorprop in Spring 1990 were fully covered in the report for years 1-3.

1.6 The data confirmed that most pesticides can translocate from the fields to the stream within a few hours of a significant rainfall event. Peak concentrations were usually associated with the peak of the stream flowrate, and on all occasions exceeded 0.1 µg 1^{-1} for short periods. Peak concentrations measured in the stream during the period covered by this report were: lindane, 0.3 µg/l; isoproturon, 17.2 µg/l, dimethoate, 3.0 µg/l; MCPA, 12.7 µg/l; oxydemeton-methyl, 0.8 µg/l; simazine, 15.3 µg/l and atrazine, 1.6 µg/l. However, in all cases, concentrations returned to background levels (generally < 0.01 µg/l) within 6-12 hours of peak flow. The total amount of any pesticide mobilised into the stream never exceeded about 5 g in any season, representing at most approximately 0.03% of the total applied.

1.7 The main analytical laboratories involved in processing samples from Rosemaund have collaborated in an intercalibration exercise using natural water samples spiked with mecoprop, dimethoate, isoproturon and simazine. The results showed good agreement between laboratories, with results generally varying by no more than a factor of 3. The exception was one laboratory where mecoprop concentrations were over-estimated. The cause of this problem has now been located and rectified.

1.8 The soil water process studies have shown that water movement in the upper metre of the soil, above drain level, is dominated by macropore pathways which bypass the very poorly conducting soil matrix. In the autumn prior to the water table rising above drain level (usually early January) heavy rainfall exceeds the acceptance capacity of the soil surface and floods down the large shrinkage cracks remaining from the summer. Such rain falling on the zone extending a metre or two on either side of the drain enters the drain due to ponding at the base of the macropore zone, although some passes on downwards to recharge the groundwater. Water falling on the inter-drain zone is absorbed into the soil peds and probably little of this goes anywhere else. The foregoing process depends on the rainfall being heavy, because prolonged light rain soaks the soil surface and causes the shrinkage cracks to close. Cultivation also probably has a similar effect, although in the former case, excess water might be expected to run off the surface to the stream, while in the latter case this is less likely.

1.9 After the water table has risen above drain level, a second macropore bypass system can come into play. This occurs in wet periods when the water table rises temporarily into the upper soil layer. This contains many worm holes, root holes and aggregate structures which, under saturated conditions, can conduct water laterally to the drain zone.

1.10 In April, when transpiration starts to exceed mean rainfall, the soil starts to dry out from the top, the water table falls below drain level and shrinkage cracks start to develop again. Once this occurs the potential for drain flow reverts to the shrinkage crack system, which may not fully develop until mid-summer.

1.11 For the reasons given above, by-pass flow appears to be the dominant transport process at Rosemaund. This explains the rapid appearance of pesticide peaks in the stream after rainfall, and has implications for the modelling.

1.12 Two broad modelling programmes are in progress, the first concerned with a relatively simple predictive approach which could be applied to assess exposure that may result from the use of new pesticides, and the second with a more complex model which is attempting to simulate the Rosemaund situation in detail. Both approaches have had some success, but neither has yet reached fruition.

1.13 The simple predictive approach is based on a modified Mackay fugacity model which assumes that the modelled system is at equilibrium (almost certainly an oversimplification) and merely aims to predict peak pesticide concentrations in the stream to within one order to magnitude. This has been used so far to model four events concerning lindane, isoproturon and mecoprop (twice). Predicted peak pesticide levels in the stream were consistently too high, but in three cases were within the desired order of magnitude. In the fourth case (one of the mecoprop datasets), the predicted level was about 20 times greater than the observed. It is felt that this approach has probably been pushed as far as it can go, and future 'simple' modelling will probably have to develop new approaches, but the fugacity concept will be tested further with future data and may be applicable for initial assessments of new pesticides.

1.14 The catchment simulation model has so far been solely based on the detailed information available on a single field at Rosemaund (Longlands). It attempts to simulate what is now known about soil hydrology and structure around and between the field drains, and includes a representation of by-pass flow. To date, it has only been used to simulate the flowrates and isoproturon concentrations in a single field drain during the period 1 September 1990 to 31 March 1991. It appears to simulate flow rate and mean isoproturon concentration well during rainfall events in the period when the sub-soil is saturated and the drain is flowing steadily.

However, it overestimates both flowrate and concentration during the transition period before normal drainflow. Although probably too detailed for initial exposure assessments of pesticides, this model shows promise for catchment-specific simulations. It is intended in the future to extend it to simulate the entire catchment, and to test it for a wider range of pesticides.

1.15 Practical work at Rosemaund during the 1991/92 season will monitor the pesticides carbofuran, aldicarb and atrazine, and plans are being formed to monitor a series of strongly-adsorptive products (eg. pyrethroid insecticides) during the 1992/93 season. These latter substances are of interest because they have been found in Rosemaund stream sediments by the Institute of Freshwater Ecology (A. House, pers. comm.) and are postulated to reach the stream via the drains adsorbed on soil particles that move by by-pass flow.

1.16 No bioassays were run in the stream during the 1990/91 season due to lack of resources, but they will be used during the carbofuran/aldicarb experiments in 1991/92 because these insecticides are considerably more toxic to crustacea than most of the pesticides monitored previously. Sediment bioassays will probably be used during the pyrethroid experiments in 1992/93.

1.17 In summary, the work to date at Rosemaund has shown that many pesticides reach the stream with a speed and at a concentration which had not been expected on the basis of classical ideas of pesticide behaviour in soils. The soil hydrology studies confirm that water and its associated solutes and suspended matter can under certain conditions rapidly by-pass the main soil blocks and lead to transient contamination of the stream during rainfall events. This complex situation is difficult to describe mathematically, but progress is being made with both a simple exposure model and a more sophisticated catchment simulation model.

2. INTRODUCTION

2.1 The use of pesticides in agriculture has risen dramatically in recent years. This has been due mainly to the introduction of effective annual grass weed herbicides in the early 1970s which allowed the continuous growing of autumn-sown crops on heavier soils and effective cereal fungicides in the mid-1970s. This increase in pesticide usage has lead to serious concern about possible contamination of the environment by these chemicals. One important area at risk from contamination with pesticides is in the aquatic environment, and the effect of pesticides in water, on both aquatic life and potable water supplies are of particular concern.

2.2 Reviews of pesticides in drinking water sources in England and Wales (Lees and McVeigh, 1988; Drinking Water Inspectorate, 1992) have indicated that a number of sources 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 ug/l and a MAC of 0.5 ug/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.

2.3 The Water Act 1989 (and subsequently the Water Resources Act 1991) allows for the Secretary of State to derive a classification system for controlled waters and to set Water Quality Objectives (WQOs) for those waters. The Department of the Environment has indicated its intention to introduce WQOs from 1992 onwards and the consultation process has begun. The NRA will be responsible for ensuring compliance with these statutory WQOs and has published consultation proposals for WQOs which include: a new general classification scheme for controlled waters, use related objectives and standards and incorporation of the requirements of relevant EC Directives.

2.4 Some pesticide standards already exist for the protection of aquatic life, and for surface waters used for potable water abstraction (see above paragraph) and, if the NRA proposals are implemented, they may be incorporated in to the WQOs for appropriate rivers. Pesticide limits may also be included in other use related objectives and EC Directives, yet to be defined. It is vital therefore 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.

2.5 Pesticide registration authorities in the UK are having to react to this possible risk situation by a further increase in standards 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. However, 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 absorbed onto eroded soil particles.

2.6 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 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.

2.7 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 National Rivers Authority (NRA) in England and Wales and the River Purification Boards in Scotland.

2.8 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 Experimental Husbandry Farm at Rosemaund 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 pesticide movements and effects at Rosemaund.

2.9 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.

2.10 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.

2.11 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 new 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.

2.12 This report is the second joint summary of progress to date by all the organisations which have collaborated in the Pesticide Run-off Study at ADAS Rosemaund between Autumn 1989 and Spring 1991. It is intended that joint reports in a similar format to this one will be produced annually until the completion of the study. 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 run-off 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 run-off 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 (eg. *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 HISTORY AND ROLE OF ADAS ROSEMAUND

In 1949, the Ministry of Agriculture purchased Rosemaund Farm for the purpose of conducting experiments on agricultural research and development. A number of farms were purchased around the country and named Experimental Husbandry Farms (EHFs). Each EHF reflected the farming in its own locality, including regional specialisations. They are co-ordinated nationally to cover all important enterprises, thus providing the necessary depth for quality experimental work.

4.2 LOCATION, RELIEF AND CATCHMENT

Rosemaund is located in the West Midlands mid-way between Hereford and Bromyard, near the village of Preston Wynne, and at a generally low altitude (on average 84 m above sea level). The farm covers some 176 ha lying in a broad undulating valley which is dissected by a stream running from east to west, which ultimately drains into the River Lugg. The catchment itself drains approximately 180 ha which is almost entirely comprised of Rosemaund land. A location and field plan showing the boundary of the catchment can be found in Appendix I.

4.3 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.

Mean monthly rainfall values are given in Table 1 below. 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.

Table 1. Mean monthly averages of rainfall (mm) - 1951-1991

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
61	44	51	43	52	52	51	57	60	56	65	64	657

Detailed meteorological data for Rosemaund from 1989 to 1991 are presented in Appendix II.

4.4 GEOLOGY

Rosemaund is underlain almost entirely by Devonian rocks composed of soft siltstones and mudstones of Downtonian 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 from drift deposits though occasional drift pebbles can be found and are probably of local origin. A narrow strip of clayey or silty alluvium flanks the stream that runs through the farm.

4.5 SOILS

A soil map and report was prepared for the farm in 1989 by J M Hodgson incorporating data from earlier surveys. For the purpose of describing the particular soils central to the present study, the 1989 farm survey has been supplemented by auger bores to a depth of 2 m with a 50 m grid spacing in Foxbridge/Longlands (and Slade Meadow) and by borings at 100 m spacing in Stoney/Brushes and Moorfields and Jubilee fields. Additional bores to 1.2 m have been made at 100 m grid intersects on adjacent farmland within the stream catchment boundary. The revised catchment map is shown in Appendix III and the soils are listed in Table 2.

Most of the farm is covered by the reddish silty clay loams of the Bromyard series, and its shallow phase. Heavier soils are found in seasonally waterlogged hollows and valley bottoms.

Table 2. Classification of Soil Series

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

Detailed descriptions of the soils are given both by Hodgson (1989) and Carter and Cope (1990).

The soils have slowly permeable subsoils which require under-drainage to avoid problems of water-logging, and to achieve the highest performance under intensive agricultural practice. The majority of fields have been under drained and a general drainage plan for the farm can be found in Appendix V. Most drains were laid between 1975 and 1989, at one metre depth with permeable backfill and at an average spacing of 20 m.

When conditions allow, fields are subsoiled every other year in the autumn to a depth of 35 cm.

4.6 CROPPING

The soils at Rosemaund are capable of growing very good crops if carefully managed and Table 3 below lists the diversity of crops grown in 1990.

Table 3. Farm cropping 1990

Crop	Ha	% of total
Arable		
Winter wheat	40	23
Winter barley	22	13
Winter Oats	7	4
Spring barley	1	0.5
Oilseed rape	15	8
Winter beans	8	5
Peas	3	2
Root crops	2	0.5
Hops	12	7
Forage		
Italian ryegrass	10	6
Forage maize	4	2
Fodder beet	2	1
Longterm grass	45	25
Woodlands, road, buildings	7	4
Total	176	

In the UK the past decade has seen a marked expansion of winter sown cereals and oilseed rape, and there has recently been a rapid increase in the area of dry harvest peas and winter/spring sown beans. The balance of arable crops to forage and grassland at Rosemaund reflects this national trend. For example, forage crops occupied two-thirds of the farm area at Rosemaund in 1975 and had declined to one-third by 1988. The recent introduction of a Red Deer enterprise has reversed this trend slightly.

An arable rotation at Rosemaund operates to maximise the research and development opportunities rather than demonstrate any best commercial practice. This accounts for about 60 ha of the prime arable fields and is detailed in Table 4 below, which also shows the change from a five to a six year rotation in 1987.

Table 4. Arable rotation at Rosemaund

Year	Rotation (1981-86)	Rotation (1987-90)
1	Oilseed rape	Oilseed rape
2	Winter wheat	Winter wheat
3	Winter wheat	Winter cereals (Wheat/barley/oats)
4	Winter barley	Beans and peas
5	Winter barley	Winter wheat
6	-	Winter barley

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

4.7 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 variety of crops grown at Rosemaund inevitably leads to the use of a wide range of pesticides at different times of the year. Winter cereals receive on average one or two autumn pesticides (herbicides, insecticides) normally as one application. There are usually a further two or three applications the following spring and summer (herbicides, fungicides and growth regulators). Hops are a high value, high risk crop requiring numerous treatments to achieve a high-grade product at harvest. However, these treatments are restricted largely to the summer months with only one or two winter applications of herbicide. By contrast, grass production requires very little use of pesticides.
The main pesticides applied to the major crops at Rosemaund in 1986-87 are listed in Appendix VI.

4.8 LEACHING POTENTIAL AND SELECTION OF PESTICIDES FOR STUDY

In the prevailing climate, the maximum leaching potential of a pesticide tends to coincide with autumn and winter applications where rainfall, soil moisture and ground water levels are all high. In addition, the individual properties of an applied pesticide are very important as some exhibit a much higher potential to leach to water courses than others. This is due to a number of individual physico-chemical factors, namely its solubility in water, its vapour pressure, its octanol-water partition and soil adsorption coefficients; its persistence in both soil and water, and the rate, timing and conditions of its application. All these factors combine to make the accurate prediction of pesticide leaching extremely difficult.

The rates and timing of the main pesticides used at Rosemaund have already been referred to in Appendix VI. A number of properties for selected pesticides, together with their total usage in this country, are given in Appendix VII.

Clearly, a great deal of information was needed before the selection of pesticides for monitoring in this study could be made. Some were easily excluded. For instance, some pesticides (like metsulfuron-methyl and mepiquat chloride) are applied at such low rates that they are unlikely to be detected in a water course, despite their high leaching potentials. Others, like oxamyl, break down very quickly in the soil and are extremely difficult to trace.

Consequently, a short list could be drawn up from this kind of data alone, and a number of studies (eg. Bird and Whitehead, 1985) confirmed which pesticides were widely found in UK water. One complicating factor was the additional need to study pesticides less prone to leaching in order to provide a broad database for validating leaching models. The final short list for the study at Rosemaund was drawn up in 1987 and is shown in Table 5 below.

Table 5. Short list of pesticides to monitor

HERBICIDES -	Atrazine+
	Chlorotoluron
	Isoproturon*
	MCPA
	Mecoprop*
	Simazine*+
INSECTICIDES -	Aldicarb
	Carbofuran
	Demeton-S-methyl
	Dimethoate
	Lindane+
GROWTH REGULATORS -	Chlormequat

* priority

\+ On the Red List of substances most dangerous to the aquatic environment.

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. Clearly the above list was expected to be subject to some alteration as the study developed.

5. SUMMARY EXPERIMENT REPORTS

5.1 EXPLANATION OF SUMMARY REPORTS

A number of experiments were carried out between Autumn 1989 and Spring 1991. They have all been reported in this section in summary form to present an overall picture of the findings in this study. Soil and soil hydrology surveys carried out by IH and SSLRC are reported first followed by summary reports of pesticide monitoring.

The pesticide monitoring summary reports have been placed in chronological order, each one covering a season of experiments, typically Spring and Autumn.

Each summary is divided between the two main reporting groups (A) MAFF Fisheries and BRE, and (B) NRA and IH as each group has different objectives (described in Section 3.2), and thus different monitoring regimes. For clarity, the experiments reported in the summaries are separated along these lines:-

1. MAFF/BRE EXPERIMENTS SERIES A
2. NRA/IH EXPERIMENTS SERIES B

Each summary report uses the following format:-

1. Introduction
2. Methods
3. Results and Discussion
4. References.

5.2 DETAILS OF PESTICIDE APPLICATION APPERTAINING TO THE STUDY

Most of the monitoring in this study concentrated on pesticides applied to fields at the upper end of the catchment (Foxbridge and Longlands, Stoney and Brushes). By and large, monitoring followed the normal use of pesticides as they were required on the farm. They were applied using the farm sprayer (a tractor-mounted Hardi with a 12 m boom, subsequently updated to a self-propelled Chaviot sprayer in Spring 1990). The pesticide applications pertinent to the monitoring programmes are given in Table 6 below.

Table 6. Details of pesticide applications monitored each season

Season	Pesticides monitored	Rate of active ingredient (kg/ha)	Product name	Fields	Crop	Date of application
Autumn 89						
	ISOPROTURON	1.0	Panther	F & L	WW	1.11.89
	ISOPROTURON	0.375	Hytane	S & B	WW	17.11.89
	LINDANE	0.5	Gammacol	F & L	WW	1.11.89
	DELTAMETHRIN*	200 ml	Decis	F & L	WW	18.10.89
	MECOPROP*	30	CMPP	S & B	WW	17.11.89
	DELTAMETHRIN*	240 ml	Decis	S & B	WW	17.11.89
Spring 90						
	DICHLORPROP	2.60)	Campbell's)	F & L	WW	20.3.90
	MECOPROP	0.65)	CMPP/DP)	S & B	WW	22.3.90
	CHLORMEQUAT*	1.8	CCC	F & L	WW	21.3.90

Table 6 (continued)

Season	Pesticides monitored	Rate of active ingredient (kg/ha)	Product name	Fields	Crop	Date of application
Autumn 90						
	ISOPROTURON	1.0	Panther	S & B	WB	11.10.90
	ISOPROTURON	2.13	Panther + Hytane	F & B	WB	23.11.90
	DIMETHOATE	0.34		S & B, F & B	WB	28.11.90
	DELTAMETHRIN*	200 ml	Decis	S & B	WB	11.10.90
				F	WB	11.10.90
	DELTAMETHRIN*		Decis	L	WB	18.10.90
Spring 91						
	MCPA	1.68		S & B, F & L	WB	28. 2.91
	OXYDEMETON-METHYL	0.114	Metasystox	S & B, F & L	WB	1. 3.91
	CHLORMEQUAT*	700 ml	CCC	S & B		21. 3.91
	SIMAZINE	2.2	Gesatop 50 WP	Windsor		13. 3.91
	SIMAZINE	1.1	Gesatop 50 WP	Coronation		15. 3.91
	SIMAZINE	3.1	Gesatop 50 WP	Balmoral		23. 3.91
	SIMAZINE	1.6	Gesatop 50 WP	Windsor		27. 3.91

* Stream monitoring of usual farm practice, not specific field monitoring of pesticides applied to the top of the catchment.

Key

S & B	Stoney and Brushes	WB	Winter barley
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, has resulted in separate sampling sites and monitoring regimes for both. In general, MAFF/BRE monitored the movement of pesticides down the soil profile and to the stream, and NRA/IH concentrated largely on looking at the catchment as a whole.

A detailed plan of all the sampling and monitoring sites can be found in Table 7. Each site is given an eight digit Ordnance Survey reference number, as well as being referred to by a 'descriptive name' in the reports and tables of data. For convenience, these are listed below in Table 7.

Table 7. Sampling sites - Ordnance Survey reference numbers and descriptive names

OS reference number	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	Ditch, Site 3 (MAFF)
SO 5688 4847	Foxbridge and Longlands drain outfall: Site 4 - left hand drain (MAFF); Site 5 - right hand drain (IH,MAFF); Site 6 - middle drain (MAFF & IH)
SO 5702 4843)	(Nos. 1-6)
SO 5697 4839)	Soil suction samplers (Nos. 7-12) (SSLRC)
SO 5698 4848)	(Nos. 16-21)
SO 5693 4844)	(Nos. 22-27)

5.4 SOIL AND SOIL HYDROLOGY SURVEYS

Surveys of the soil and soil hydrology were carried out in 1990-91 to provide an insight into the processes and pathways controlling the movement of soil water (and hence, of dissolved agro-chemicals and their derivatives). Investigations by IH and SSLRC are described below.

5.4.1. IH The Soil Hydrology of 'Longlands'

Following a pilot study carried out in the previous year, a soil hydrological study was carried out by IH in Longlands field. The objectives of this study was to identify the real processes of water transport over, within and below the soil. The experimental programme comprised of two components:

1. A study of the dynamic behaviour of the soil water reservoir in relation to the effects of a representative field drain throughout the crop cycle.
2. A preliminary, semi-quantitative study of surface run off to assess its importance and relationships with antecedent surface soil water content and short-term rainfall intensity and amount.

The report is reproduced in full in Appendix IX.

5.4.2. SSLRC Soil Characterisation

5.4.2.1 Introduction

The SSLRC contribution is focused on characterising the soils, particularly their distribution and hydrology within the Rosemaund catchment area. A major part of the work is to sample soil water from a range of locations and depths for determination of the applied pesticides by Birmingham University under contract to MAFF. Further detailed investigations of soil characteristics were made regarding water regime, hydraulic conductivity, soil physical and chemical properties and general profile features, particularly structure. These data were obtained in order to provide a better understanding of soil, water and pesticide interactions.

5.4.2.2 Water Sampling and Methodology

Inert stainless steel/teflon suction samplers have been used since autumn 1989 at the Rosemaund site to obtain 'mobile' soil water. The installation and sampling procedures were described by Carter and Cope (1990). Water samples were transported to the University of Essex and later Birmingham University for analyses in refrigerated containers using an express freight carrier. The Meteorological Office Rainfall Evaporation Calculation System (MORECS) was used (square 135) to estimate prevailing weekly Soil Moisture Deficits (SMDs) in order to assess the likelihood of mobile water being available for sampling.

Spring 1990

Soil water suction samplers remained in situ in the Foxbridge and Longlands field on two soil types - Bromyard and Bromyard shallow phase. Each site comprised water samplers at 50, 100 and 150 cm depth. The herbicides mecoprop and dichlorprop (2.6 and 0.65 kg/ha respectively) were applied as Campbells CMPP/DP to the winter wheat crop on 20 March 1990 (MORECS soil moisture deficit of 13 mm). Water samples were taken on 21 March 1990, 18 April 1990 and 21 May 1990. No trigger rainfall events (a volume greater than 10 mm in a 24 hour period or 15 mm over a 72 hour period) were recorded until 12 April when rain fell for several days. This initiated the sampling of 18 April 1990. No significant rain fell until 15 May 1990 and the site was sampled on 21 May 1990. No further sampling took place after this time due to the high Soil Moisture Deficit (93 mm 22 May 1990 MORECS). Sample volumes and herbicide concentrations are listed in Table 1 (Appendix X).

Autumn 1990

The Foxbridge and Longlands site was ploughed in September after the removal of all SSLRC instrumentation. A winter barley crop was drilled and the sampling equipment was reinstalled following any necessary repairs and cleaning. The suction samplers were relocated to four new positions. Site A located on the Bromyard 'normal' phase, B on the Bromyard 'shallow' phase, D and E at the foot of the hillslope on the Middleton (variant) soil series. Duplicate suctions samplers at 50, 100 and 150 cm depth were installed at each site with dip wells at 60, 100 and 140 cm depth at the Middleton sites only. Three additional samplers at 50, 100 and 150 cm depth were installed at site C on the Bromyard series in response to a request from the Institute of Hydrology to enable a more detailed investigation of the effect of the sampling process to take place. A pre-spray sampling was attempted on 16 November 1990 - (MORECS SMD c.50 mm) but no samples were obtained. The herbicides isoproturon (IPU) and diflufenican (DFF) were applied on 23 November 1990 in a tank mix of Hytane and Panther. This is equivalent to 2.1 kg/ha of IPU and 50 g/ha of DFF. The organophosphorus insecticide dimethoate was applied on 28 November 1990 at 0.85 l/ha giving a rate per hectare of 340 g. Water samples were obtained on four occasions, 12 December 1990, 4 January 1991, 15 January 1991 and 21 February 1991, in response to a 10.7 mm trigger event on 10 December 1990, various rainfall events 24 December 1990-1 January 1991, 15.9 mm on 8 January 1991 and a routine sampling respectively. Pesticide concentrations are given in Tables W12 and W13 (Appendix XI) respectively.

Soil water samplers remained in situ and sampling continued for the spring 1991 period following the application of the herbicide MCPA and the organophosphorus insecticide oxydemeton-methyl on 28 February 1991 to Foxbridge and Longlands field. MCPA was applied as Atlas MCPA equivalent to 1.68 kg/ha and oxydemeton-methyl as Metasystox R equivalent to 114 g/ha. Water samples were obtained on three occasions, 21 March 1991, 22 April 1991 and 7 May 1991 as routine monthly samples. The March sampling coincides with a rainfall total of 20.7 mm over 16-18 March 1991, but four significant events (4 March 1991 - 11.5 mm, 6-7 March 1991 - 26.7 mm, 2-6 April 1991 - 22.7 mm and 29 April 1991 - 24.8 mm) were not responded to as unfortunately, the notification system for flow events to the NRA malfunctioned, it was disconnected and SSLRC were not informed of any events during the Spring 1991 period. The previous rainfall trigger system will be used in future, since it is known that pesticide movement in soils at Rosemaund can occur independently of stream flow events. Concentrations of MCPA are given in Table W18 (Appendix XI). No oxydemeton methyl was detected.

5.4.2.3 Soil water regimes

Autumn 1989-Spring 1990

Dipwells lined with 10 cm slotted drainage pipe were installed on each of the Bromyard experimental areas in nests at 30, 60, 100 and 140 cm depth and the water-table height in each hole was recorded on each site visit.

Measurements of saturated horizontal hydraulic conductivity (Ksat(h)) were made when draw down could be made within each discrete soil horizon. The inverse auger hole method was used to measure the vertical saturated hydraulic conductivity (Ksat(v)) of soil horizons with no water-table using a Guelph permeameter.

Methylene blue dye was applied to six 1 x 1 meter squares in order to identify the pathways of water movement. The dye (5.0 g/l) was applied in 5 or 10 litres of water using a watering can with a rose attached. Two squares were focused around suction samplers 18 and 20, two on the Bromyard normal phase and two on the shallow phase. The squares were excavated on 7 June 1990 after 10 weeks and 62.3 mm of rainfall. The high SMD (102 mm) and crop growth prevented the squares from being left longer.

Autumn 1990-Spring 1991

Dipwells were installed at 60, 100 and 140 cm depth on the Middleton soil series only. Water-table height for each hole was recorded on each site visit.

Methylene blue was applied in powder form (5 g m^2) to allow natural rainfall water movement to be traced at 6 locations in Foxbridge and Longlands during early spring 1991.

5.4.2.4 Suction samplers and flow regimes

Soil water suction samplers have been used for many years to obtain samples of 'mobile' soil water. However, little is known about the effect of sampling on the soil hydrology, particularly the nature and volume of the water supply zone. A laboratory experiment was set up to investigate the effect and extent of water removed around a suction sampler installed in packed medium sand. Soil water suction was recorded around the sampler using septum tensiometers and a Thies pressure transducer tensiometer system. Following the normal field practice a suction of 700 mb was applied to the sampler, left 'overnight' and the sampler evacuated. Tensiometers were read at regular intervals.

Soil Characterisation

In September 1990 four soil profile pits (one each on representative locations of the Bromyard normal and shallow phases, Middleton and Compton series) were dug in order to sample soil for physical and chemical anaylses. Detailed descriptions of profile characteristics, particularly structure, the presence of fissures and macropores were made and can be found in Carter and Beard (1992).

5.4.2.5 Results and discussion

Soil water sampling

The soil water data are reported in sections 5.5, 5.6 and 5.7.

All data sets emphasise:
the reliance of this sampling system on accurate and prompt reporting of events;
the need for pre-spray sampling to establish a 'base line' or identify residual concentrations;
the need for more intensive sampling following spray application;
the continuation of analysis until zero or base line levels are attained. The limited sampling ability of the existing equipment when more than one pesticide is investigated.

The results from the laboratory study suggest that the suction sampler imposes a U-shaped field of influence on water potential in the surrounding soil. The shallow tensiometers close to the sampler show little effect when suction is applied or the sampler evacuated. Effects on soil water suction after sampling of approximately 20 mb were seen up to 15 cm distance at both depths and the full extent of influence may be greater in a field situation. Data from the Institute of Hydrology field experiment will further develop an understanding of the effect of the suction sampler on the surrounding area.

Soil water regimes

The saturated hydraulic conductivity provides an indication of the relative permeability of a soil. When combined with information on pore size distribution it can also indicate the expected rate of movement of water in soils which are not saturated. Details of the conductivities measured in the Bromyard shallow and normal phase soils are given in Carter and Beard (1992). Results do indicate that vertical conductivity is greater than horizontal conductivity. Topsoil conductivity is variable according to cultivation and animal activity (1-190 cm/day). Upper subsoil conductivity suggests conductivities of 30 cm/day decreasing to < 1 cm/day in the lower subsoil on both Bromyard phases.

Methylene blue studies

The dry spring of 1990 did not allow full penetration of the methylene blue down the soil profile. The maximum depth observed was 49 cm where dye was observed to have penetrated along a structural faces and fissures. The initial point of entry to the lower soil was determined by irregularities, crop and other existing voids. Dye occurred in the general soil matrix to a shallower depth of approximately 23 cm. Soil excavation during this exercise revealed significant channels of approximately 5 cm at depths of 19 cm created by animal activity. The presence of these channels helps to explain the very rapid topsoil saturated hydraulic conductivities which were observed. Dye was also observed in worm channels and blue stained worms were noted at lower soil depths.

The spring 1991 study with powder form methylene blue dye showed that on excavation several weeks later the dye had virtually degraded and no trace could be seen in any of the profiles.

Further studies will use the dye tracing technique to provide semi-quantitative assessments of the number and importance of by-pass channels.

5.4.2.6. References

Carter, A D and Cope, D W (1990). Interim report on the fate and behaviour of pesticides within a small catchment at Rosemaund EHF, Herefordshire (1989-1990). SSLRC Research contract 82/3823, undertaken for the Ministry of Agriculture Fisheries and Fisheries and Food. Silsoe.

Carter, A D and Beard, G R (1992). Interim report on the soil water sampling and soil characterisation programme within a small catchment at Rosemaund EHF, Herefordshire (1990-1991). SSLRC Research Contract 82/3823, undertaken for the Ministry of Agriculture Fisheries and Food. Silsoe.

5.5 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS - ISOPROTURON/LINDANE EXPERIMENT - AUTUMN 1989

5.5.1. MAFF/BRE Experiment Series A

5.5.1.1. Introduction

The rationale behind this work has been fully described elsewhere by Brooke and Matthiessen (1991). In summary, the purpose of the project is to provide validation data for computer models which can be used to predict surface-water concentrations of new pesticides before they are used in the environment. Models are therefore restricted to operation with simple physicochemical data and the model currently being investigated employs a modification of the simple Mackay fugacity approach.

The fieldwork involves the application of known amounts of pesticide (at MAFF-approved rates) to the upper part of the Rosemaund catchment (Stoney and Brushes, and Foxbridge and Longlands), and the measurement of residue levels in soil, drainage water, sediments and biota. The Rosemaund catchment appears to be almost ideal for this purpose because it lies largely within the boundary of the farm, thus allowing good control over inputs. Also, the soil is relatively low in organic matter, fairly steeply sloping, drained by a network of field drains, and underlain by a largely impervious clay/siltstone layer. All of these factors will tend to maximise pesticide concentrations appearing in the stream, an important consideration for models which are to be used for pesticide hazard assessment.

The pesticides chosen for study in Autumn 1989 were the herbicide isoproturon and the insecticide lindane.

Isoproturon (as Panther, which includes diflufenican) was applied to Foxbridge and Longlands at 1.0 kg ai ha^{-1} on 1 November 1989, and to Stoney and Brushes at 0.375 kg ha-1 on 17 November 1989. Lindane was applied as Gammacol to Foxbridge and Longlands alone at 0.5 kg ai ha^{-1} on 1 November 1989. The applications were to winter wheat.

5.5.1.2. Methods

These are fully described in the Report for years 1-3. The fish and sediment samples have still not been analysed.

5.5.1.3. Results and Discussion

Manual samples

Data on the levels of isoproturon and lindane in the soil were presented in the Report for years 1-3. The results for isoproturon are described in the Report for years 1-3 but are tabulated here again alongside the recently available results for lindane.

Water

Samples taken manually from stream and field drains between rainfall events are shown in Table W1. The maximum concentration of lindane seen in the stream at site 1 was 0.11 µg l^{-1} on 9 November 1989, although higher maximum concentrations were seen on various dates in the field drains at sites 3, 4, 5 and 6 (0.39, 0.33, 0.21 and 0.30 µg l^{-1} lindane, respectively). Background concentrations of lindane dropped to below 0.04 µg l^{-1} by the end of January 1990, and to below 0.007 µg l^{-1} by mid-February 1990.

Rainfall event on 8 November 1989

Automatic samples were only taken successfully from the Site 3 field drain (Table W2, Appendix XI and Fig. W1). Following 28.5 mm rainfall in the early hours of 8 November 1989, lindane concentrations in drain water peaked immediately at 4.46 µg l^{-1}, but dropped within 2 hours to 0.3 µg l^{-1} and reached 0.04 µg l^{-1} after 18 hours before starting to rise again at 20 hours. The peak lindane concentration slightly preceded the peak water flowrate (2.3 l sec^{-1}). Altogether, approximately 7 mg of lindane flowed out of the drain at site 3 during this event.

Rainfall event on 9 November 1989

This occurred about 10 hours after the event on 8 November 1989, and the drain flow had not yet returned to zero. Automatic samples were only taken from the drain (Table W3, Appendix XI and Fig. W2). Although the peak flow rate after the 10.5 mm rainstorm was less than on the previous day, the peak concentration of lindane (4.14 µg l^{-1}) in the drain at Site 3 was almost as large. Once again, however, the lindane concentration declined rapidly to approximately 0.1 µg l^{-1}. Approximately 27 mg of lindane flowed from the drain at site 3 during this event. Taking the 8 November 1989 and 9 November 1989 events together, approximately 100 mg of lindane were mobilised via this drain.

Rainfall event on 13-14 December 1989

This large event consisted of two storms separated by 5 hours and totalling 52.5 mm. Automatic samples were obtained from both the stream at Site 1 and the drain at Site 3 (Table W4, Appendix XI and Figs. W3 and W4). In the stream, the flow was slow to reach a peak, but finally attained flowrates in excess of 30 l sec^{-1} approximately 28 hours after rainfall began. Lindane concentrations in the stream peaked only about 10 hours after rainfall began (peak = 0.27 µg l^{-1}), but peaked again at 0.29 µg l^{-1} after the second rainstorm.

Fig.W1. Rosemaund Site 3. Isoproturon/Lindane Experiment 7.11.89 - 9.11.89

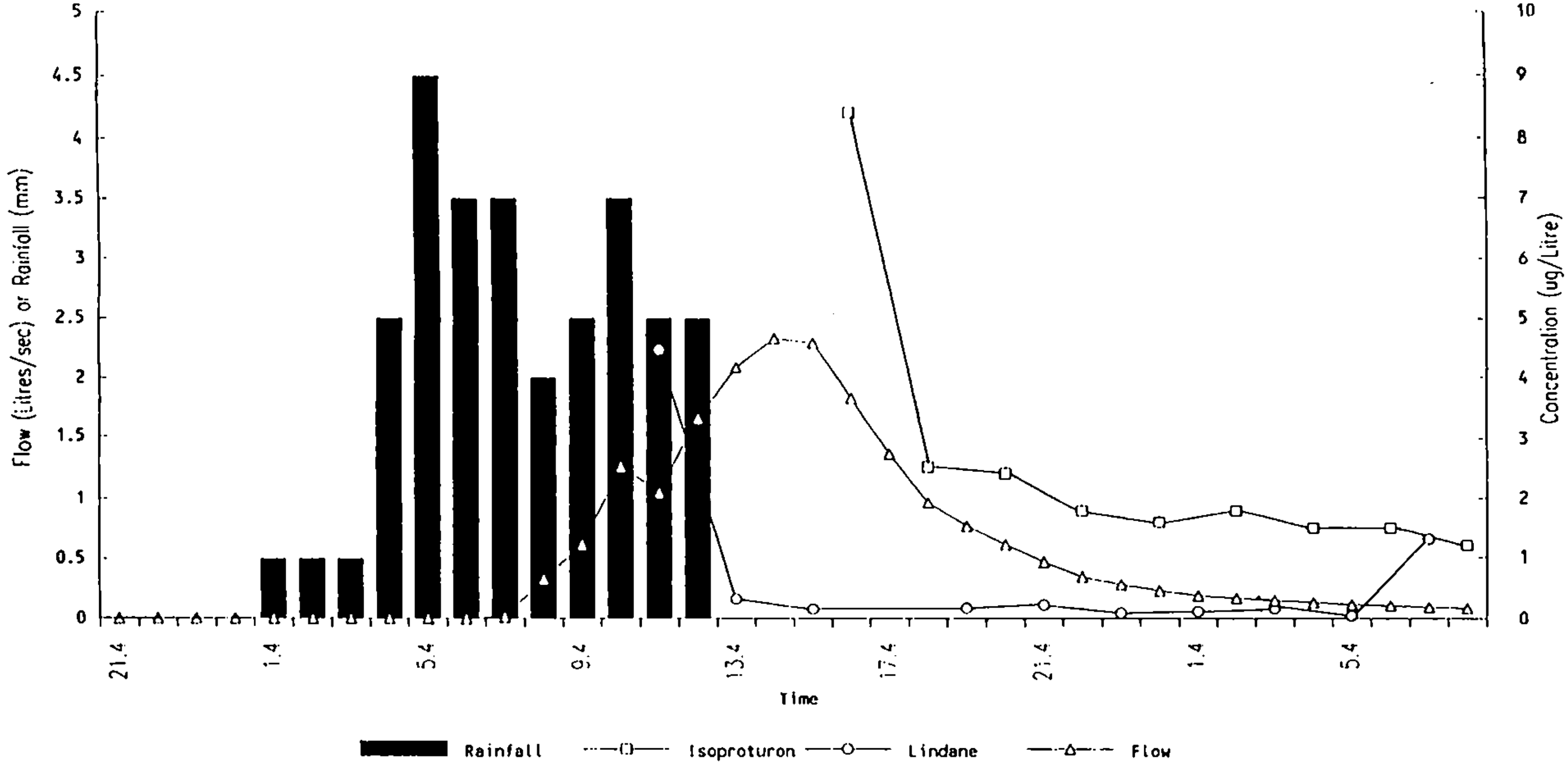


Fig.W2. Rosemaund Site 3. Isoproturon/Lindane Experiment 9.11.89 - 10.11.89

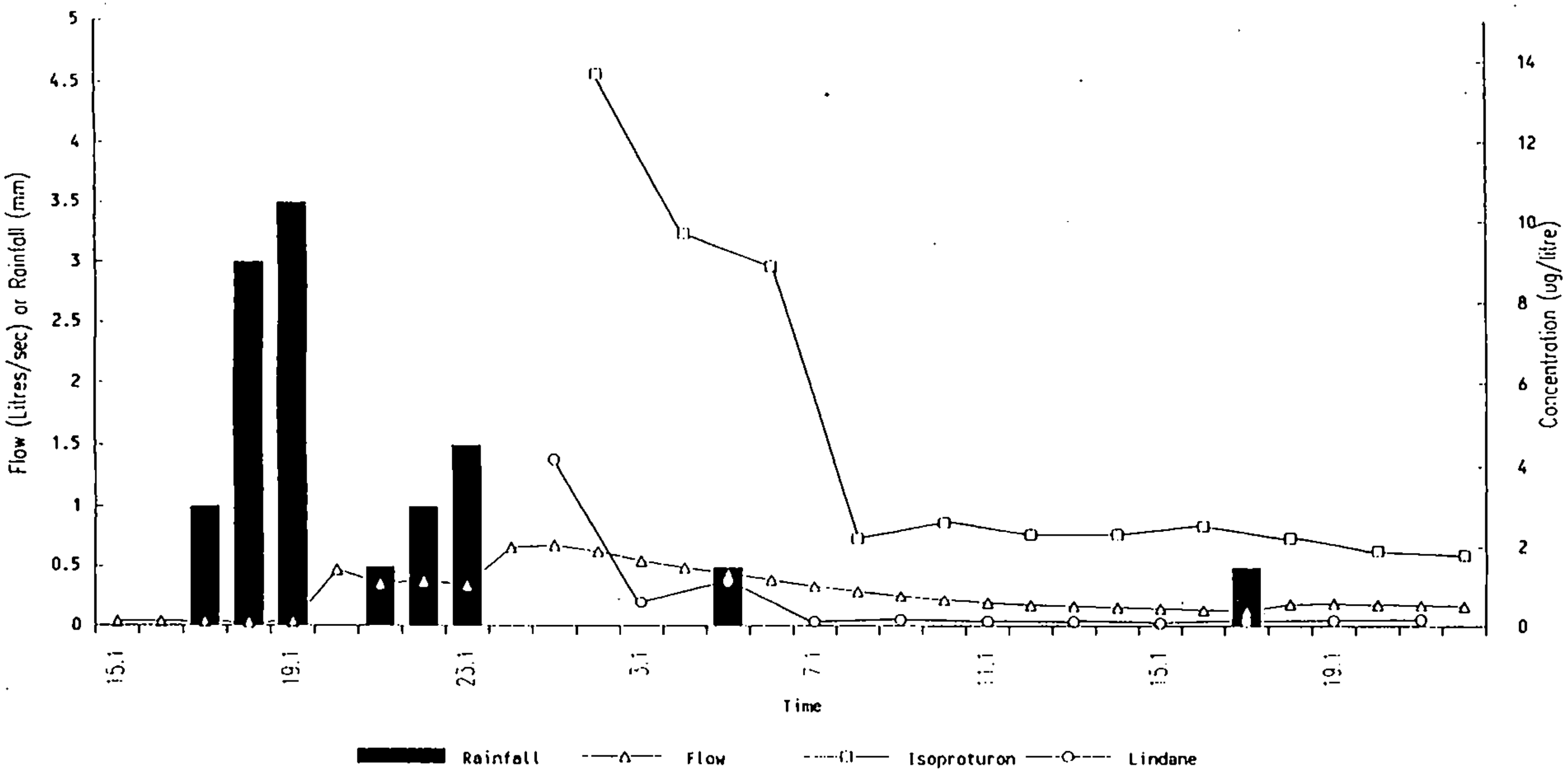


Fig.W3. Rosemaund Site 1.Isoproturon/Lindane Experiment.13.12.89-14.12.89

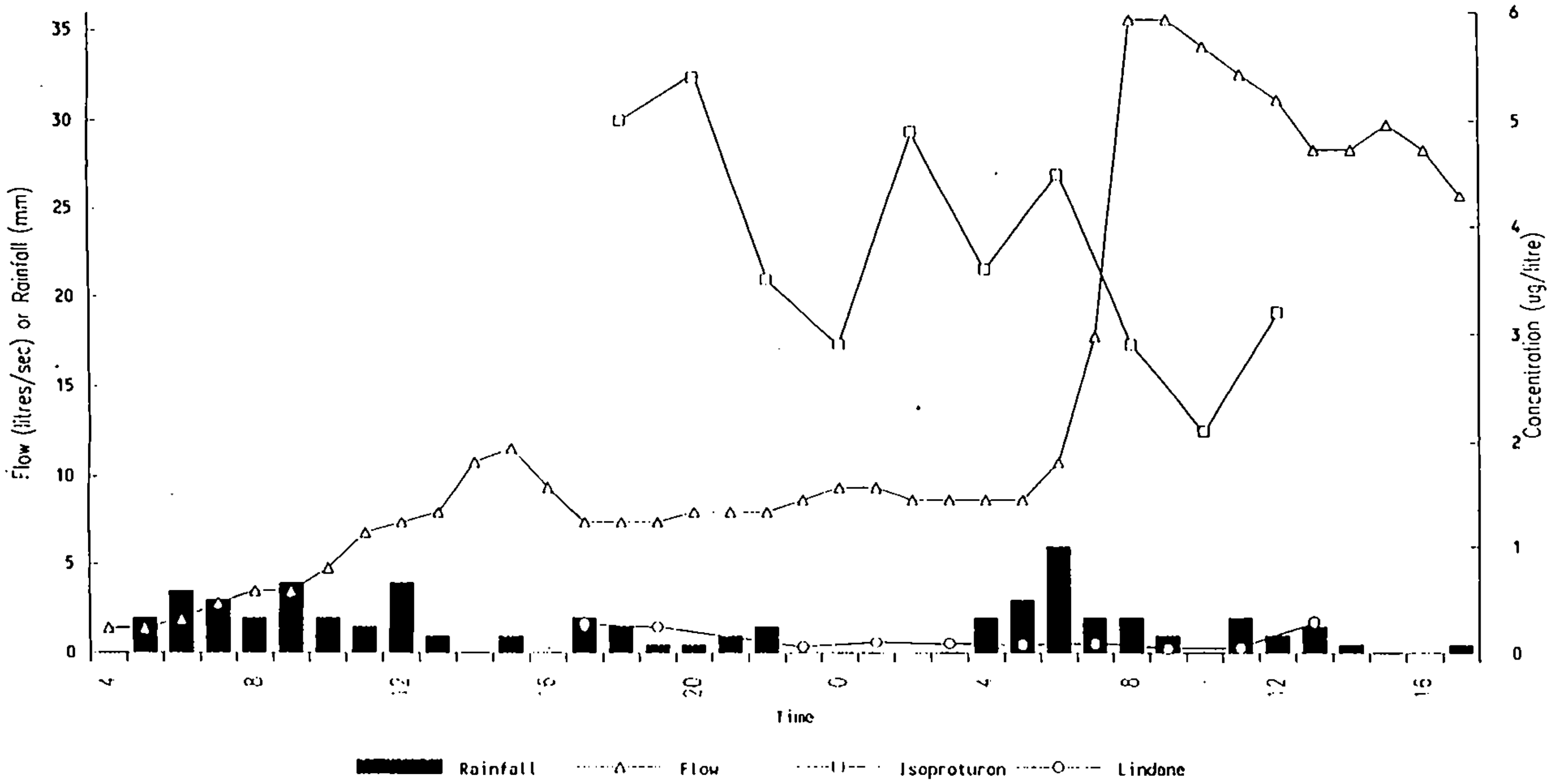
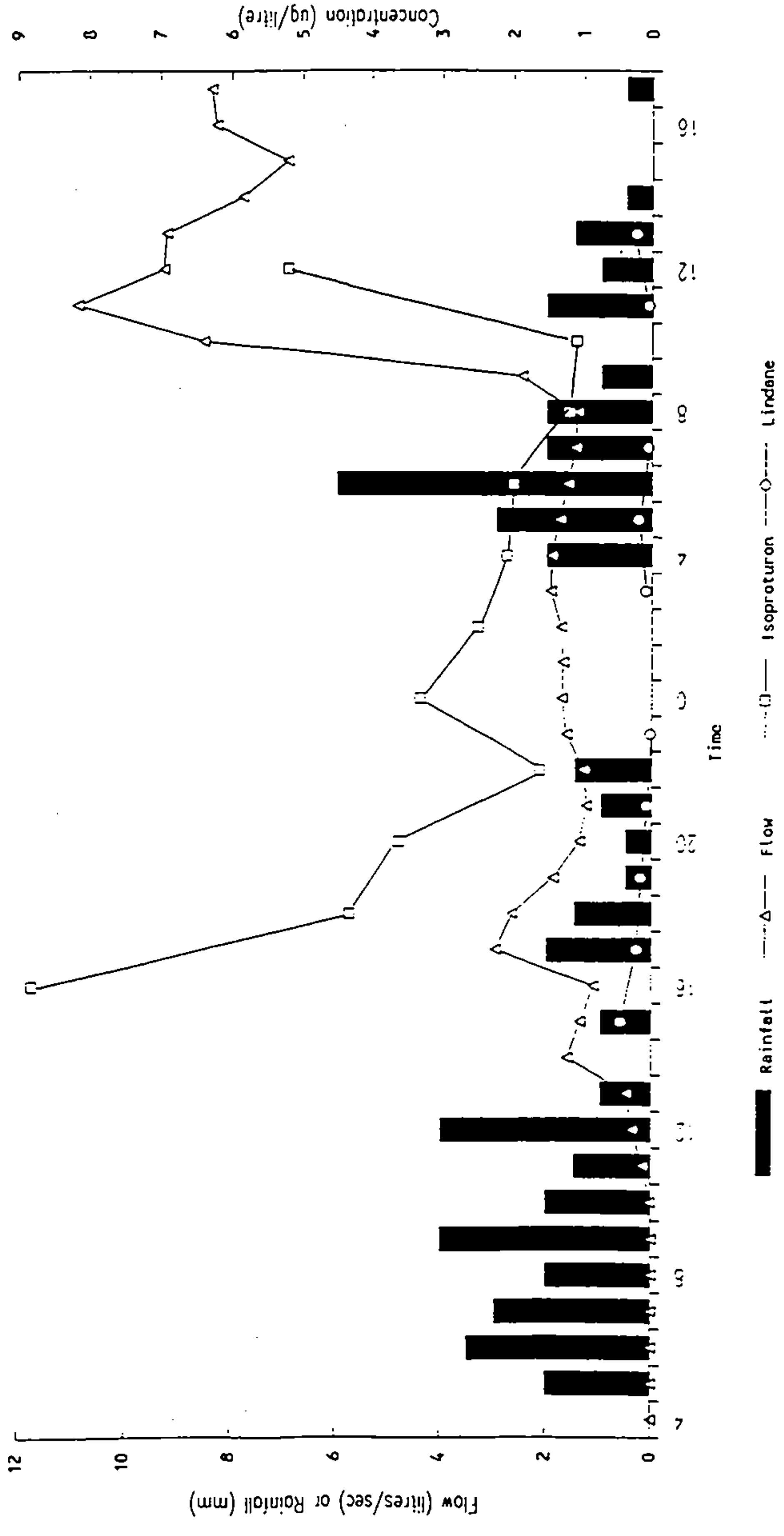


Fig.W4. Rosemaund Site 3.Isoproturon/Lindane Experiment.13.12.89-14.12.89



Approximately 156 mg of lindane flowed in the stream during this event, although it should be noted that water flowrates were still very high when sampling ceased.

The pattern of water flow rates and lindane concentrations seen in the drain at Site 3 was similar to the stream, although peak concentrations were somewhat higher (0.45 and 0.29 µg l^{-1}) and water flowrates lower (peak = 10.9 l sec^{-1}). Approximately 34 mg lindane flowed in the drain during this event, so 4.5 times as much lindane flowed in the stream. Site 3 drains roughly 50% of the area sprayed with lindane, implying that a considerable proportion of the lindane reaching the stream did so by non-drain routes (eg. overland flow).

Rainfall event on 19 March 1990

This was a small event (9.0 mm), but again, both sites 1 and 3 were sampled (Table W5, Appendix XI, and Figs. W5 and W6). By this date, lindane concentrations in the field had markedly declined, and concentrations appearing in the stream and drain were therefore low (max = 0.02 and 0.03 µg l^{-1} respectively). In both cases, there was a lindane peak which was associated with peak water flowrates, and in the case of the stream there was a second peak which just preceded a small subsidiary water flowrate peak. The total amounts of lindane mobilised were 0.7 mg in the stream and 0.08 mg in the drain, again implying a degree of transport via overland flow and other non-drain routes.

Between the spraying date and the 19 March 1990 event, despite gaps in the data, it is estimated that 0.6 g of lindane were mobilised from the field during rainfall events. Between events, it is estimated that a further 0.1-0.2 g were mobilised in all, giving a total of 0.7-0.8 g for the whole experiment. This represents about 0.03% of the total applied to Foxbridge and Longlands. Some of these data were presented in Williams _et al_ (1991).

Fig.W5. Rosemaund Site 1.Isoproturon/Lindane Experiment.19.3.90-20.3.90.

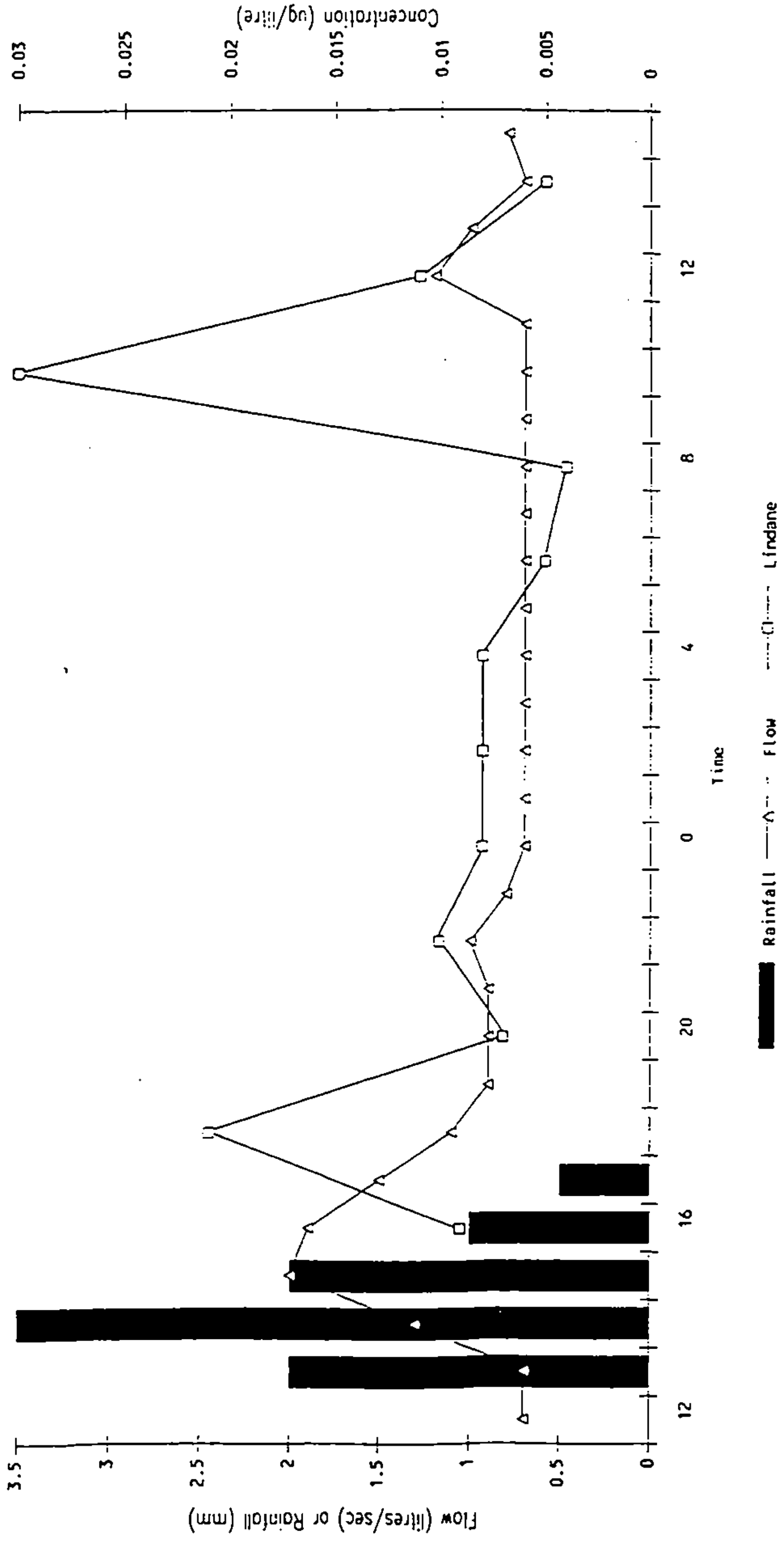
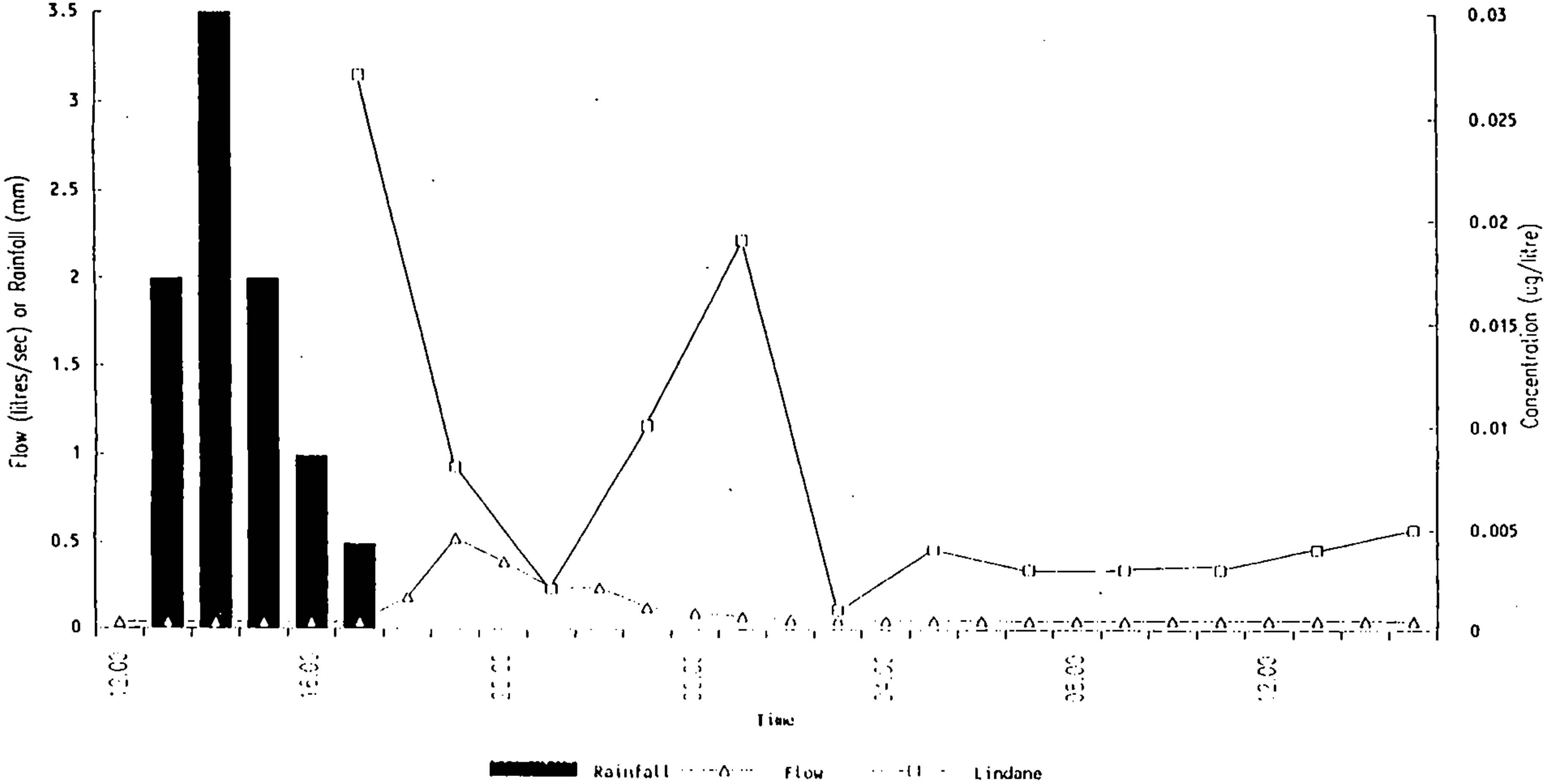


Fig.W6. Rosemaund Site 3.Isoproturon/Lindane Experiment.19.3.90-20.3.90



5.5.2 NRA/IH Experiment Series B

Results described in previous annual report.

5.6 ISOPROTURON/DIMETHOATE EXPERIMENT, AUTUMN 1990

Isoproturon was applied to Stoney and Brushes as Panther at 1.0 kg ai ha^{-1} on 11 October 1990, and to Foxbridge and Longlands as Hytane + Panther at 2.13 kg ai ha^{-1} on 23 November 1990. Dimethoate was applied to both fields at 0.34 kg ai ha^{-1} on 28 November 1990. The sprayed crop was winter barley.

5.6.1 MAFF/BRE Experiment A

5.6.1.1. Methods

Soil

Soil samples were taken from both areas to a depth of 1 metre, using a stainless steel corer. Sites were chosen at random from the intersects of a 25 metre grid superimposed on a map of the field. One site per visit was sampled in 25 cm sections, to give four depth profile sections. The samples have been stored at -35 °C since collection; no analysis has been carried out thus far on these samples.

Water

The sampling strategy and techniques remained essentially the same as in the 1989/90 season.

Isoproturon analysis

1 l samples were stabilised in the field by the addition of 2 ml '880' ammonia solution followed by 50 ml dichloromethane (DCM). The samples were transferred in the laboratory to a 2 l bottle and mechanically shaken for 15 minutes after which the organic layer was separated off in a separating funnel. A further 50 ml of DCM was used to rinse out the original sample bottle and this was then added to the sample. After a further 15 minutes shaking the organic layers were combined and dried over sodium sulphate (previously dried in a muffle furnace at 400 °C for 4 hours). This extract was

stored at -20 °C in the dark. The final reduction was achieved by rotary evaporation of the DCM under vacuum to approximately 5 ml. This was then transferred by rinsing with a further 5 ml of DCM to a small vial, placed in a water bath at 40 °C, and reduced to dryness under a stream of clean, dry nitrogen. The analyte was redissolved in the mobile phase for chromatographic analysis.

Analysis of isoproturon was by high pressure liquid chromatography (HPLC) using a 25 cm C18 reversed phase column with UV detection at 240 nm. The instrument used was an LDC series 111 HPLC pump linked to an LDC spectromonitor 3100 detector. The mobile phase was a 1:1 ratio of acetonitrile and distilled deionised water (DDW) run isocratically. This was filtered through Whatman 41 filters and degassed continually by helium. A flow rate of 1.5 ml min^{-1} was used unless the pressure increased above 5000 psi at which point the flow was reduced to 1.2 ml min^{-1}. The injection volume was 100 µl.

Standard solutions of isoproturon were made up in the mobile phase from a reference standard. All solvents used were of HPLC or glass distilled grade.

Results were calculated from a standard chart recorder print out by measuring peak heights with reference to a calibration curve generated by injection of known standards of the relevant concentrations. Calibration standards were obtained from Greyhound Chromatography and Allied Chemicals. All samples were analysed in duplicate and the mean result taken. The detection limit of the analytical method was below 0.1 ppm, thus giving a detection limit below 0.1 µg/l in most samples. Soil water sample volumes were often less than 1 l therefore detection limits were reduced correspondingly.

A test for extraction efficiency using environmental lake water from the University site gave a mean recovery of 95% +/- 1.7%.

This was determined by spiking 1 l of lake water with isoproturon reference standard to a concentration of 10 ppb. The number of parallel extractions was 8 and 2 blank extractions. Blank levels were 0.2 ppb in both cases. The limit of detection for this method was 0.01 mg l^{-1} for samples of 1 l, soil water samples of less volume had correspondingly higher detection limits.

Dimethoate analysis

1 l samples were stabilised in the field by the addition of 2 ml concentrated hydrochloric acid followed by 50 ml dichloromethane (DCM). The extraction procedure was similar to that used for isoproturon, being a two fold liquid/liquid extraction into DCM, and reduction to 1 ml of the mobile phase for chromatographic analysis.

Extracted samples in hexane were analysed by a Hewlett Packard 5890 gas chromatograph equipped with a nitrogen/phosphorus detector. The column used was an HP-5 (25 m x 0.2 mm x 0.33 mm) with helium carrier gas. The injection volume was 1.5 ml and the injector temperature was 153 °C. The oven was set at 150 °C and run isothermally. Quantitative results were gained from a standard calibration curve calculated by a Hewlett Packard 3396A integrator. Calibration standards were obtained from Greyhound Chromatography and Allied Chemicals.

Recovery tests yielded an extraction efficiency of 91% (σ = 3% n = 3) from 2 µg l^{-1} spiked concentration into DDW. The results given have not been corrected for these recoveries. The detection limit for the method was initially 0.05 µg l^{-1} but was improved to 0.01 µg l^{-1} for later samples by development of the method. The value of 0.01 µg l^{-1} was, to some extent, dependent upon clean samples, being based on 3 times baseline noise. The soil water samples which were less than 1 l had correspondingly higher limits of detection.

5.6.1.2. Results and Discussion

Soil water samples

Soil water from the soil suction samplers situated in Foxbridge and Longlands was obtained on four occasions between 12 November 1990 and 28 February 1991. Isoproturon concentrations are given in Table W12, and show that there was some residual herbicide at 0.5 m depth on 12 November 1990 (presumably originating from the 1.0 kg ha^{-1} application on 1 November 1989). Throughout the experimental period, the soil was very dry and prevented samples being taken from many samplers. It is therefore difficult to discern patterns, but it is clear that (as in Autumn 1989) concentrations of up to 18 µg l^{-1} were able to penetrate to the depth of the field drains (1.0 m) within 5 weeks of spraying. However, it should be noted that the application rate in the present case was twice that in 1989. Furthermore, the high concentrations seen at 1.5 m depth in 1989 (up to 54 µg l^{-1}) were not present in 1990/91 (max = 9.4 µg l^{-1}). As in 1990, the concentrations of isoproturon in soil water were extremely variable, indicating a considerable variation in the soil water flow regime, depending on the precise location with respect to field drains. The dimethoate data (Table W13, Appendix XI) are too sparse to be subjected to detailed analysis, peaking at 0.25 µg l^{-1} at field-drain level, and 0.16 µg l^{-1} at 1.5 m. By 28 February 1991, all concentrations were below the detection limit (0.01 µg l^{-1}).

Manual samples

The isoproturon results from these samples are shown in Table W6, and the dimethoate results in Table W7 (Appendix X). Rainfall was low for several months after spraying, so manual samples could not be collected from most of the field drains until January 1991. Isoproturon concentrations in the stream were in the range 0.04-1.50 µg l^{-1}. Isoproturon concentrations in the drains and ditches varied from <0.01 to 26.2 µg l^{-1}, with no clear correlation with rainfall events. It is apparent, however, that the drain discharges were being considerably diluted by relatively uncontaminated water, some of which was undoubtedly derived from the ditch at Site 2. This ditch water arises from a perennial spring that is almost certainly fed in part from outside the catchment.

Dimethoate concentrations in the manual stream samples were generally below the limit of detection (0.01-0.05 µg l^{-1}), but peaked at 0.1 µg l^{-1} on one occasion. Dimethoate concentrations were also low in the Site 2 ditch, but reached peaks of 2.85, 1.25 and 1.10 µg l^{-1} in the drains at Sites 3, 4 and 5 respectively. Again, dilution of the drain water by the ditch discharge was clearly occurring.

Rainfall event on 25 December 1990

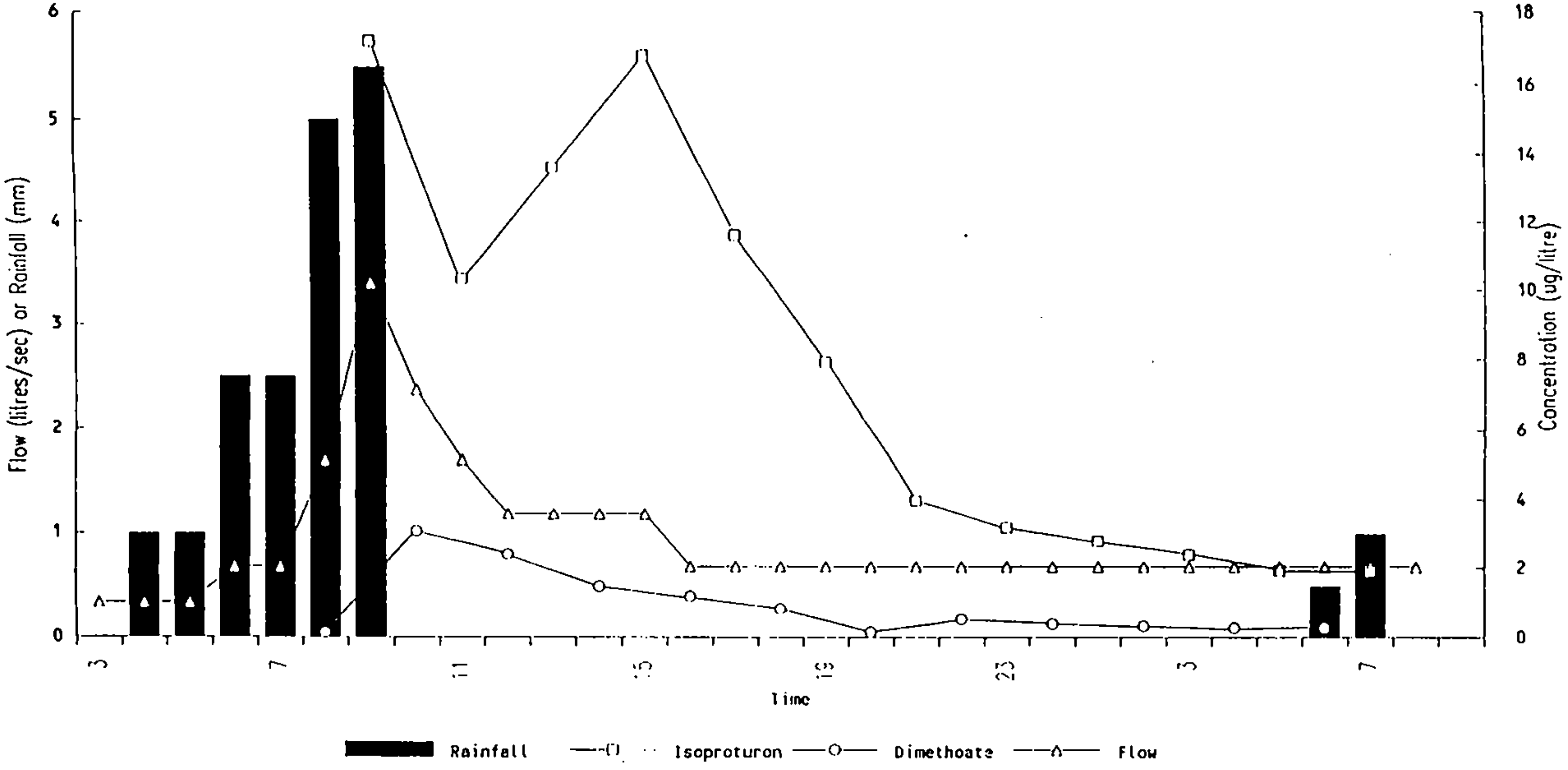
MAFF/BRE Experiment Series A

Automatic water samples were only obtained from the stream at Site 1 (Table W8, Appendix XI and Fig. W7). The rainfall event was 17.5 mm, with a further 1.5 mm about 24 hours later. As in previous events, isoproturon concentrations peaked at approximately the same time as the flowrate peak (17.2 µg l^{-1} and 3.40 l sec^{-1}, respectively). A further peak of 16.8 µg l^{-1} was observed after 6 hours, followed by a rapid decline to approximately 2 µg l^{-1}. The dimethoate peak (3.05 µg l^{-1}) was also roughly coincident with the flowrate peak, declining thereafter to approximately 0.3 µg l^{-1}. A total of 869 mg of isoproturon and 99 mg of dimethoate flowed down the stream during this event.

NRA/IH Experiment Series B

10.5 mm of rain fell on the catchment between 0400 and 0900 on 25 December 1990. The subsequent rise in stream level caused the automatic sampler on the main gauging site (GR SO 5598 4789) to trigger at 0815 on 25 December 1990. Samples were taken each hour for 24 hours. The automatic sampler on the Longlands field drain (GR SO 5688 4847) was not triggered by this rainfall event.

Fig.W7. Rosemaund Site 1.Isoproturon/Dimethoate Experiment.25.12.90-26.12.90



Results

The results of the analysis of the samples taken from the main gauging site are given in Table A1, Appendix XII.

Isoproturon

The levels of isoproturon measured were generally low with a maximum of 1.76 µg l^{-1} and the bulk of the samples between 0.5 and 1.0 µg l^{-1}. The distribution of concentrations through the event showed no correlation with stream discharge or rainfall.

Dimethoate

No values of dimethoate were measured above the detection limit of 0.02 µg l^{-1}.

Simazine and Atrazine

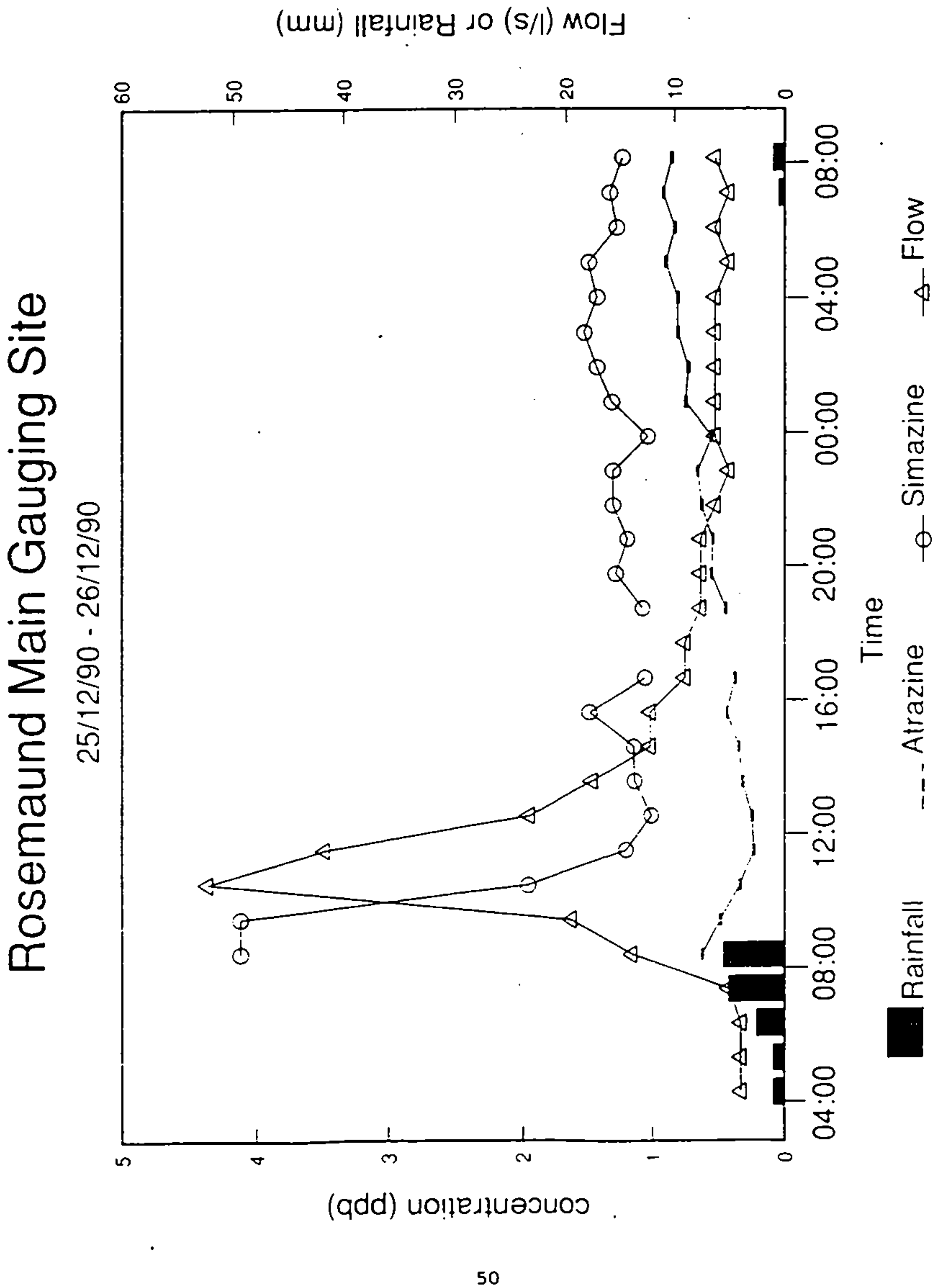
The peak simazine concentration of 4.12 µg l^{-1} was measured in the first two samples. The majority of the samples were around 1 µg l^{-1}. The concentrations seem to be strongly associated with rainfall. The peak concentration occurring at the end of the rainfall and before the maximum flow value (Fig. A1). This observation was also made in the last Rosemaund Report (Bird et al, 1990). Atrazine levels were lower than for simazine with values around 0.5 µg l^{-1}. There is the suggestion of a depression of atrazine concentrations coinciding with the peak flowrate. This could suggest a contribution of atrazine to the stream through base flow, being diluted by lower concentration water from the surface and quick flow routes.

Event 5 January 1991

MAFF/BRE Experiment Series A

No data generated.

Figure A1.


Rosemaund Main Gauging Site
25/12/90 - 26/12/90
concentration (ppb)
0
1
2
3
4
5
Flow (l/s) or Rainfall (mm)
0
10
20
30
40
50
60
04:00
08:00
12:00
16:00
20:00
00:00
04:00
08:00
Time
Rainfall
Atrazine
Simazine
Flow

NRA/IH Experiment Series B

Rainfall

34.5 mm of rain fell between 25 December 1990 and 4 January 1991. Due to the Christmas holidays the sampler was not reset until 2 January 1991. 9.5 mm of rain fell between 0300 and 1400 on 5 January 1991 causing the automatic sampler to trigger at the main gauging site. Samples were again collected each hour for 24 hours. The Longlands field drain autosampler was not triggered.

Results

The results of the chemical analysis of these samples are given in Table A2, Appendix XII.

Isoproturon

The levels of isoproturon were very low, less than 0.2 $\mu g\ l^{-1}$, with the exception of two values towards the end of the sampling run, which were of 2.5 and 5.2 $\mu g\ l^{-1}$. The occurrence of isoproturon bore no relationship to either the rainfall or the stream flow.

Dimethoate

No concentrations were found above the limit of detection.

Simazine and Atrazine

Simazine levels were lower than in the previous event, as would be expected since no more applications had been made. The peak value was 1.5 ug/l, with the rest of the higher values occurring with the rainfall. Atrazine concentrations were around 0.5 ug/l as in the previous event with a peak value of 0.8 ug/l. In this event, however, the atrazine concentrations increased with stream flow.

Rainfall event on 8 January 1991

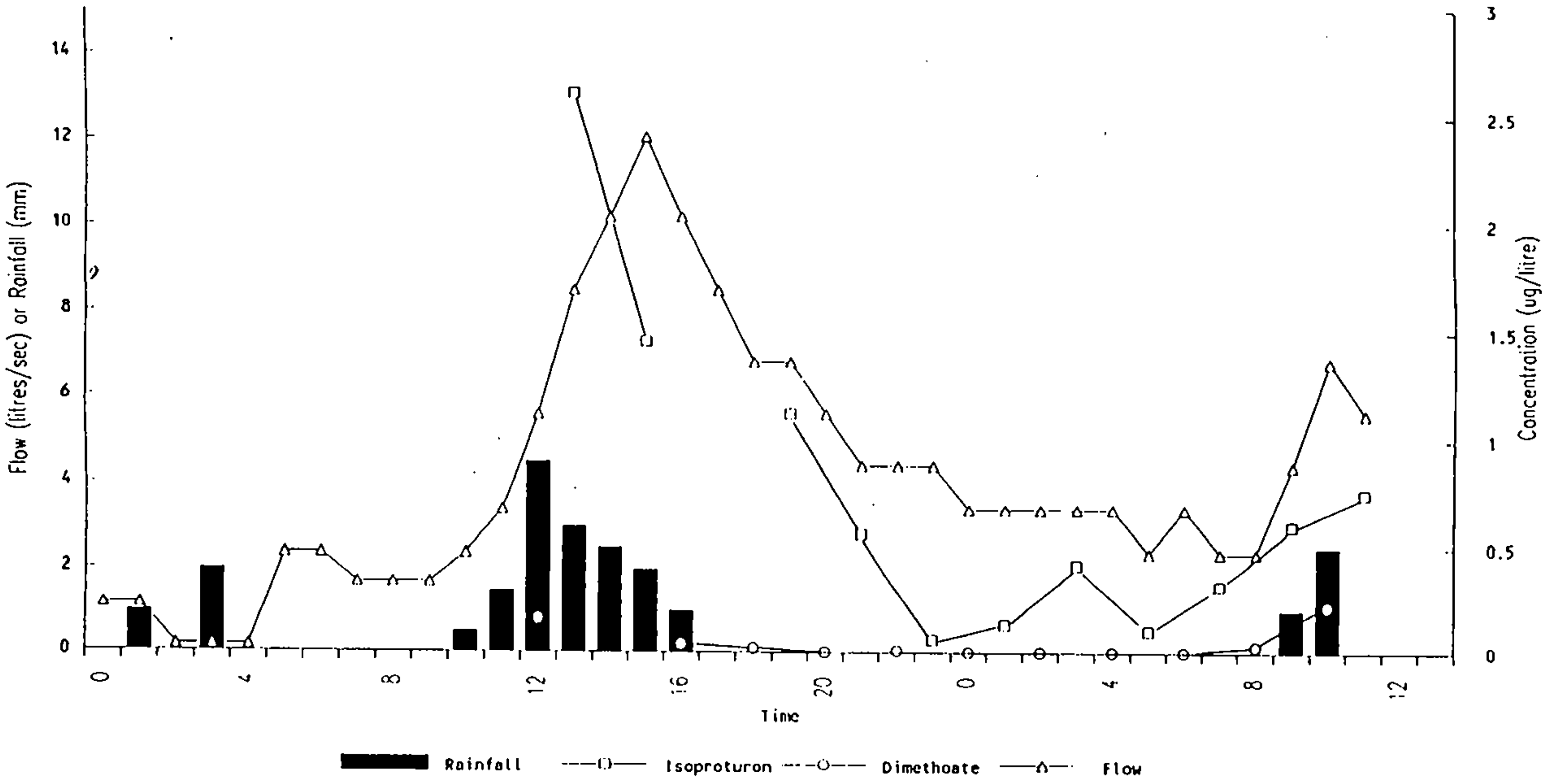
MAFF/BRE Experiment Series A

A full set of automatic water samples was obtained from the stream at site 1, but the sampler on the drain at site 3 had to be triggered manually and only obtained an incomplete set. Water flow rates were not recorded automatically at site 3 (Tables W9 and W10, Appendix XI and Fig. W8). The rainfall event was 18 mm, followed by a further 3.5 mm some 17 hours later. Isoproturon concentrations in the stream peaked at 2.6 µg l^{-1} just before the water flowrate peak (12.1 l sec^{-1}), and then declined rapidly to about 0.1 µg l^{-1}, followed by a slight increase to 0.7 µg l^{-1}. In contrast, the peak level of isoproturon in the site 3 drain appeared to be at least 12.1 µg l^{-1}, with a more gradual decline to 0.5 µg l^{-1}. Dimethoate concentrations in the stream started at 0.16 µg l^{-1}, thereafter declining rapidly to below the detection limit, and recovering to 0.22 µg l^{-1} at the end of the sampling period. For both pesticides, the slight increase at the end appeared to be associated with the increased flowrate derived from the second burst of rain. As with isoproturon, peak levels of dimethoate in the drain were slightly higher than in the stream (0.58 µg l^{-1}). 519 mg of isoproturon were mobilised into the stream during this event, compared with 31 mg of dimethoate.

NRA/IH Experiment Series B

15 mm of rainfall fell between 1000 and 1600 hours on 8 January 1991 causing the automatic samplers to trigger at both the main gauging site (1315 hours) and the Longlands field drain (1300 hours). Twenty-four hourly samples were taken at the main gauging site but only 11 from the Longlands drain due to sampler failure. A further 5.5 mm of rain fell between 0600 and 1000 hours on 9 January 1991 towards the end of the sample run.

Fig.W8. Rosemaund Site 1.Isoproturon/Dimethoate Experiment.8.1.91-9.1.91



Results

The results of the analysis of the samples from the main gauging site are given in Table A3, Appendix XII and those from Longlands drain in Table A6.

Isoproturon

Main Gauging Station

The concentrations showed a similar pattern to the previous event; very low concentrations initially and much higher concentrations at the end of the sampling run. In this case however the peak concentration of 6.7 µg l^{-1} coincided with a small rainfall event (Fig. A2).

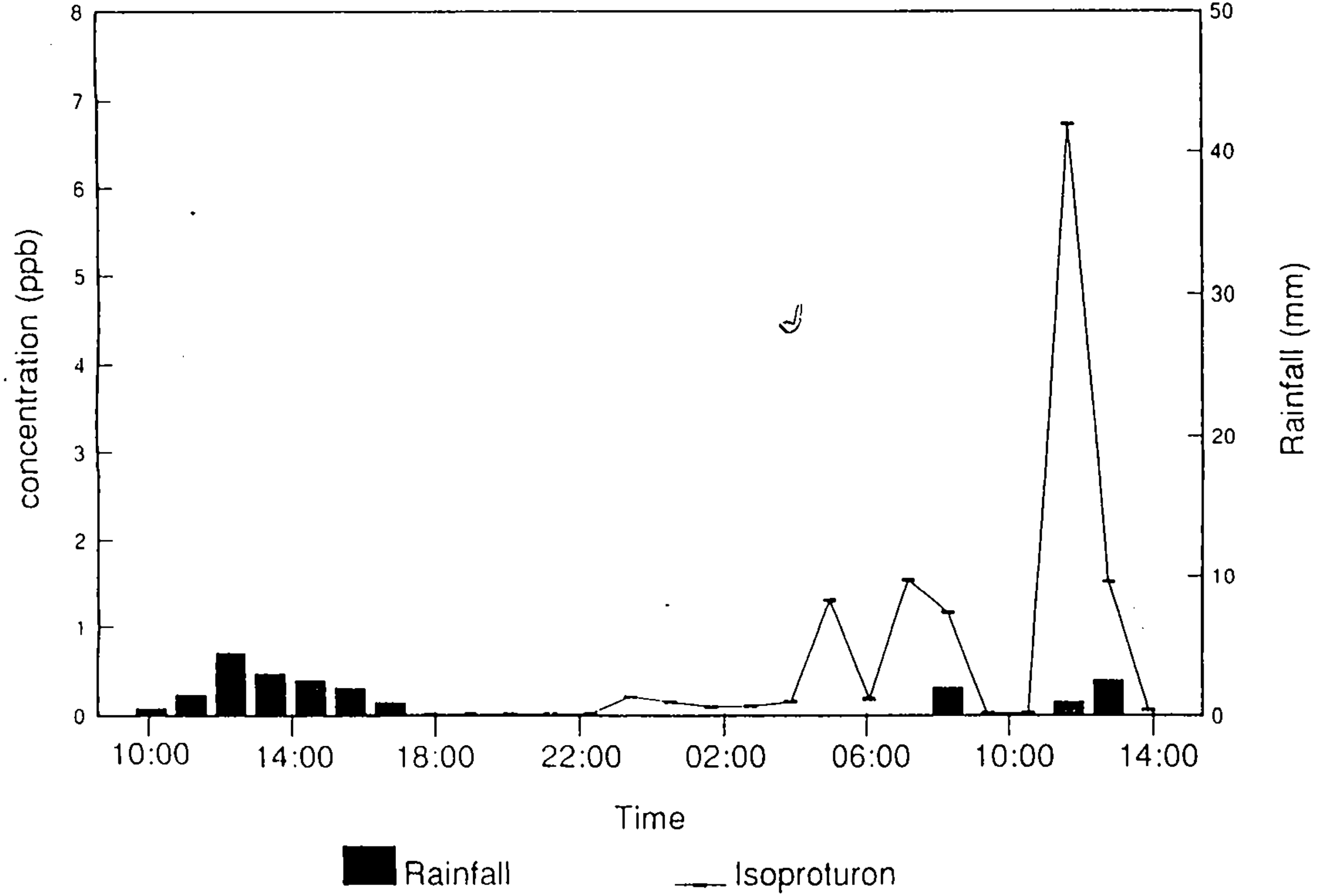
Longlands Drain

Concentrations were generally low in all the samples collected with a maximum value of 0.38 ug l^{-1}. The concentrations showed no obvious relationship with either rainfall or flow.

Figure A2

Rosemaund Main Gauging Site

08/01/91 - 09/01/91



Dimethoate

No concentrations of dimethoate were measured above the detection limit at either the main gauging site or Longlands field drain.

Simazine and Atrazine

Main Gauging Site

Concentrations of simazine were once again lower than in the previous event with a peak value of 0.8 µg l^{-1}. Once again peak simazine concentrations coincided with rainfall events (Fig. A3). Atrazine levels were also low at around 0.1 to 0.2 µg l^{-1}. In this case the atrazine concentrations once again showed a decrease with the initial rainfall event but an increase with the small amount of rainfall at the end of the sample run.

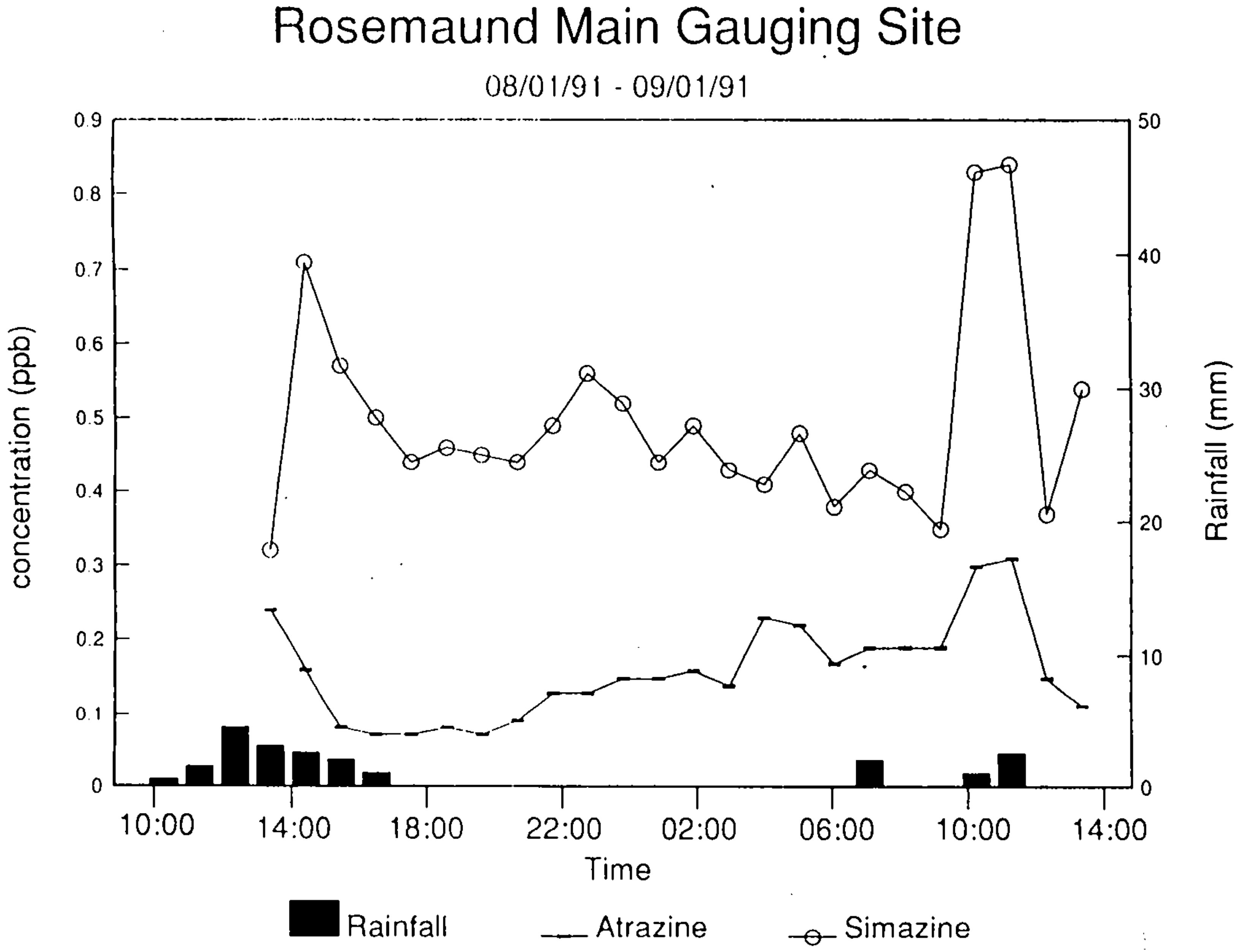
Rainfall event on 21 February 1991

MAFF/BRE Experiment Series A

On this occasion, automatic water samples were obtained only from the stream at Site 1 and only isoproturon was looked for (Table W11, Appendix XI and Fig. W9). The event consisted of 11.5 mm of rain. As before, isoproturon concentrations peaked (2.07 µg l^{-1}) at about the same time as the water flow rate (9.1 l sec^{-1}), and then declined fairly rapidly to 0.4 µg l^{-1}. The total amount of isoproturon mobilised during this event was 398 mg.

The total amounts of isoproturon and dimethoate mobilised during rainstorms in this experiment were approximately 1.8 g and 0.1 g respectively. Taking a mean between-storm stream flowrate of 0.5 l sec^{-1} and a mean concentration of isoproturon of 0.5 µg l^{-1}, the total between-storm flux would have been approximately 2.4 g up to 21 February 1991, giving an overall isoproturon total of 4.2 g. Similarly, the between-storm flux of dimethoate was approximately 0.2 g, giving an overall dimethoate total of 0.3 g. These values represent approximately 0.02% and 0.005% of the isoproturon and dimethoate applied, respectively.

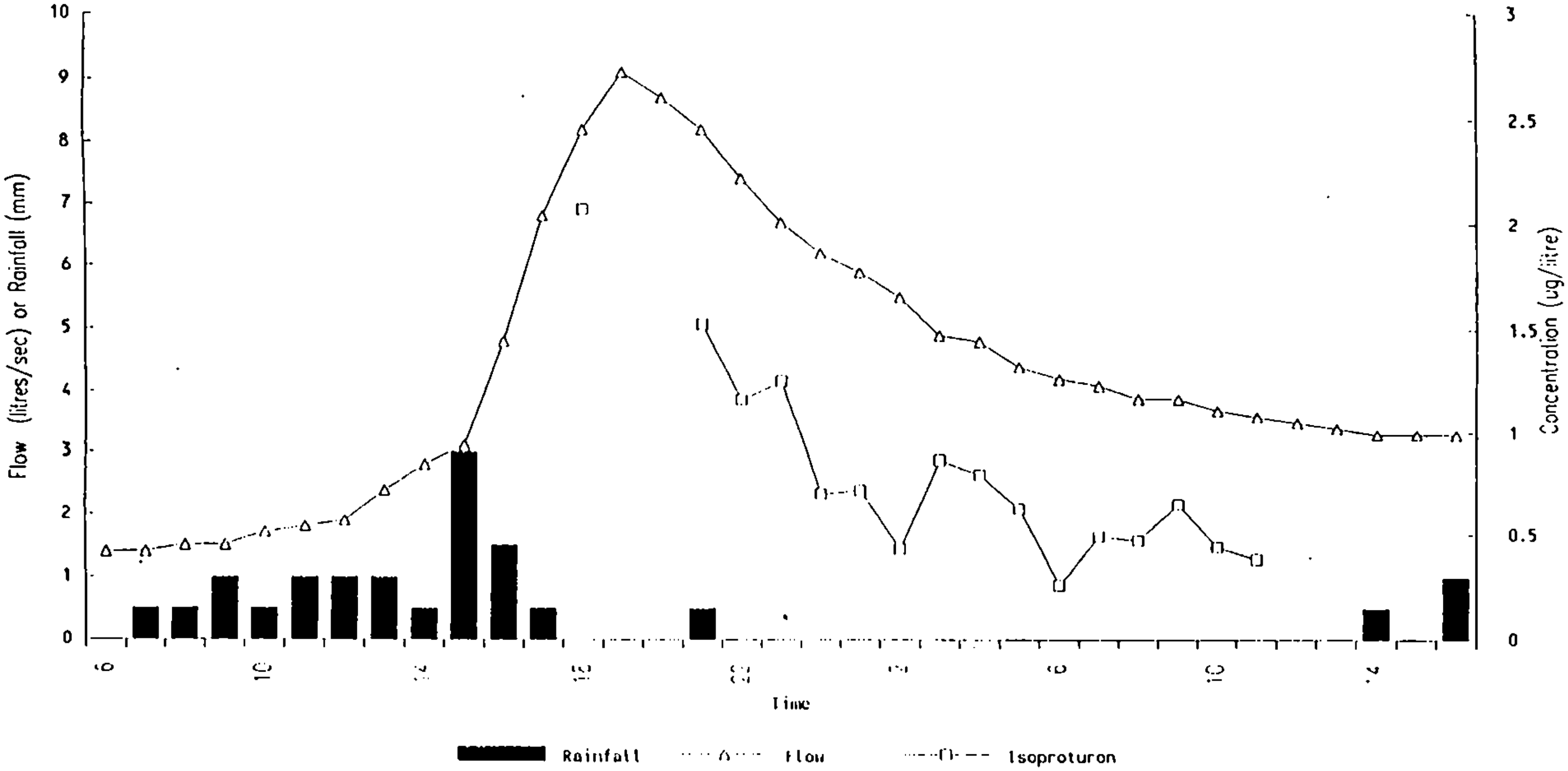
Figure A3.



Rosemaund Main Gauging Site

08/01/91 - 09/01/91

Fig.W9. Rosemaund Site 1.Isoproturon/Dimethoate Experiment.21.2.91-22.2.91.



NRA/IH Experiment Series B

11.5 mm of rain fell between 0600 and 2100 on 21 February 1991 causing both automatic samplers to trigger, 1600 at the main gauging site and 1330 at Longlands drain. Due to sampler failure only 6 samples were taken from the main gauging site and 20 from Longlands drain.

Results

The results of the analysis of the samples is given in Table A4 for the main gauging site and Table A7 for Longlands drain, Appendix XII.

Isoproturon

Main Gauging Site

None of the samples contained concentrations above the detection limit.

Longlands Drain

The first 5 samples had very low concentrations around the detection limit of 0.02 µg l^{-1}. Subsequent samples had values around 2 µg l^{-1} with a peak value of 2.7 µg l^{-1} (Fig. A4).

Dimethoate

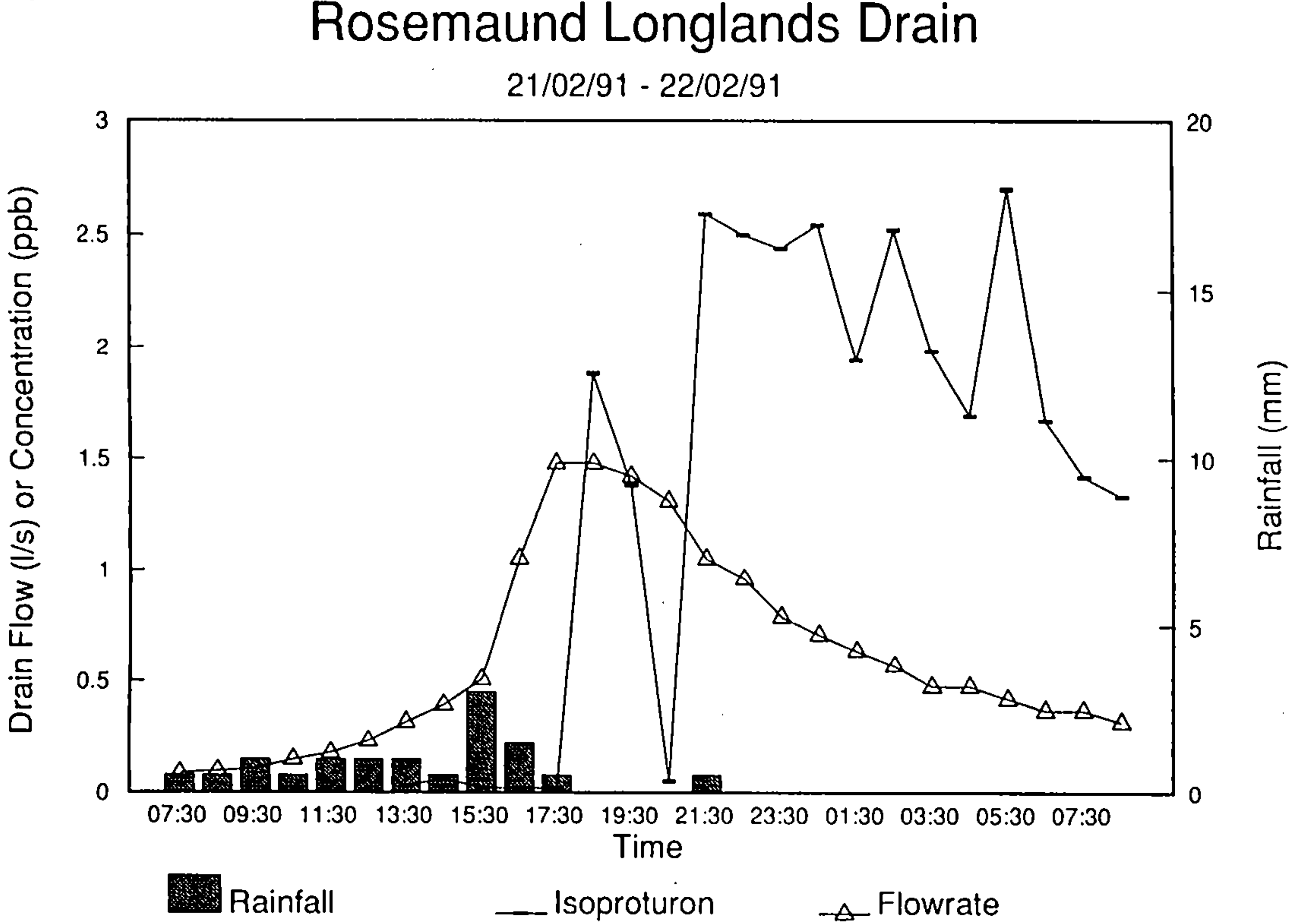
No samples had concentrations above the limit of detection at either the main gauging site or Longlands drain.

Simazine and Atrazine

Main Gauging Site

The simazine concentrations were again low with a peak concentration of 0.37 µg l^{-1} occurring with the peak stream flow. Atrazine concentrations were very low, less than 0.1 µg l^{-1} for most of the samples.

Figure A4.


Rosemaund Longlands Drain
21/02/91 - 22/02/91
Drain Flow (l/s) or Concentration (ppb)
3
2.5
2
1.5
1
0.5
0
Rainfall (mm)
20
15
10
5
0
07:30
09:30
11:30
13:30
15:30
17:30
19:30
21:30
23:30
01:30
03:30
05:30
07:30
Time
Rainfall
Isoproturon
Flowrate

5.7 MCPA/OXYDEMETON METHYL EXPERIMENT, SPRING 1991

5.7.1 MAFF/BRE Experiment Series A

MCPA was applied to Stoney and Brushes and Foxbridge and Longlands at 1.68 kg ai ha^{-1} on 28 February 1991 and 1 March 1991 respectively. Oxydemeton-methyl was applied to the same fields at 0.114 kg ai ha^{-1} on the same dates. The crop (winter barley) was the same as that sown in Autumn 1989.

5.7.1.1. Methods

The sampling strategy and techniques were the same as for the Autumn 1989 experiments.

Oxydemeton-methyl analysis in water

1 l water samples were acidified in the field with 2 ml concentrated hydrochloric acid followed by the addition of 50 ml dichloromethane (analytical grade, glass re-distilled). The stabilised samples were stored in the dark and then extracted with further dichloromethane, after which the combined extracts were evaporated to incipient dryness. The residue was dissolved in 1 ml methanol and stored at -20 °C to await analysis.

The methanol extract was added to 10 ml distilled deionised water (DDW) to which was then added 2.5 ml of 0.1 N potassium permanganate and 0.2 ml concentrated sulphuric acid. After 40 minutes oxidation, the resulting sulphone derivative was separated off in a preconditioned C18 SPE cartridge and eluted with 7 ml dichloromethane. This was evaporated to incipient dryness at 40 °C in a stream of oxygen-free nitrogen. The final extract was redissolved in a known weight of ethyl acetate (0.3-0.5 ml).

The quantification needs to be understood in the light of the total extraction procedure. Initial liquid/liquid extraction efficiency was not quantified, although past experience with the technique would indicate a value around 70%. The efficiency of the oxidation step was quantified using freshly prepared standards of oxydemeton methyl and demeton-S-methylsulphone. The efficiency was low at 39% with standard deviation of 9% (n=5). Due to these factors, and the low stability of these samples in water, the true environmental concentrations at the time of sampling could be higher than the results obtained. The sulphone was not detected at any time in environmental samples, so the present method involving an oxidation step to the sulphone was adopted as a technique for quantifying oxydemeton methyl.

GC-MS analysis using a Hewlett Packard 5890 Mass Selective Detector (MSD) operating in single ion mode allowed for a limit of detection of 0.15 $\mu g\ l^{-1}$. The column used was an HP-5 (25 m x 0.2mm x 0.33 mm) with helium carrier gas. Quantification from known standards of the sulphone was performed using the Hewlett Packard MSD software.

MCPA analysis in water

All samples were delivered to the laboratory without prior treatment and were stored at 4 °C in the dark. A solid phase extraction (SPE) system was used for this compound. The technique has advantages over traditional liquid/liquid extraction in terms of time, minimal use of solvents and reduced sample volumes. The Bond Elute cartridges were obtained from Varian UK Ltd.

A 250 ml portion of each sample was filtered through a Whatman GF/A glass fibre filter (12.5 cm). To the filtrate was added 0.75 ml concentrated hydrochloric acid and 12.5 ml methanol. Octadecyl (C18) SPE cartridges were preconditioned by passing in turn through the cartridge acetone (5 ml), methanol (5 ml) and deionised distilled water (DDW) (5 ml). A water jet pump was used to supply vacuum to apparatus supporting the cartridges. The sample was then allowed to pass through the cartridge at a rate of around 10 ml min^{-1}. The cartridge-bound pesticide was eluted in 0.5 ml methanol, to which was added 0.5 ml DDW containing 1% trifluoroacetic acid and 0.32M potassium chloride. The resulting 1 ml extract was stored in a vial ready for HPLC analysis.

Analysis for MCPA was performed by Reversed Phase HPLC with UV detection on an LDC system using a 25 cm C18 column. The mobile phase was an isocratic 62:38 ratio of methanol to DDW containing 0.08% trifluoroacetic acid and 0.16M potassium chloride. This ratio was developed to separate interfering peaks found in some samples. The flow was set at 1.25 ml min^{-1} and ran at a pressure of around 5000 psi. The variable wavelength UV detector was set at 230 nm. Quantification of sample concentrations was calculated from a calibration curve of known standards by peak height on a strip chart recorder. The reference standards were obtained from Greyhound Chromatography and Allied Chemicals.

The recovery of MCPA by the SPE technique was determined by spiking water obtained from a stream-fed lake on the University of Essex campus. This water was heavily polluted by organic matter. The recovery was 78% (σ = 2.5%), including a blank of 0.22 µg l^{-1}. The limit of detection of the technique was 0.02 µg l^{-1} based on a quantitatively significant peak being 3 times baseline noise.

MCPA analysis in soil

Samples of soil (~10 g) were acidified with 1M sulphuric acid and shaken with dichloromethane (DCM, 10 ml) for 2-3 hours. After decanting off the DCM, the soil was rinsed with a further 10 ml of DCM and the extracts combined. Mecoprop was added as an internal standard. The extracts were then evaporated to dryness under nitrogen. Derivitisation was carried out by adding 1 ml of a 25% solution of α-bromo-2,3,4,5,6-pentafluorotoluene to the residue, together with a drop of saturated sodium carbonate solution. The mixture was kept at 60 °C for 40 minutes, and then allowed to cool. 10 ml of distilled water was added, and then 1 ml of iso-octane. After shaking, the iso-octane layer was removed for GC analysis.
GC equipment: Carlo Erba Fractovap 4160 series GC, BP-1 capillary column, electron capture detector, TRIO computing integrator.
GC conditions: column temperature 155 °C, detector temperature 240 °C, injection direct on to column.

5.7.1.2. Results and Discussion

Soil samples

Data on the levels of MCPA measured in the soil samples are presented in Table S1, Appendix XI. The initial level on the day after spraying in Foxbridge and Longlands was 190 µg/kg wet weight. Degradation was fairly rapid, with levels below the detection limit (1 µg/kg) after 40 days. Assuming first order degradation, the half life of MCPA was 90-100 hours. Profile samples showed significant levels of MCPA below the surface layers shortly after application.

Soil water samples

The soil water suction samplers were in the same positions as in the Autumn 1990 experiments, and soil water samples taken on three dates between 21 March 1991 and 8 May 1991 were sampled and analysed for MCPA alone (Table W18). It is apparent that, as with isoproturon, significant though lower concentrations of MCPA were able to reach 1.0 and 1.5 m below the surface within three weeks of spraying (max. values of 1.26 and 2.58 µg l^{-1} respectively). These had declined to the detection limit in many cases by seven weeks post-spray, although samples from one site (number 9; 1.5 m) were still just above 2 µg l^{-1} after ten weeks. The mean MCPA concentration on 21 March 1991 at the level of the field drains (1.0 m) was 0.3 µg l^{-1}, corresponding reasonably well to the between-peak concentrations found the stream.

Manual water samples

Oxydemeton-methyl was not detected in manual samples taken on 20 March 1991, but the MCPA results are shown in Table W14, Appendix X. The 7 March 1991 samples were taken during a rainfall event (see below), but the other two datasets represent between-event samples, with a maximum of 0.4 µg l^{-1} of MCPA in the stream at site 1 and 4.75 µg l^{-1} in the drains.

Rainfall events on 4 March 1991 to 8 March 1991

These events consisted of a total of 43.5 mm distributed in three main bursts (Table W15, Appendix XI and Figs. W10 and W11). However, stream and drain flowrates did not peak until after the second burst which occurred in the early hours of 7 March 1991. Taking MCPA first, concentrations peaked soon after the first burst, at 12.44 and 18.80 µg l^{-1} for stream (site 1) and drain (site 3) respectively. Concentrations the declined to about 0.4-0.6 µg l^{-1} before the start of the second burst of rain. After a gap in sampling, a further set of autosamples was obtained from the stream immediately after the second burst of rain, and this set overlapped with the final burst. The MCPA peak was lower than previously (2.0 µg l^{-1}) although the highest levels may not have been sampled, but concentrations of approximately 1.0 µg l^{-1} were then maintained until after the final burst, which led to an upturn in MCPA to 2.2 µg/l^{-1}.

The only complete oxydemeton-methyl dataset concerns the stream at Site 1 during the first series of samples. There was an initial peak of 0.8 µg l^{-1} which rapidly declined below the detection limit with a brief reappearance at 0.2 µg l^{-1}.

A total of 374 mg MCPA flowed down the stream during the two sampling runs, and if one allows an estimate of 75 mg for the period between the sampling runs, this gives a total for the whole event of approximately 450 mg MCPA. During the first sampling run, approximately 5-10 mg of oxydemeton-methyl were mobilised into the stream.

NRA/IH Experiment Series B

12 mm of rain fell between 1000 hours and 2100 hours on 4 March 1991 causing the automatic sampler on Longlands drain trigger at 2030 hours the same day. A sample was taken each hour for 24 hours. The sampler at the main gauging site was not triggered.

Fig.W10. Rosemaund Site 1,MCPA/Oxydemeton-methyl Experiment.4.3.91-8.3.91

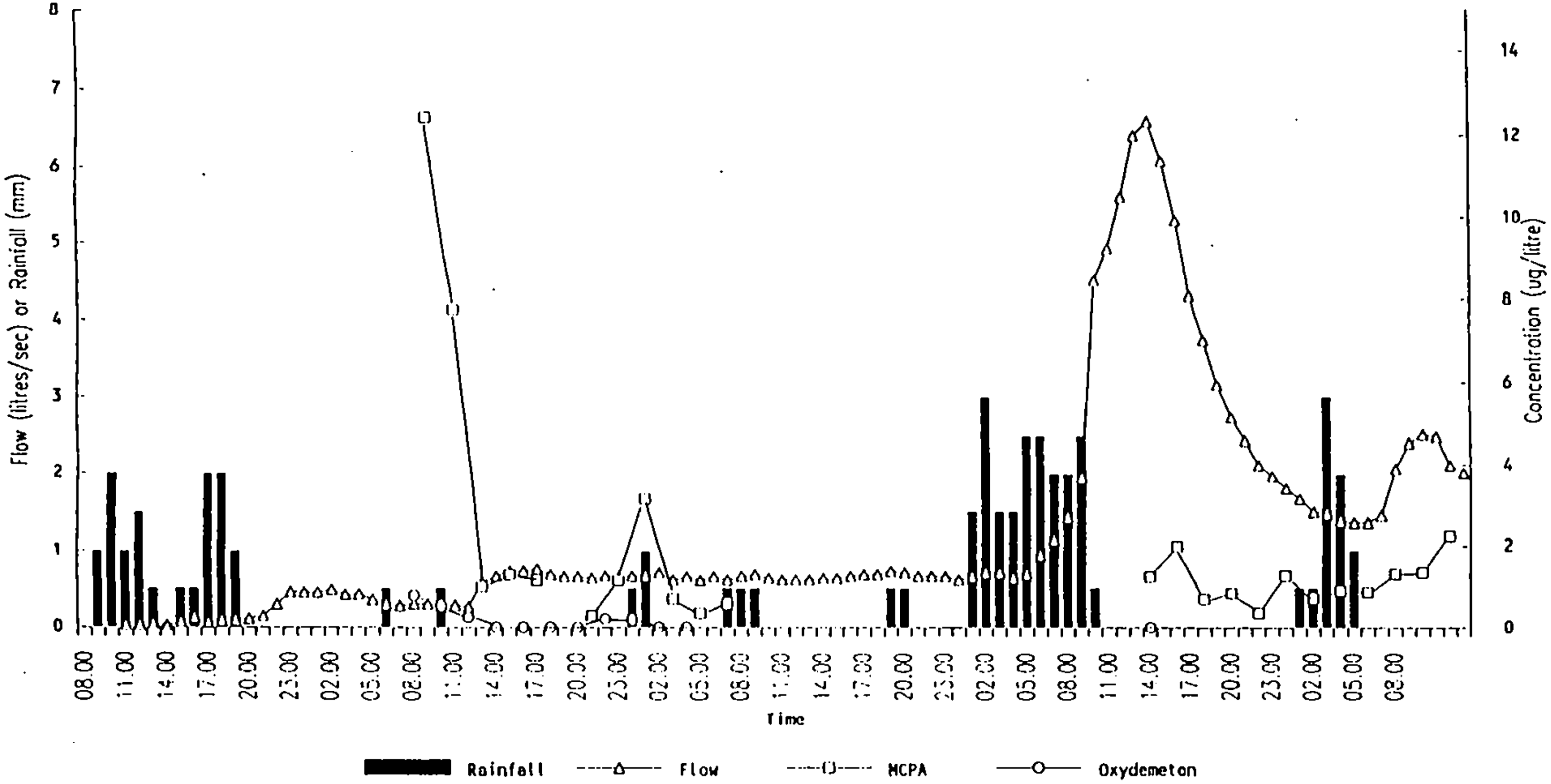
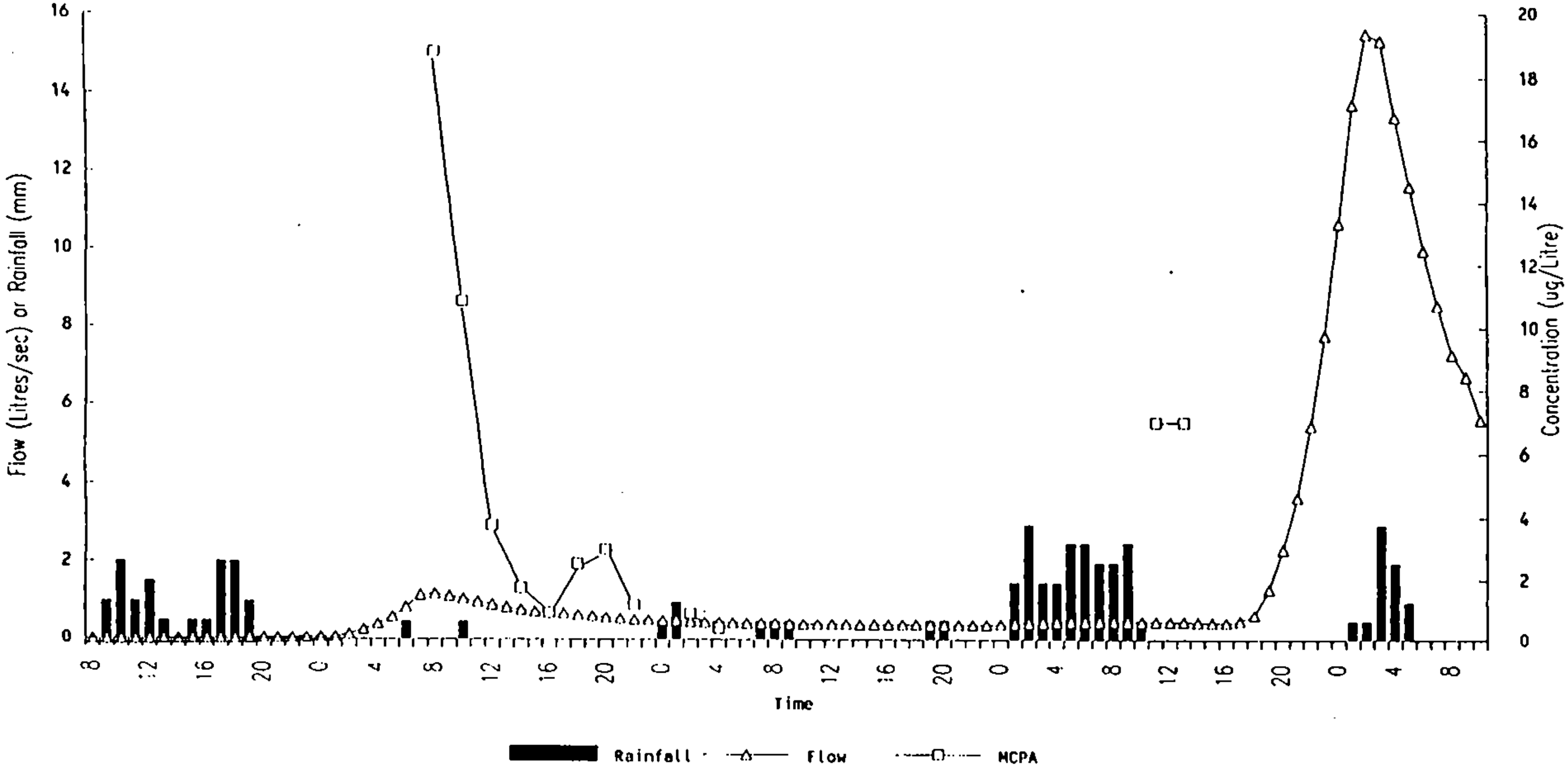


Fig.W11. Rosemaund Site 3. MCPA/Oxydemeton-methyl Experiment.4.3.91-8.3.91



Results

The results of the analysis of the samples are given in Table A8.

Isoproturon

The concentrations of isoproturon showed no pattern through the event. Concentrations varied considerably with a maximum value of 2.5 µg l^{-1}.

Dimethoate

No samples had concentrations above the detection limit.

Oxydemeton Methyl

No samples had concentrations above the detection limit of 10 µg l^{-1}.

Rainfall event on 16 March 1991

MAFF/BRE Experiment Series A

This 10 mm event was followed by a smaller burst of rain (6 mm) approximately 24 hours later (Table W16, Appendix XI and Fig. W12). Samples were only obtained from the stream at Site 1. MCPA peaked immediately at 12.7 µg l^{-1} and then very rapidly declined to approximately 0.3 µg l^{-1}. A few samples from the start of the sampling run were analysed for oxydemeton-methyl, but all concentrations were below the detection limit. Approximately 681 mg of MCPA was mobilised into the stream during this event.

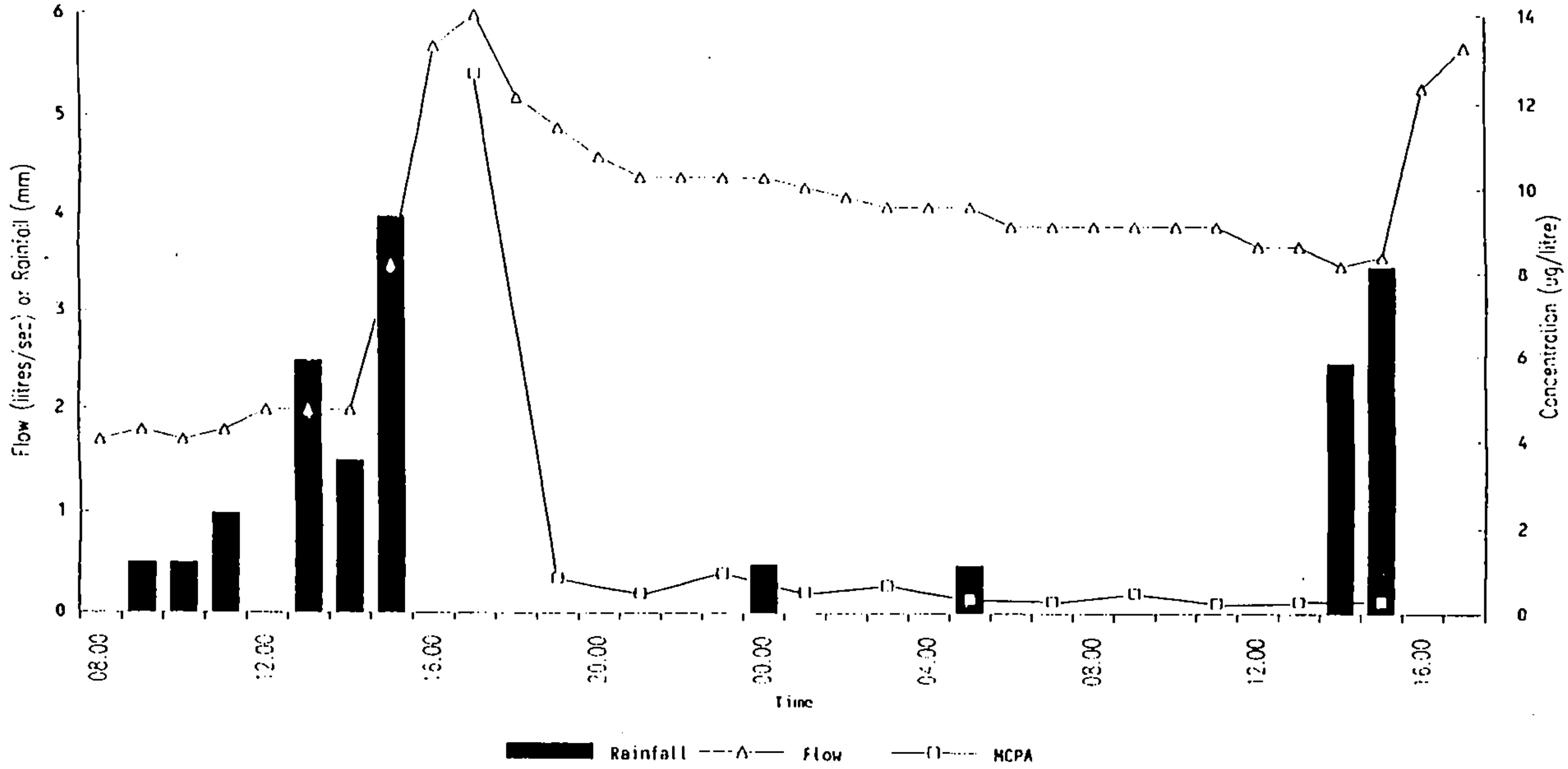
NRA/IH Experiment Series B

10 mm of rain fell between 0900 hours and 1600 hours on 16 March 1991 causing the automatic sampler to trigger at the main gauging site at 1515 hours the same day. A sample was taken each hour for 24 hours. A further 3.5 mm of rainfall fell during the sampling run.

Results

The results of the analysis of the samples is given in Table A5.

Fig.W12 Rosemaund Site 1.MPCA/Oxydemeton-methyl Experiment.16.3.91-17.3.91



Isoproturon

This event gave the highest isoproturon concentrations despite occurring more than three months after its application. Generally levels were around 5 µg l^{-1} with a peak value of 16.2 µg l^{-1}. There was no obvious relationship between the concentrations and either the flow or the rainfall (Fig. A5).

Dimethoate

No concentrations were measured above the detection limit.

Oxydemeton Methyl

No concentrations were found above the detection limit.

Simazine and Atrazine

Simazine showed a marked peak concentration of 15.3 µg l^{-1} which coincided with the rainfall and preceded the peak stream flow (Fig. A6). The levels fell rapidly back to 1-2 µg l^{-1}. This increased concentration was as a result of applications of simazine made in the previous weeks to the hopyards. Atrazine peaked with simazine to 1.6 µg l^{-1} and fell quickly to 0.4 µg l^{-1} (Fig. A6).

Rainfall event on 19 March 1991

MAFF/BRE Experiment Series A

The sampler on the drain at site 3 was triggered manually at 1000 hours on 19 March 1991 during a period of moderate flow (0.9 l sec^{-1}) following intermittent rain (4.5 mm in the preceding 24 hours) (Table W17, Appendix XI and Fig. W13). Oxydemeton-methyl was not determined, but MCPA concentrations were initially high (15-47 µg l^{-1}), thereafter declining rapidly to an average of about 5 µg l^{-1}.

A total of approximately 1.1 g of MCPA flowed down the stream during the two main rainfall events between the spraying date and 19 March 1991. Assuming the mean between-storm flowrate to be 0.5 l sec^{-1} and the mean MCPA concentration to be 0.3 µg l^{-1}, the total flux of MCPA during this 19 day period is estimated to have been approximately 1.3 g, equivalent to 0.005% of the total applied

Figure A5

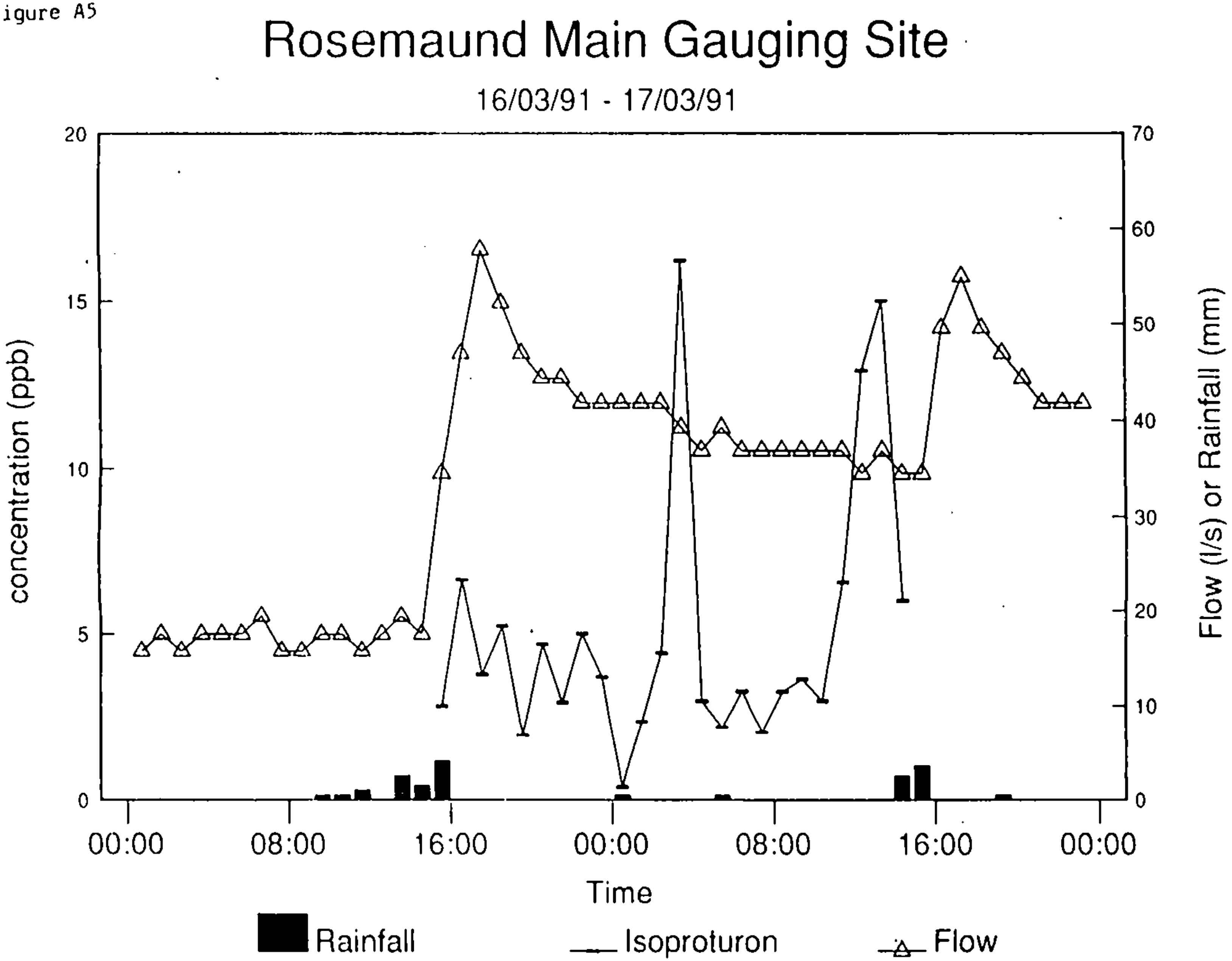

Rosemaund Main Gauging Site
16/03/91 - 17/03/91
concentration (ppb)
0
5
10
15
20
Flow (l/s) or Rainfall (mm)
0
10
20
30
40
50
60
70
00:00
08:00
16:00
00:00
08:00
16:00
00:00
Time
Rainfall
Isoproturon
Flow

Fig.W13 Rosemaund Site 3.MPCA/Oxydemeton-methyl Experiment.19.3.91-20.3.91

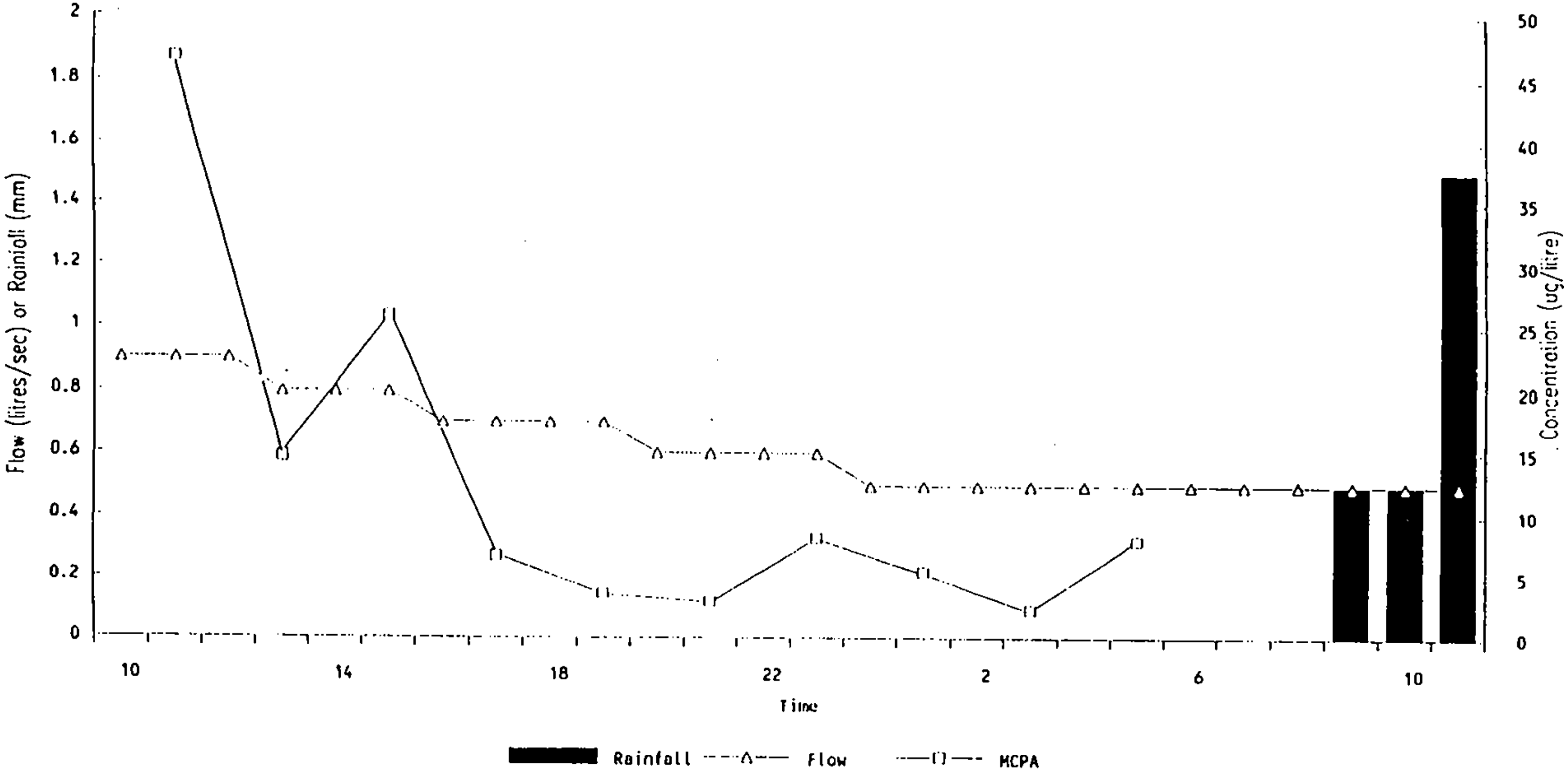
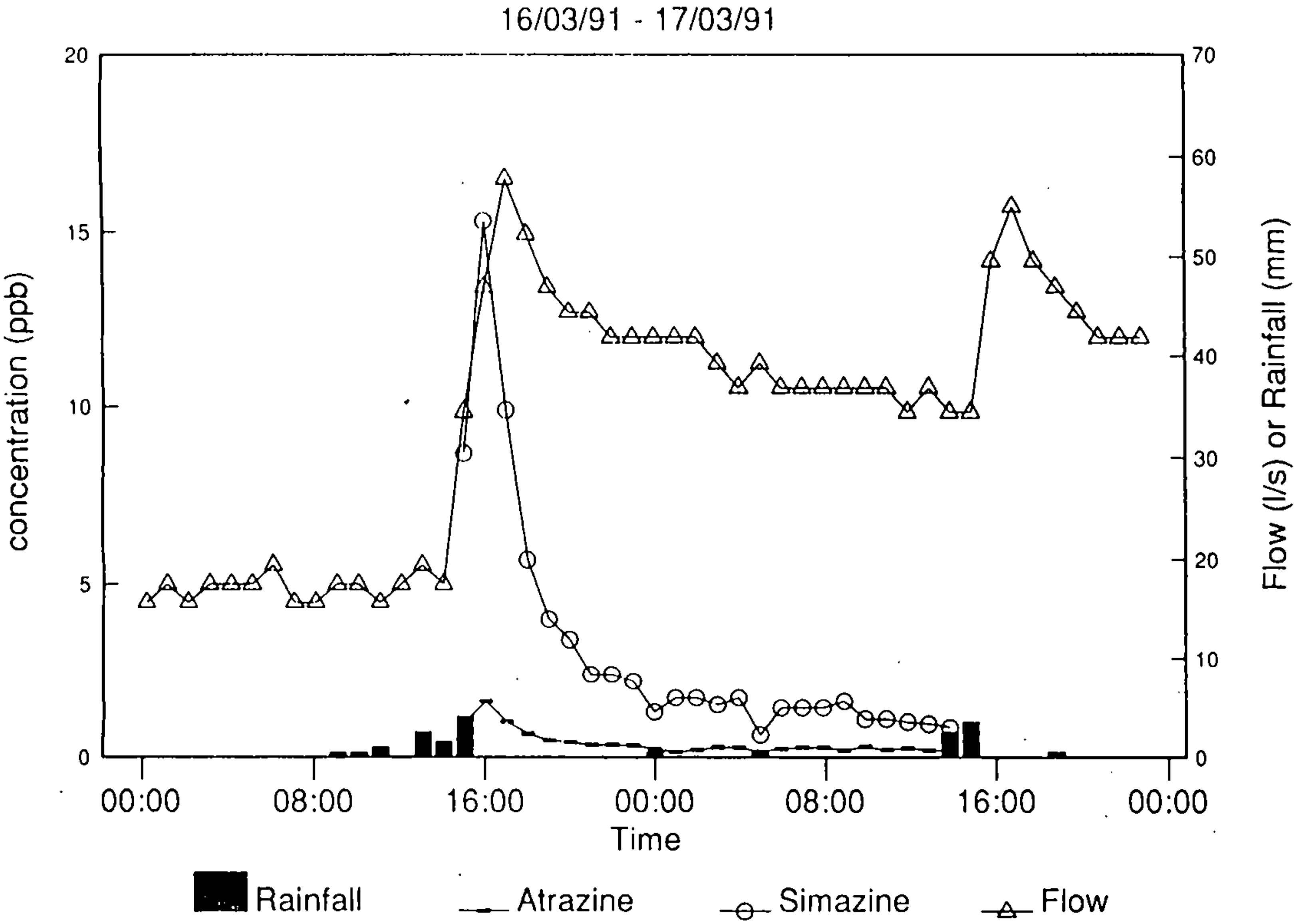


Figure A6.

Rosemaund Main Gauging Site



to the fields. Insufficient data are available to make reliable estimates for oxydemeton-methyl, but it is unlikely that more than 0.005% of this substance found its way into the stream.

References

Williams, R. J., Brooke, D. N., Glendinning, P. J., Matthiessen, P., Mills, M. J. and Turnbull, A. (1991). Measurement and modelling of pesticide residues at Rosemaund Farm. Brighton Crop Protection Conference Proceedings, No. 18-21 1991, Vol. 2, pp 507-514, British Crop Protection Council. 14

Brooke, D. and Matthiessen, P. (1991). Development and validation of a modified fugacity model of pesticide leaching from farmland. Pesticide Science 31, 349-361.

5.8 QUALITY ASSURANCE

The Pesticide Run Off Study at Rosemaund involves a number of participating organisations which collect a range of samples from the site. These samples are analysed by different laboratories which use different analytical techniques. Under circumstances such as this the difference in techniques can be used as a method of verifying the results and validating the data as well as checking for errors in the analysis.

In order to check that the analytical techniques being followed by the different laboratories produced consistent results across the collaborating bodies, an inter-laboratory calibration exercise was organised. Samples spiked with known concentrations of pesticides were sent to each laboratory for analysis. The results of this exercise are reported in Appendix XIII.

6. MODELLING

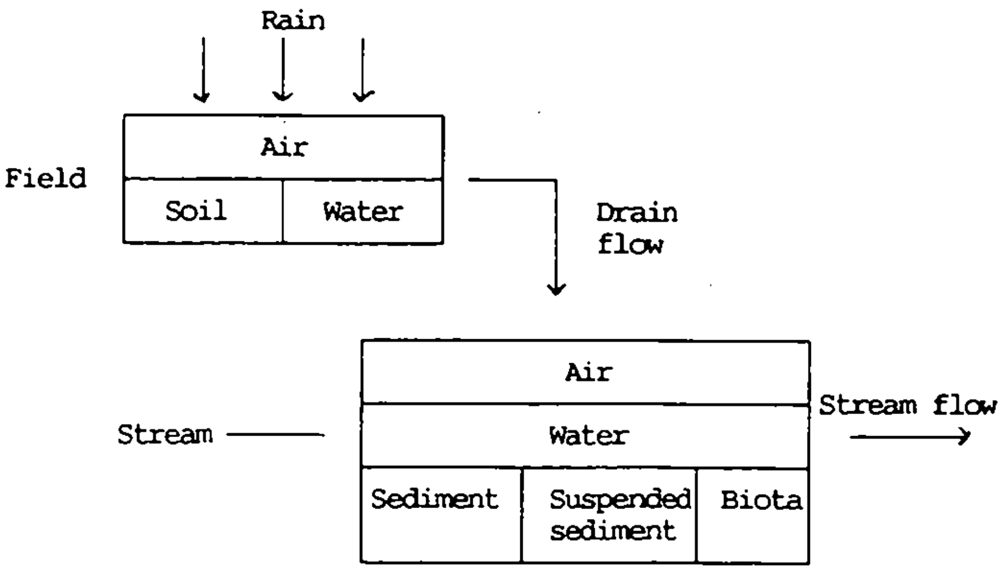
6.1 FUGACITY MODELLING

One of the objectives of the Rosemaund study is to test the validity of simple models against the actual behaviour of pesticides in a field situation. The aim is to identify or develop a model or models which can be used to predict realistic worst case estimates of pesticide levels in watercourses. Such a model would have obvious application in the assessment of new pesticides before they came into widespread use, and could also be useful in the assessment of the fate of chemicals in general.

The work described here has concentrated on the application of a fugacity based model to the upper area of the farm (the fields Foxbridge and Longlands, and Stoney and Brushes). This type of model was chosen for study because of its widespread use in chemical assessments, and the limited data requirements as regards the chemical of interest and other inputs. It is recognised that as a simple equilibrium model, it may be too great an oversimplification of this situation; the approach adopted has been to modify the model to improve the agreement with actual behaviour, whilst attempting to retain as much of the simplicity as possible. The overall aim in this modelling is to be able to predict peak levels in the stream to within one order of magnitude.

The principles of the model have been described by Mackay and co-workers (Mackay, 1979; Mackay and Paterson, 1981). It uses simple physico-chemical data on a chemical to determine its partitioning between a number of idealised phases or compartments. Removal processes such as degradation and water flow are also included. For this work, two linked models have been used (Figure 6.1A). The first of these represents the field, and consists of soil, soil water, and air above the field. The dimensions and properties of each compartment are derived from those of the site. When the chemical (pesticide) is added to the field model, it is initially partitioned between the three compartments.

Figure 6.1A. Model structure



The removal processes then act upon the appropriate compartment (eg water flow on the water compartment) for a period of time; after this, the amounts of chemical remaining in each compartment are added together and repartitioned. Rainfall is used to model the water flow into the field, carry chemical out and act as a link to the second model.

The second model, representing the stream, has five compartments (air, water, sediment, suspended sediment and biota), with properties and dimensions again determined from the site. Water from the field model enters the stream carrying the chemical, with the time of input set back relative to the rainfall to allow for the interval between rainfall and stream rise. Partitioning and removal operate in the same way as for the field model.

This modelling approach has been applied to data presented in the previous annual report (Bird et al, 1991); some of the results were presented at the BCPC in 1991 (Williams et al, 1991). The applications covered are mecoprop (Autumn 1987 and Spring 1990), and lindane and isoproturon (Autumn 1989). The physico-chemical data on the chemicals are shown in Table A. Other data used in the model, for example the soil sorption coefficient, was calculated from this data by the methods in Mackay et al, 1985. For the field model, comparisons of measured and calculated levels are shown in tables B-D, and illustrated for mecoprop and lindane in Figures 6.1B and 6.1C. The field model calculates levels of chemical in the soil and in the soil water. As the actual measurements were carried out on wet soil, a composite value from the model was calculated. For all chemicals, the dominant removal process in the model was degradation, which was modelled as a first order process. For mecoprop, the model calculation indicated that only 0.4% of the chemical applied was removed by water flow; the figure for lindane was 0.26%. It is notable that in all cases, the concentrations calculated shortly after application are lower than those actually measured. It is not clear why this should be so; in fact the opposite would be expected to be true, with some losses in the field due to drift or interception by

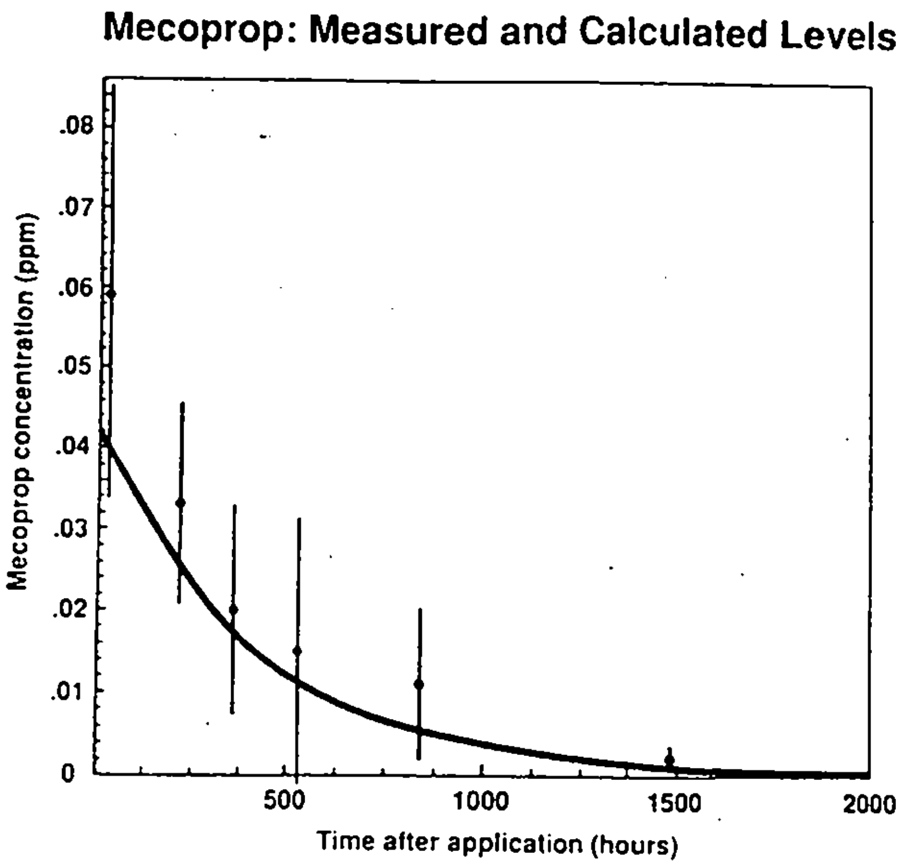


Fig 6.1B Mecoprop application in Spring 1990. Measured (points) and calculated (line) levels in soil.

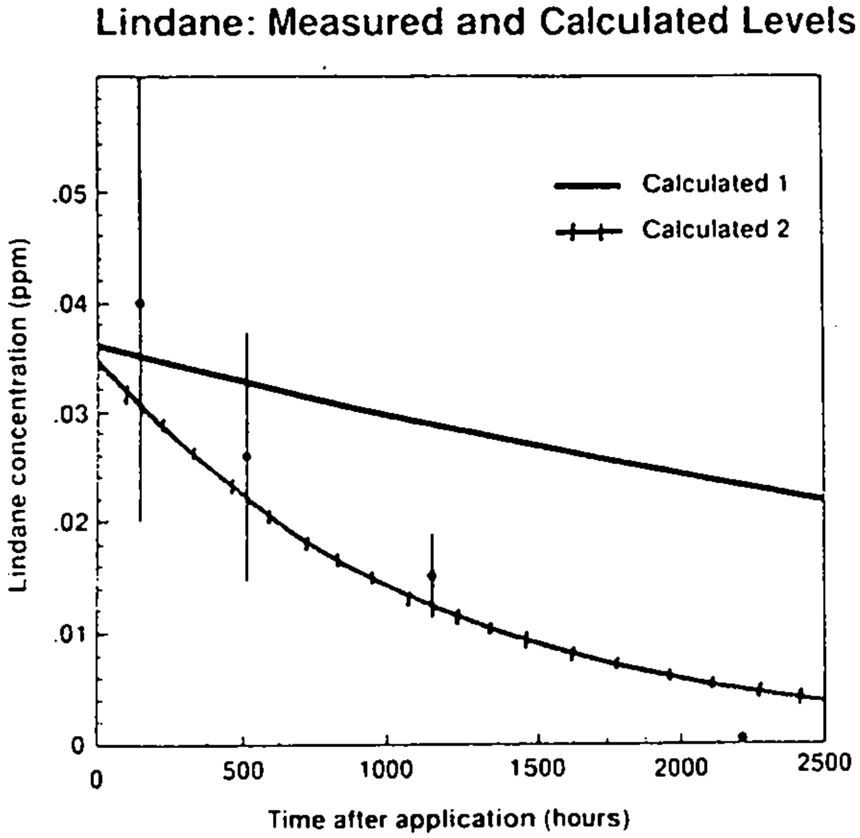


Fig 6.1C Lindane application in Autumn 1989. Measured (points) and calculated (lines) levels in soil.

the crop. However, these differences between calculated and measured values are not great, and as the purpose is to estimate concentrations before use, no adjustments have been made to the amounts added to the model to make them agree better with the measurements.

For lindane, the rate of disappearance from the field was much greater than that predicted from the literature degradation rate. It is not considered likely that this is due to physical removal of the chemical from the field, and so a new degradation rate was calculated from field measurements, and used to recalculate the levels in the field model. Calculations with both rates are shown in Figure 6.1C.

The water in the field model carries chemical out of the model, and is thus analogous to the drains. It is of interest to compare the concentrations predicted for field water with those measured in the drain water. Measured values for isoproturon in 1989 ranged from 1.1 to 8.8 µg/l, compared to model levels of 4.4 to 4.7 µg/l. For lindane, measured levels lay in the range 0.02 to 0.45 µg/l, and calculated levels were around 0.4 µg/l.

The chemical washed out from the field model was added to the stream model. Study of the rainfall and stream flow data showed a delay of six hours between the onset of rain and the flow rate increasing significantly for the isoproturon/lindane events in Autumn 1989, and a shorter delay of 3 hours for the mecoprop event in Spring 1991. These delays were built into the model. In earlier work (Bird et al 1991; Brooke and Matthiessen 1991), all the water falling as rain was assumed to carry chemical from the field to the stream. This is obviously not the case in reality, with losses occurring by evaporation and through water moving below the drain level. From a study of the rainfall and stream flow data, a run-off coefficient of 0.2 appears to be appropriate for this part of the catchment. This has been included in the stream modelling by only allowing 20% of the chemical removed from the field model to enter the stream in each time period. The factor was included in this way for reasons of convenience in changing the input data; tests carried out later in which the water flow through the field model was reduced to 20% of the rainfall gave virtually identical results.

Comparisons between measured and calculated values are shown for lindane and mecoprop (two different applications) in Figures 6.1D-F. From the aim of the project, it is interesting to compare the peak concentrations. For lindane, the peak measured concentration was 0.29 µg/l, whilst that calculated was 0.47 µg/l, a ratio of 1.6. Mecoprop in Spring 1990 gave a ratio of 20.4 (measured 1.4 µg/l, calculated 28.6 µg/l), while for the same chemical in Autumn 1987 the ratio was 5.8 (measured 11.7 µg/l, calculated 67.5 µg/l). For isoproturon in Autumn 1989 (not shown), the ratio was 3.0, the measured peak level being 5.4 µg/l compared with 16.7 µg/l calculated. In three out of these four cases, the agreement was within the order of magnitude which was the target. For mecoprop the agreement for the Spring application was much worse than that for the Autumn experiment. Differing behaviour of the water regime in the field has been noted for different seasons (see Appendix IX), and it may be that other seasonal factors need to be incorporated. It is notable that the levels in the stream following the Spring application are lower than those in the Autumn.

Work on this model so far has produced some success within the targets set out. However the levels predicted in the water are consistently higher than those measured, and in one case beyond the order of magnitude aimed for. The data from the applications included in this report and those planned will be used to further test this approach, to determine if there is a pattern to the differences between the measured and calculated levels. If results show a reasonably consistent pattern, then this method may have some use in initial assessments. For example, the data in this report for the MCPA application may help to determine the difference between Spring and

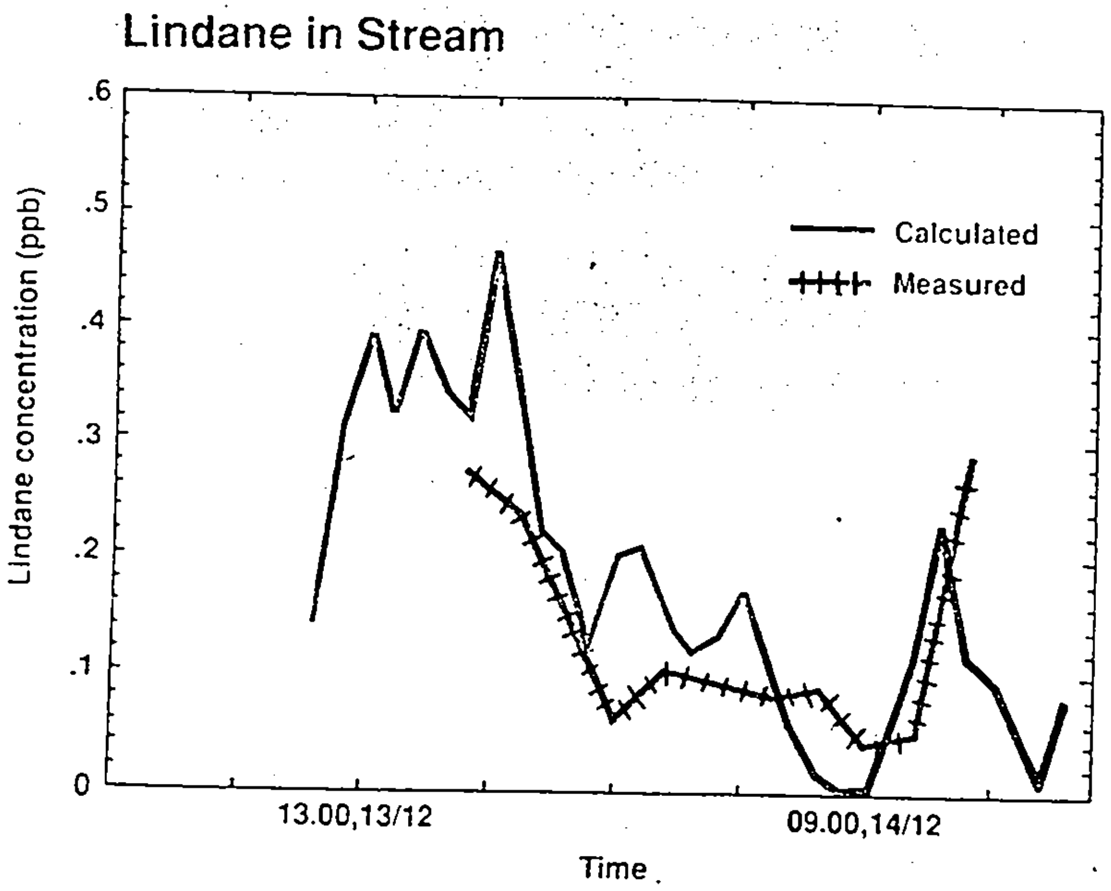


Fig 6.1D Lindane levels in stream following rainfall event of 13 December 1989.

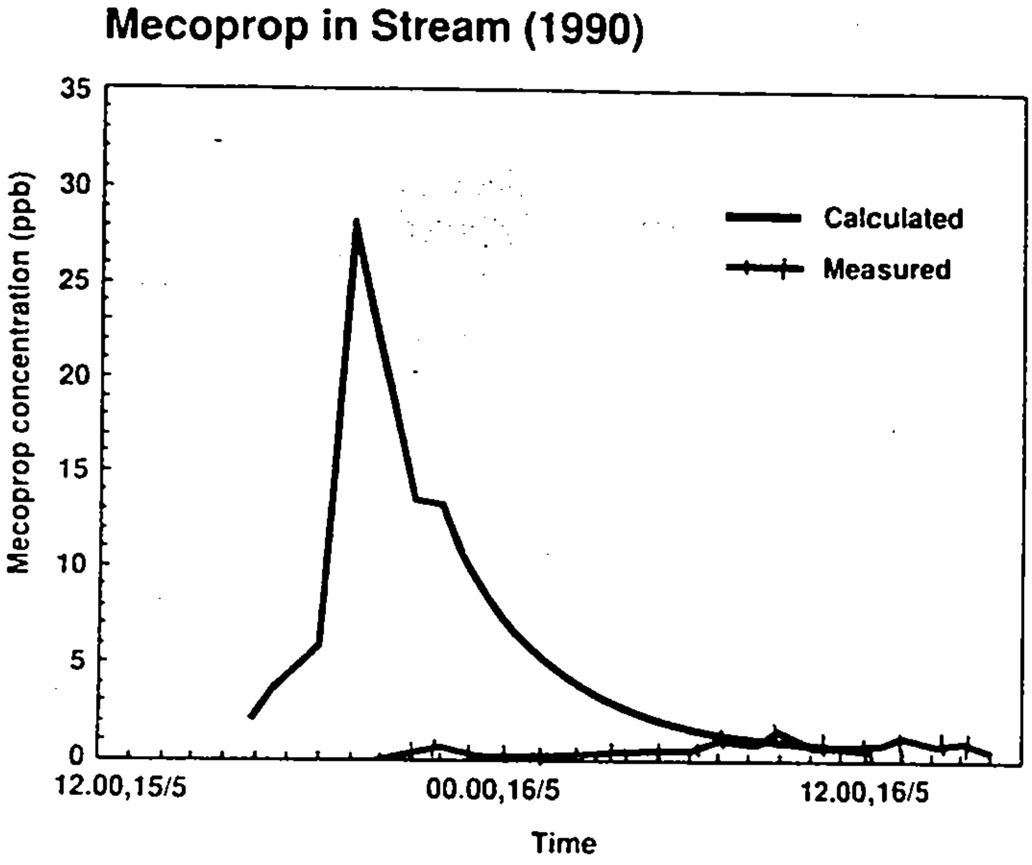


Fig 6.1E Mecoprop levels in stream following rainfall event of 15 May 1990.

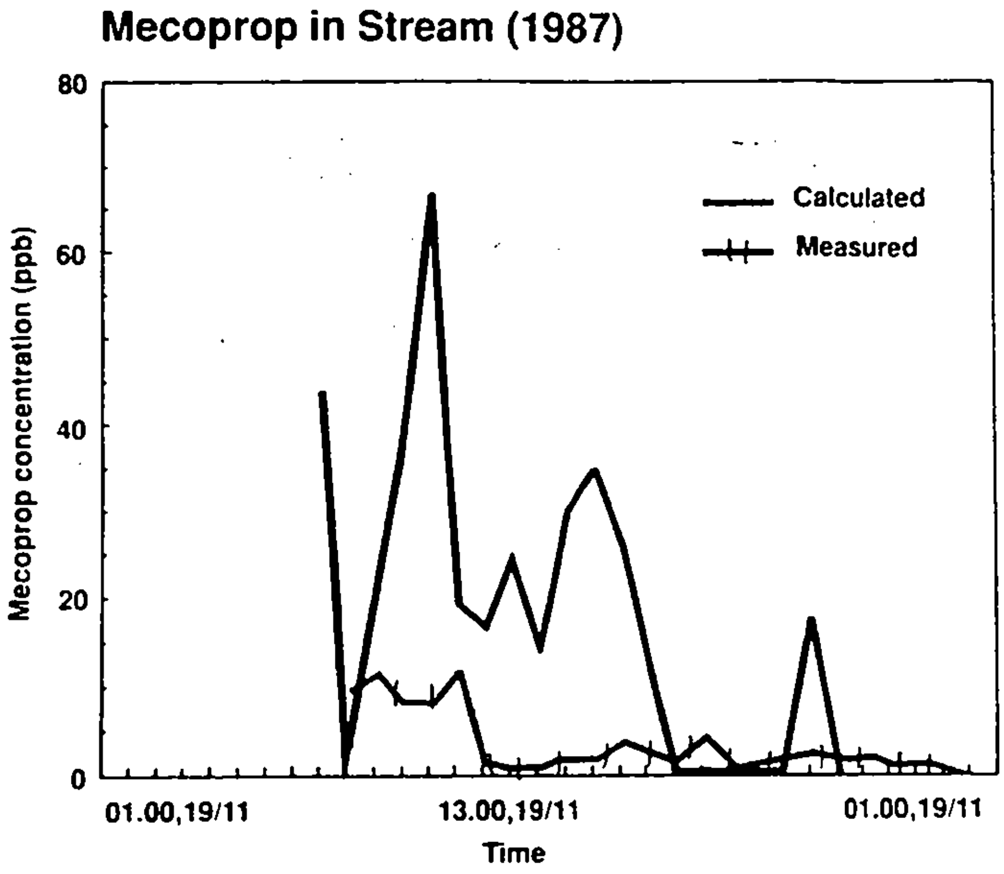


Fig 6.1F Mecoprop levels in stream following rainfall event of 19 November 1987.

Autumn applications is consistent, as this was a Spring application of a chemical with similar structure and properties to mecoprop. However, in this work this type of model has probably been pushed as far as it can be in attempting to model situations such as this.

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Bird et al - last annual report

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6.2 CATCHMENT MODELLING

6.2.1. Introduction

The end objective of the Institute of Hydrology/National Rivers Authority part of the Rosemaund Study is to develop a simple model of pesticide run-off from catchments. This model could then be used to help the NRA develop sampling strategies for pesticides within surface waters based on some knowledge of pesticide use. Clearly this end objective is very ambitious and the work to date has been directed at developing a model that will simulate pesticide concentrations at Rosemaund Farm.

The soils at Rosemaund are predominantly clay/loam in texture and from the Bromyard series (see Appendix III). These soils are prone to seasonal water logging and subsequently nearly all the fields at Rosemaund are drained, (typically 1 m depth, 20 m spacing). During the summer the soils can crack and these cracks may persist at depth through part or all of the drainage period. There are also macro-pores extending to depth and spaces around soil peds in the lower parts of the profile. It is obvious therefore that the route water takes to the drains and the stream will influence its pesticide concentration and that any reasonable model must attempt to describe these different water pathways.

6.2.2 Model Structure

The model structure presented here is derived from detailed measurements of soil water movement and distribution made in Longlands field over successive winters by members of the Agrohydrology section of the Institute of Hydrology (Appendix IX). Broadly an underdrained field consists of two types of soil profile 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 they 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 6.2A. 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 divided into two to represent the fast and slow parts of the soil profile described above. The slow portion of the field is considered to be up-slope of the fast part and the subsequent possible direction of water movement are shown by the arrows in figure A1. The dotted arrows indicate the possibility of water directly to lower layers without interacting with intervening layers via macropores and/or cracks. 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 timestep. The model keeps account of the amount of water and dissolved and adsorbed pesticide in each box and calculates changes to these depending on a mass balance of inputs, outputs and internal sources and sinks.

To explain the details of water and pesticide movement it is best to consider a single box from the model (Figure 6.2B).

6.2.3 Water Movement

The change in soil water content of box i, S_i is given by;

$$\frac{dS_i}{dt} = q_{i-1} - qbp_i + d_u - q_i - d_l + qbm_{i-1}$$

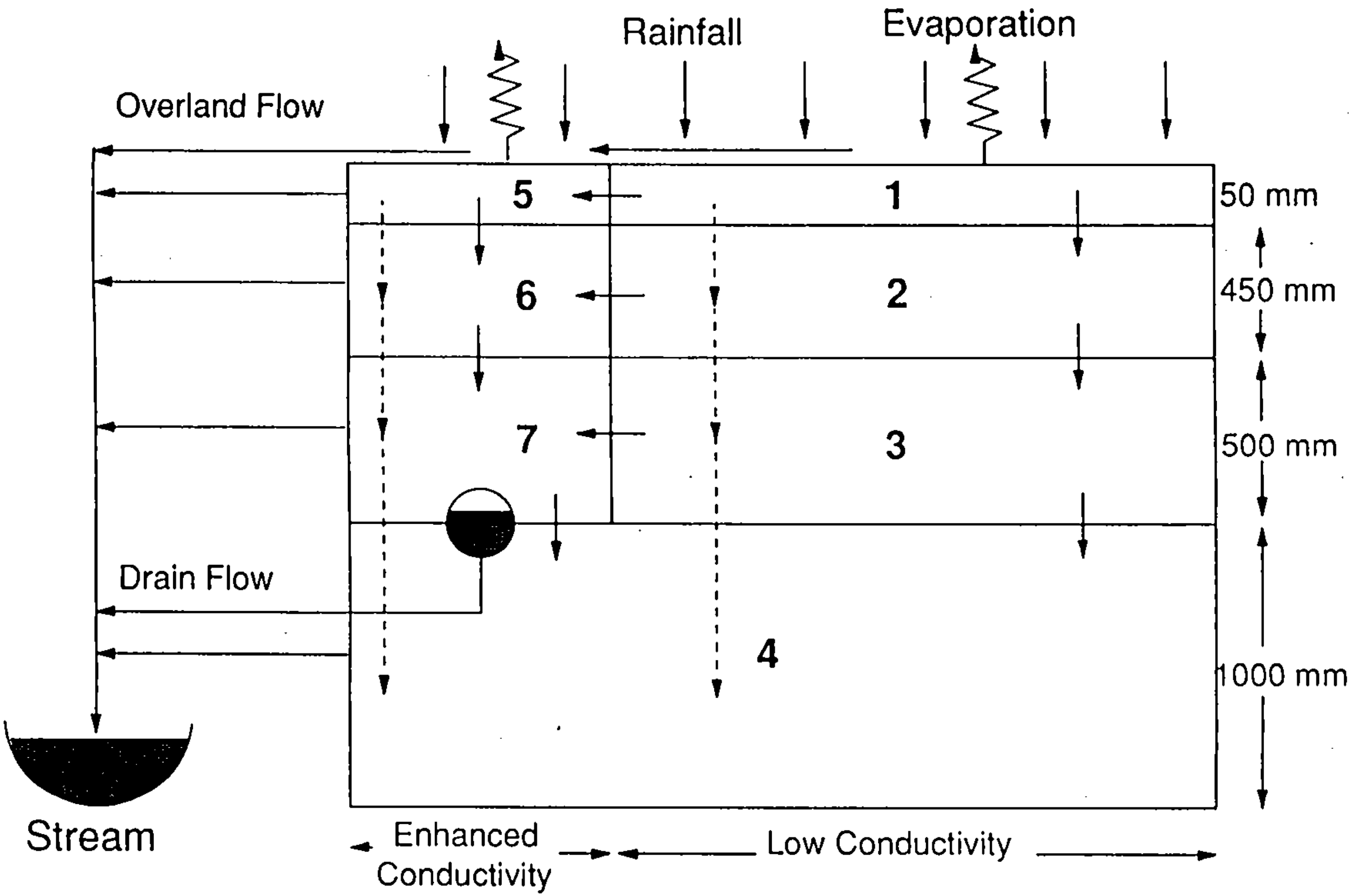
Rainfall
Evaporation
Overland Flow
5
1
50 mm
6
2
450 mm
7
3
500 mm
Drain Flow
4
1000 mm
Stream
Enhanced Conductivity
Low Conductivity

Figure 6.2A

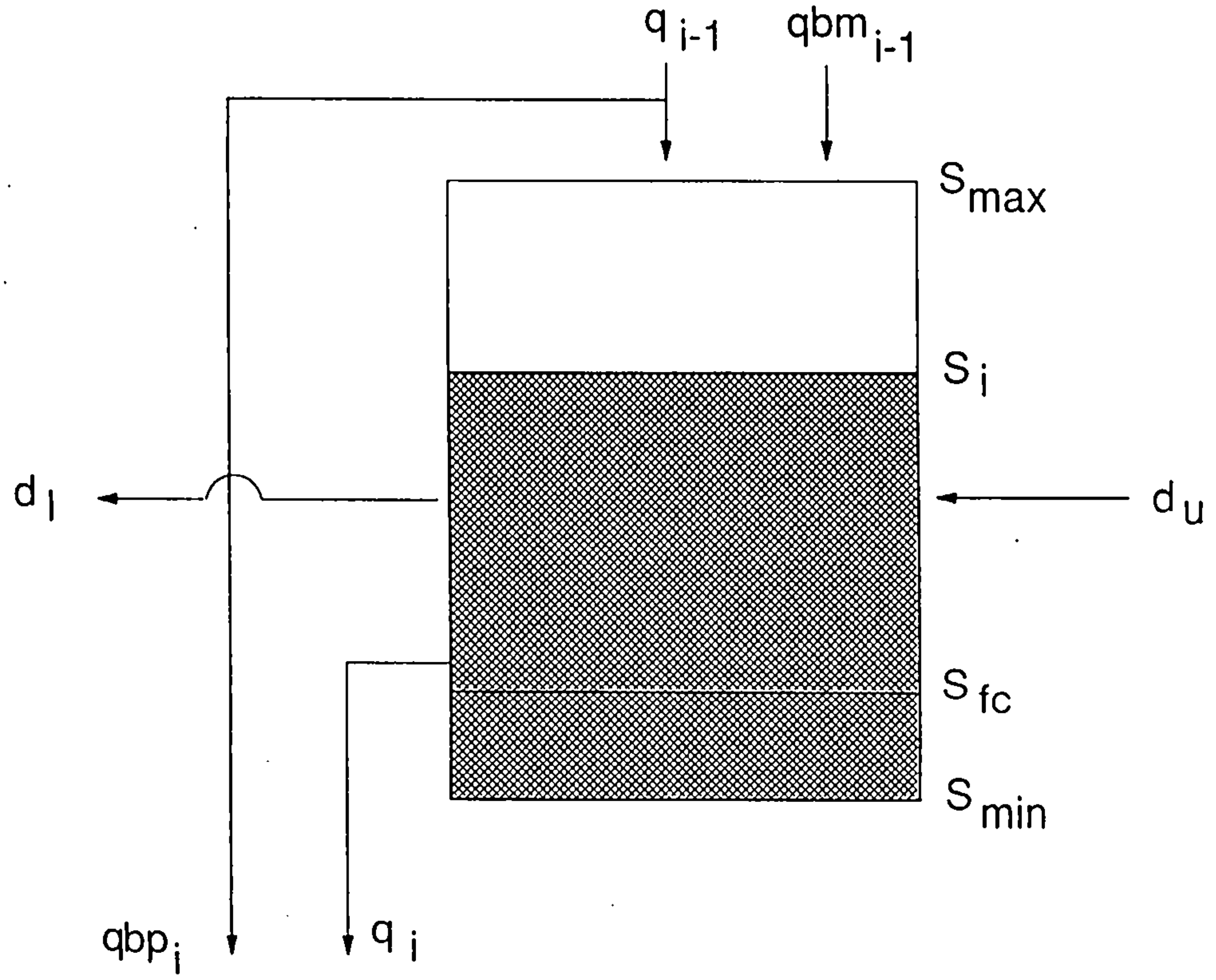

Figure 6.28

where q_i is the flow per unit (mm) area from box i, d_u is the flow per unit area (mm) from an upslope box, d_i is the flow to a downslope box or stream, qbp_i is the flow from box i-1 that by-passes box i in cracks or macro-pores, qbm_{i-1} is the flow that was in by-pass routes in box i-1 that return to the soil matrix in box i and t is time (hours). Flow may only occur from box i, either vertically, q_i or laterally, d_l when $S_i > SFC_i$, where SFCi is the field capacity of box i. Flow from box i depends on the water content of box i and is given by;

$$q_i = k_v(S_i - SFC_i)(1-\tan(\alpha))$$

where k_v (hours^{-1}) is a measure of the vertical conductivity of box i, and is the average slope of the field. Similar the down slope drainage d_l is given by;

$$d_l = k_h(S_i - SFC_i)\tan(\alpha)$$

where k_h is a measure of the horizontal conductivity of box i. A fraction of water may by-pass a given layer through macro-pores and cracks. The fraction of by-pass flow through a box is related to the soil water content of the box, such that the drier the box the more by-pass flow can occur. This feature of the model is to take some account of the swelling nature of the soil. The by-pass flow fraction CF_i is given by;

$$CF_i = CFMIN_i + G_i(S_i - SMIN_i) \text{ where}$$
$$G_i = (CFMIN_i - CFMAX_i)/(SMAX_i - SMIN_i)$$

where $CFMIN_i$ is the minimum bypass flow fraction occurring at maximum water content, $SMAX_i$ and $CFMAX_i$ is the maximum bypass flow fraction occurring at minimum soil water content $SMIN_i$. Therefore,

$$qbp_i = CF_i q_{i-1}$$

The continuity of cracks through layers is given by the ratio, CF_i/CF_{i-1} to a maximum of unity. Thus once in a crack water is assumed to remain there until the crack ends. Hence,

$$qbm_i = 1 - \frac{CF_i}{CF_{i-1}} \; qbp_{i-1}$$

Water may only enter a box if it is not saturated ie $S_i < SMAX_i$. $SMAX_i$ is given by;

$$SMAX_i = \Theta_i V_i$$

where Θ_i and V_i are respectively the porosity and volume (mm) of box i.

6.2.4 Pesticide Movement

Pesticide is added to the model by assuming that the amount applied is well mixed into the top layer of the model (boxes 1 and 5, Fig 6.2A) and partitioned following a reversible instantaneous linear adsorption isotherm.

$$PS_i = PW_i Kd_i \text{ and}$$
$$k_i = k_{oc} OCi$$

where PS_i is the pesticide concentration in the soil phase, PW_i is the concentration of the dissolved phase, kd_i is the adsorption coefficient, k_{oc} is the absorption coefficient normalised for organic carbon content, OC_i.

The rate of change of mass of dissolved pesticide in the ith box, $S_i PW_i$ is given by,

$$\frac{dS_i PW_i}{dt} = (q_{i-1} - qbp_i)P_{i-1} + d_u PW_u - (q_i + d_1)P_i + qbm_{i-1} PW_{bm} - R_d PWi$$

where, P_i is the pesticide concentration per unit area of the ith box (µg/mm), P_u is the pesticide concentration of water draining from an upslope box, P_{bm} is the concentration of pesticide in the bypass flow and R_d is the first order rate coefficient describing degradation of the pesticide. Water moving through by-pass routes is assumed to have the same concentration as the soil water in the box with which it was last in contact. The rate of change of mass of pesticide absorbed onto the soil is given by;

$$\frac{dPS_i}{dt} = - R_d PS_i .$$

where, PS_i is the soil absorbed pesticide concentration per unit area in the ith box (µg/kg/mm²). The degradation rate of the pesticide is assumed to be the same in both the liquid and solid phase. At the end of each model time step the pesticide is repartitioned between the soil and the soil water using the linear isotherm described above.

6.2.5. Drainflow

The model only allows drainflow when the deep soil box, (box 4, Fig. 6.2A) 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.

6.2.6. Stream Flow

Stream flow is the sum of the lateral drainage from each of the boxes, overland flow 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 exceeds evaporation and either box 1 or box 2 are saturated. Water flowing overland from box 1 may infiltrate into box 5 if this box is not saturated. The concentration of pesticide in the surface run-off is assumed to be equal to the concentration of the box from which it was generated.

6.2.7. Model Application

The model has been applied over the period from 1 September 1990 to 31 March 1991 but at this stage has only been used to simulate the flow from and isoproturon concentrations in the drainage system under Longlands field. It is intended that methods will be developed to apply the model to the whole of the catchment and other pesticides.

The model is driven by hourly rainfall taken from the automatic weather station (AWS) at GR SO 5582 4789. 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 values of moisture volume fraction corresponding to SMIN, SMAX and SFC used in the model simulation are given in table 6.2.1. The values of SMIN and SMAX, with exception of Box 4, are based on the PF curves given in Appendix XIV; values of SMAX for Box 4 were adjusted to allow the prediction of the onset of drain flow to match reality. The values of SFC are best guess estimates.

Box No.	SMIN	SFC	SMAX
1 and 5	0.19	0.27	0.49
2 and 6	0.24	0.32	0.40
3 and 7	0.30	0.35	0.38
4	0.24	0.25	0.31

Table 6.2.1. Values of the moisture volume fraction equivalent to minimum water content (SMIN), field capacity (SFC) and saturation (SMAX), used in the model.

The organic carbon content of the soils in each of the model boxes was estimated from analysis of soil profiles carried out by the Soil Survey and Land Research Centre. These values are given in Table 6.2.2.

Box No.	% Organic C.
1 and 5	1.8
2 and 6	1.1
3 and 7	0.3
4	0.3

Table 6.2.2. Organic carbon content of the boxes used in the model.

The application rate of isoproturon to Longlands was supplied by ADAS Rosemaund and is reported in section 6.2. The Koc value used in the model is 130 and the degradation rate used was 1.44×10^{-3} hours $^{-1}$. The degradation rate is assumed to be the same in all boxes. No changes in degradation rate ij, are currently made as a result of changes in temperature, soil moisture content or depth.

6.2.8. Results and Discussion

The results presented here are from a very preliminary application of the model and should be viewed as an attempt at using the model outlined above. The model was run using hourly data from 1 September 1990 to 31 March 1991 and output data were produced for the entire period. The results presented here are for short periods of time, coinciding with rainfall events, for which data on isoproturon concentrations were collected. Figures 6.2C to 6.2F show simulated and observed values of drain flow and isoproturon concentration for the periods 8/9 January 1991, 21/22 February 1991 and 4/5 March 1991 respectively. For the last of these events no drain flow data are available.

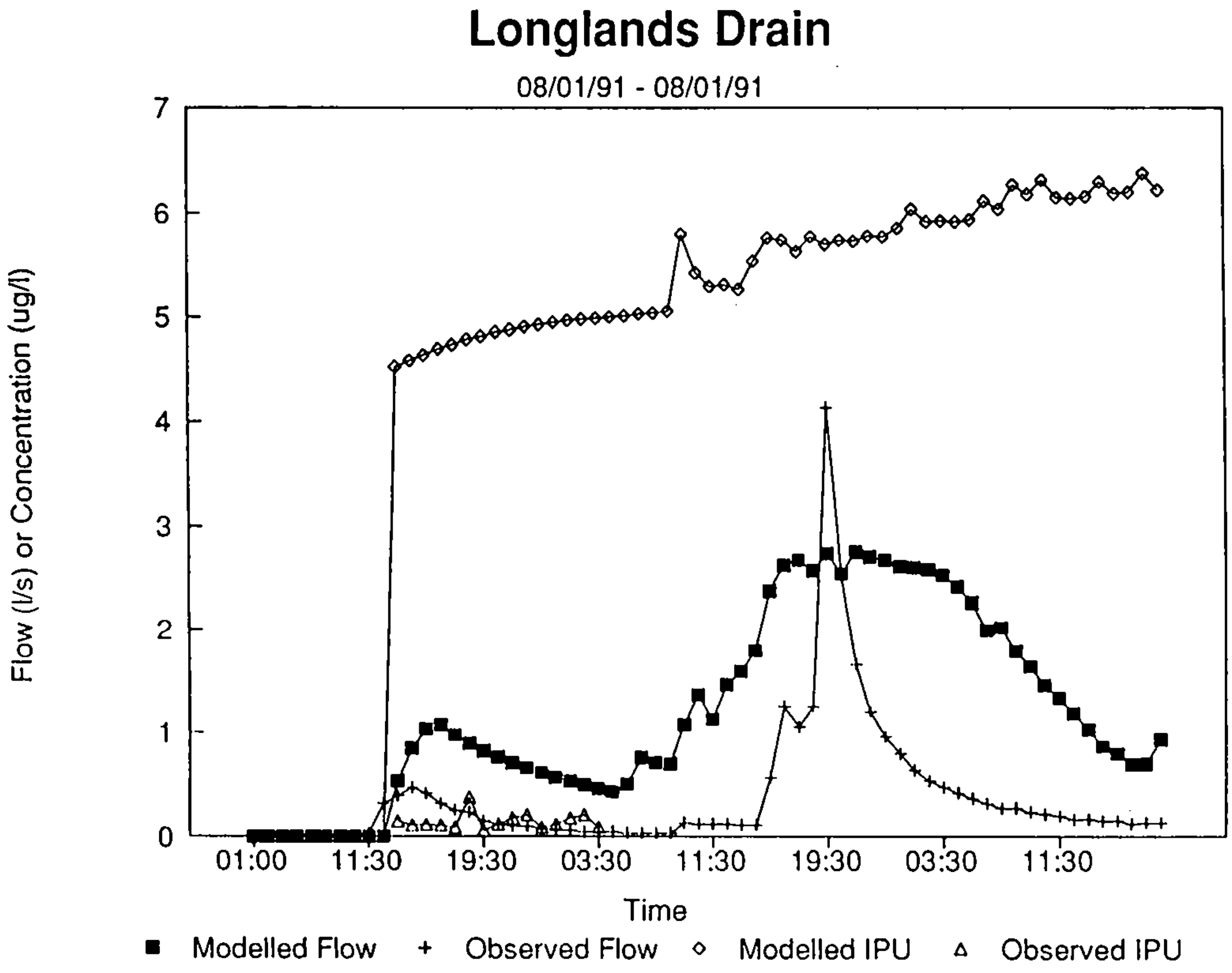
Longlands Drain
08/01/91 - 08/01/91
Flow (l/s) or Concentration (ug/l)
7
6
5
4
3
2
1
0
01:00
11:30
19:30
03:30
11:30
19:30
03:30
11:30
Time
■ Modelled Flow
+ Observed Flow
◇ Modelled IPU
△ Observed IPU

Figure 6.2C.

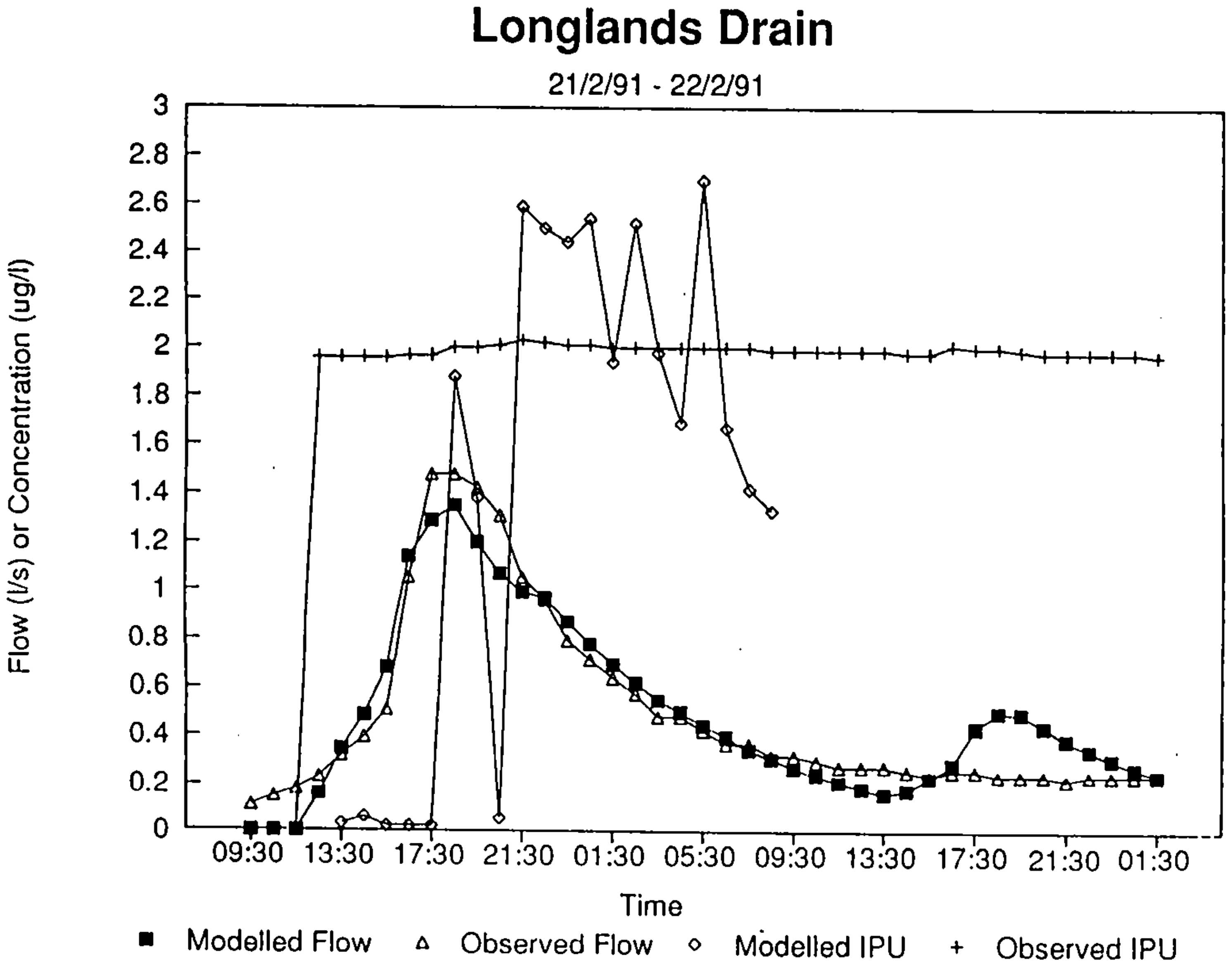
Longlands Drain
21/2/91 - 22/2/91
Flow (l/s) or Concentration (ug/l)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
09:30
13:30
17:30
21:30
01:30
05:30
09:30
13:30
17:30
21:30
01:30
Time
■ Modelled Flow
△ Observed Flow
◇ Modelled IPU
+ Observed IPU

Figure 6.2D.

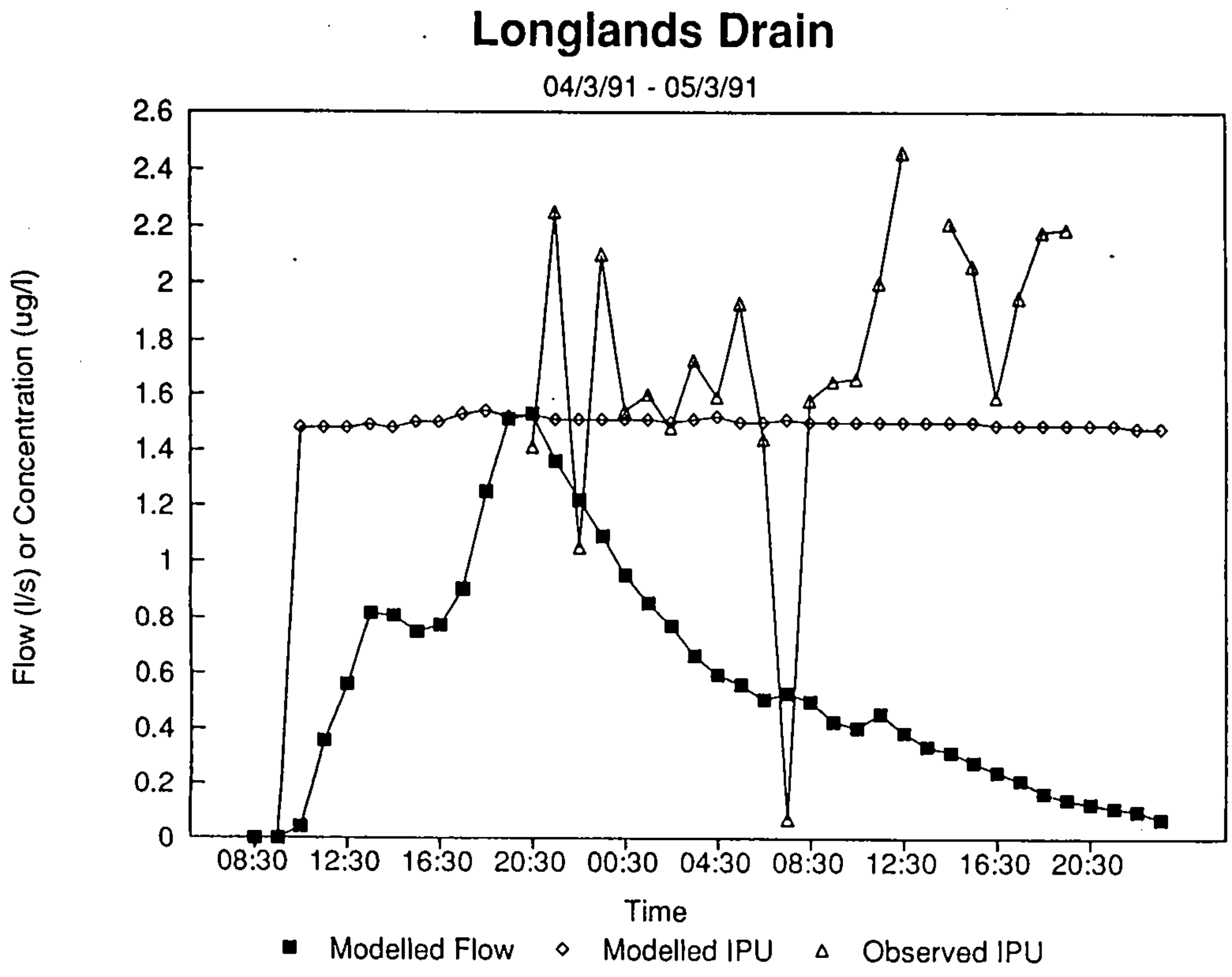
Longlands Drain
04/3/91 - 05/3/91
Flow (l/s) or Concentration (ug/l)
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
08:30
12:30
16:30
20:30
00:30
04:30
08:30
12:30
16:30
20:30
Time
■ Modelled Flow
◇ Modelled IPU
△ Observed IPU

Figure 6.2E.

6.2.9. Drainflow

Figure 6.2C shows that the model did a good job of simulating flows over this event. However the simulation shown in figure 2 is clearly less good. While the peaks of the hydrograph are simulated well temporally, the dynamic response of the model is too slow for this particular event. This may be because this was the first drainage event of any significance. The drainage system was not working in the classic way at this point ie. there was no 'gull winged' shaped water table above the drains (see Appendix IX section 1, Fig 6.2F). The soil above the drain was draining water rapidly down the profile and into the backfill and hence the drains. However, since there was no water table some of the drain water left the drain to recharge the ground water, while some exited the drainage system. This resulted in a very flashy response at the drainage outlet. Since the way the model is set up only allows water to exit the drain when there is a water table (i.e. in the classic drainage situation) then the model will do much better when this situation is reflected in the field. Therefore it should be expected to reflect reality better in the February event than in the January event, as indeed it did.

6.2.10. Isoproturon

Figures 6.2C and 6.2D show that the model does not reflect any of the variability in isoproturon concentrations measured at the drain outfall, but does seem to agree well with the mean value about which these variations occur. There seems to be no obvious physical explanation for the variability in the measured concentrations and some of it must be attributable to variability in the chemical analysis at such low concentrations. It is therefore reasonable to suggest that the model simulates these events quite well. The first event once again presents a problem with the estimated concentrations exceeding the measured values by more than a factor of 10. It is possible that this is linked to the problems noted with flow above. The model structure is such that the majority of the recharge to the bottom box is produced by the movement of a great deal of water through the high conductivity area above the drains. Consequently dissolved pesticide is transported fairly rapidly to depth and the concentration in the bottom box increases. In reality the water maybe moving rapidly in the larger pores which will not give it time to reach equilibrium concentrations with the surrounding soil. Further a proportion of water may not contact soil at all if it is moving down the middle of the larger pores.

6.2.11. Conclusions

The simple model of Longlands field constructed on the basis of the process studies carried out has shown some promise. The simulation of isoproturon and flow in periods of classic drain flow are good. More work needs to be done to model the processes that control the transition period from no drain flow to drain flow which seems to exist in Longlands.

6.2.12. Future Work

The work on this model will continue with the major objective of extending the model to the whole catchment. Steps on the way will include modelling of Longlands field for different year for isoproturon and for the same year for different chemicals. The model will also be applied to the drainage system under Foxbridge and to the subcatchment above the MAFF weir (GR SO 5665 4841). Extending the model for the catchment will involve integrating the surface run-off work into the model which will also need to be extended further to include the erosion of soil particles and adsorbed pesticide.

7. SUMMARY DISCUSSION OF EXPERIMENTAL RESULTS

Studies by IH and SSLRC into the soil and soil hydrology provided interesting results and useful pointers for the modelling group. The study by IH identified important differences in the pattern of autumn soil rewetting which was dependent on the autumn rainfall pattern. This will have important consequences for the design of models for this system. Sheet flows were thought unlikely to occur with rainfall events of less that 15-20 mm.

Soil characterisation by the SSLRC produced a list of important experimental constraints:-

- The reliance of their sampling system on accurate and prompt reporting of events;
- The need for pre-spray sampling to establish a 'base line' or identify residual concentrations;
- The need for more intensive sampling following spray application;
- The continuation of analysis until zero or base line levels are attained;
- The limited sampling ability of the existing equipment when more than one pesticide is investigated.

As with the pesticides studied in the last report, in every experiment the experimental pesticides were found in the streams and drains that were monitored following rainfall events. Movement of the pesticides to the receiving waters occurred within a few hours of rainfall and the maximum pesticide concentration measured in the stream was 17.2 ug/l (isoproturon). It should be noted that although the pesticide levels measured in the stream exceeded 0.1 ug/l during and after rainfall, this does not necessarily imply that pesticide concentrations at any drinking water intakes downstream would be in breach of the EC Drinking Water Directive (MAC). This is because peak levels are likely to receive dilution, dispersion and degradation as they travel downstream. Outwith periods of rainfall, the levels of pesticides measured in the stream were low or below detection limits.

The amounts of each pesticide accounted for in the stream were only a very small proportion of the total amounts applied to the field (maximum 0.03% for any of the rainfall events monitored).

The interlaboratory calibration exercise was very satisfactory and showed that the results from all of the laboratories were within an order of magnitude with the exception of the NRA/mecoprop problem, the cause of which has now been identified and resolved. This problem underlines the importance of such exercises and similar exercises will be carried out again.

The modelling studies are now concentrating on two main developments, the fugacity model and the catchment model. These will continue to be tested and updated as information regarding the behaviour of the soil and the catchment is obtained. As mentioned above, the work by IH and SSLRC on the soil will provide important data for the model developments.

The fugacity model has been applied to the data described in the last annual report. The levels predicted by this model were, however, consistently higher than those measured. Data from the applications included in this report and those planned for 1992/93 will be used to further test this approach. If there is a consistent pattern to the overestimation of pesticide levels in the water then this model may be of use as a qualitative, rather than a quantitative tool; for example, to estimate the difference between spring and autumn applications of MCPA. The fugacity model has probably reached the limit of its usefulness in a situation as complex at Rosemaund and further models will need to be developed using the experience gained.

The catchment model has been developed by the NRA and IH but only simulations of flow and isoproturon from the drainage system under Longlands field have so far been simulated. Results from simulations using this simple model during periods of classic drain flow have been good. More work is needed on the model, particularly on the processes that control the transition period which appears to exist in the Longlands field from no drain flow to that of classic drain flow.

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MAJOR PRESENTATIONS

December 1991. Technical Presentation Day at ADAS Rosemaund.

9. ACKNOWLEDGEMENTS

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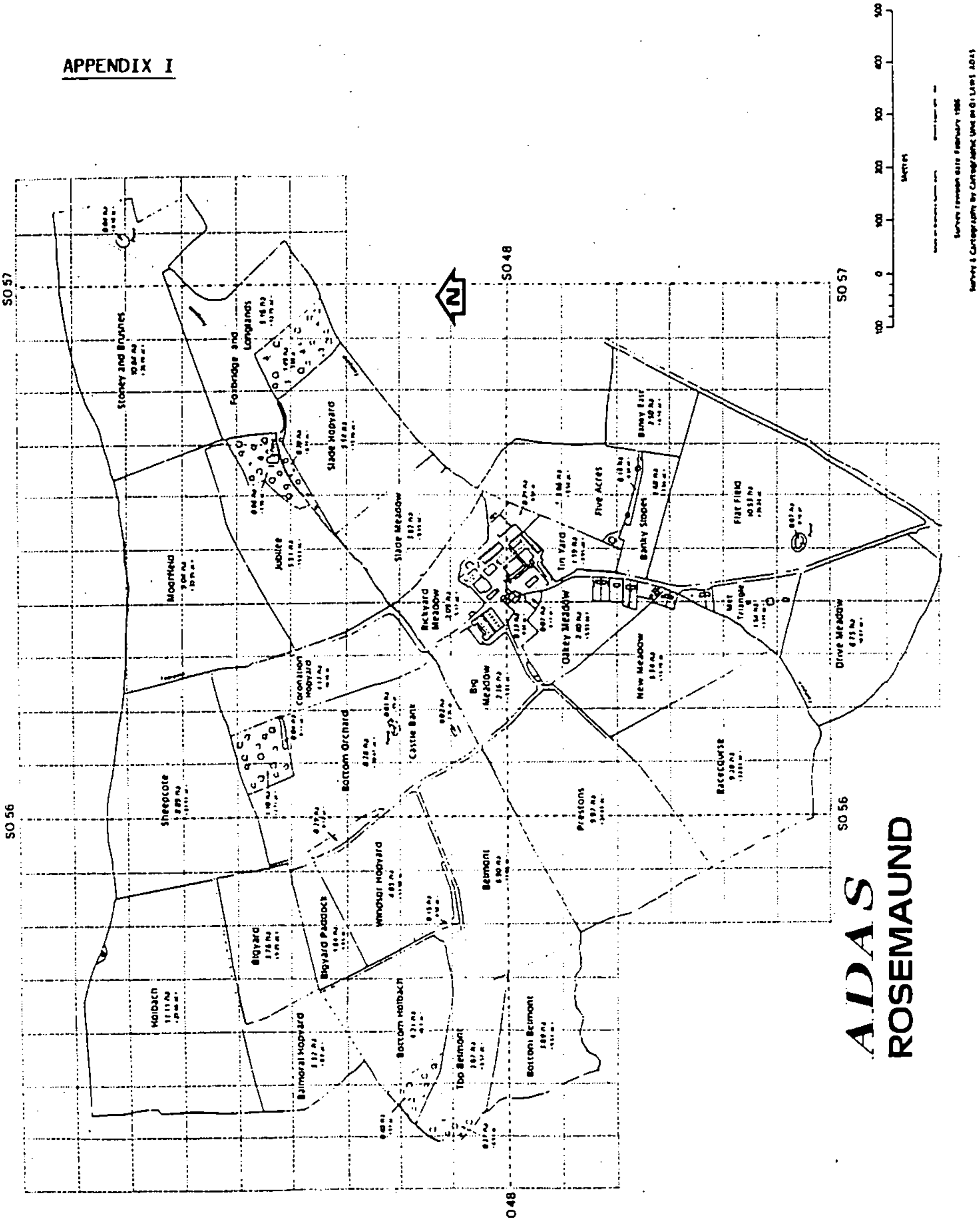
APPENDIX I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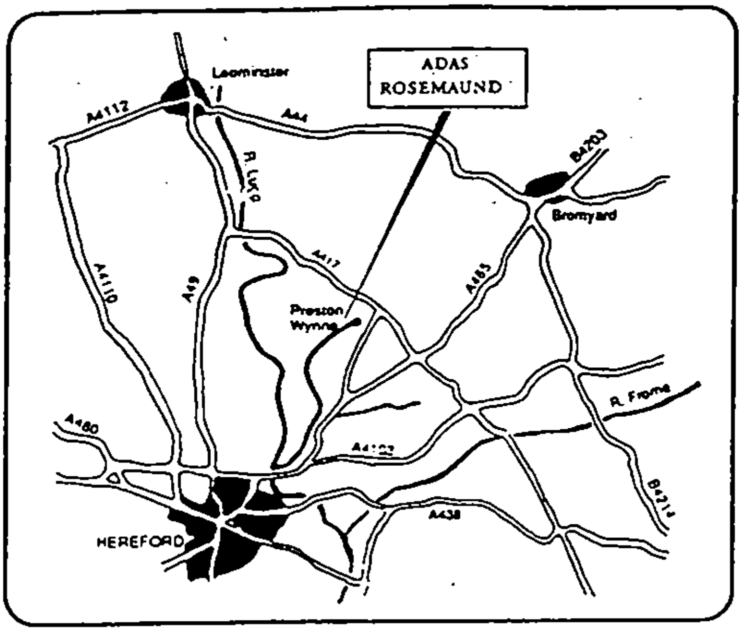
Stoney and Brushes
Footbridge and Longlands
Slade Hopyard
Slade Meadow
Jubilee
Moorfield
Rickyard Meadow
Coronation Hopyard
Bottom Orchard
Castle Bank
Big Meadow
Sheepcote
Windsor Hopyard
Belmont
Bigyard
Bigyard Paddock
Halbach
Balmoral Hopyard
Bottom Halbach
Top Belmont
Bottom Belmont
Prestons
Racecourse
New Meadow
Oakey Meadow
Tin Yard
Five Acres
Barley Slopes
Barley Rise
Flax Field
Wet Triangle
Drive Meadow

APPENDIX I

Location of Rosemaund Farm

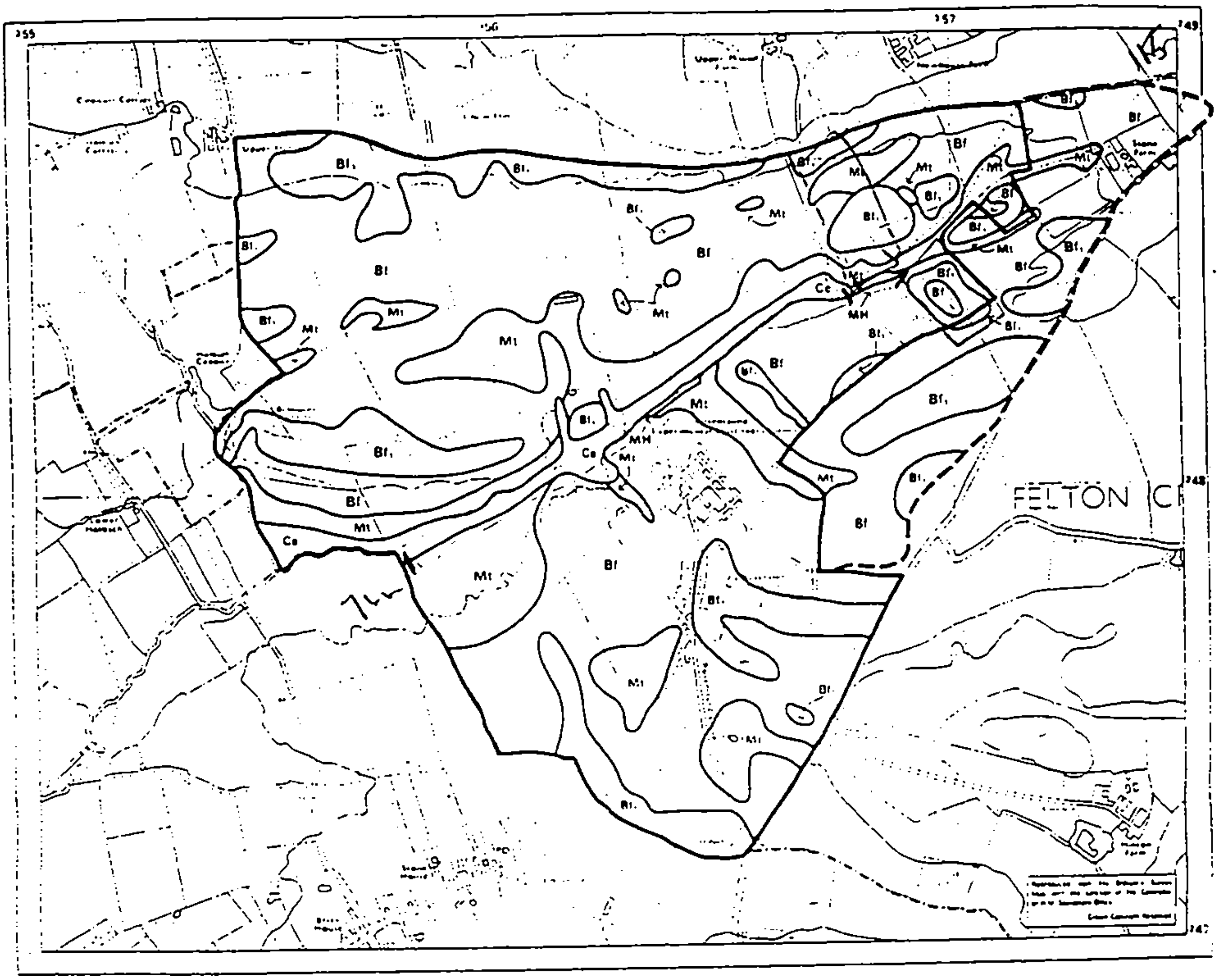


Field boundaries and extent of catchment

APPENDIX II

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 loams	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 loams	Deep moderately permeable slightly mottled stoneless reddish alluvial silty clay loams	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 III

WEATHER DATA SUMMARY FOR ADAS ROSEMAUND (1989-1991)

1989

	Rainfall(mm)		Sunshine(hrs)		Mean 10 cm Soil temp ^{o}C @ 0900 hrs GMT		No.of days rain(0.1mm or more)	No.of ground frosts	No.of air frosts
	LTM	1989	LTM	1989	LTM	1989	1989	1989	1989
January	58.4	23.7	51.8	68.0	2.7	4.7	12	12	4
February	43.6	44.6	66.5	82.6	2.8	3.9	20	19	7
March	51.0	34.2	105.0	101.3	4.2	5.8	22	18	2
April	43.4	63.2	149.1	115.4	7.1	6.3	14	21	11
May	54.8	17.4	182.7	213.6	10.8	13.5	5	11	0
June	51.6	26.5	190.1	212.7	14.4	16.0	12	5	0
July	50.9	59.0	186.1	280.3	16.2	18.3	5	0	0
August	59.7	42.2	168.3	229.7	14.9	16.1	8	1	0
September	60.9	33.7	128.9	118.5	12.4	13.2	9	4	0
October	56.3	95.9	94.5	83.8	9.4	10.7	20	6	0
November	66.2	51.9	61.7	76.1	5.74	5.1	15	16	5
December	65.9	158.2	45.4	10.1	3.77	4.4	15	17	8

Summary: January to March very dry and mild; cool and wet in April; all summer very hot and dry; September dry; very wet October; November average; December very wet and cold.

LTM = Longterm mean since 1951.

1990

	Rainfall(mm)		Sunshine(hrs)		Mean 10 cm Soil temp ^{O}C @ 0900 hrs GMT		No.of days rain(0.1mm 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 = Longterm mean since 1951.

1991

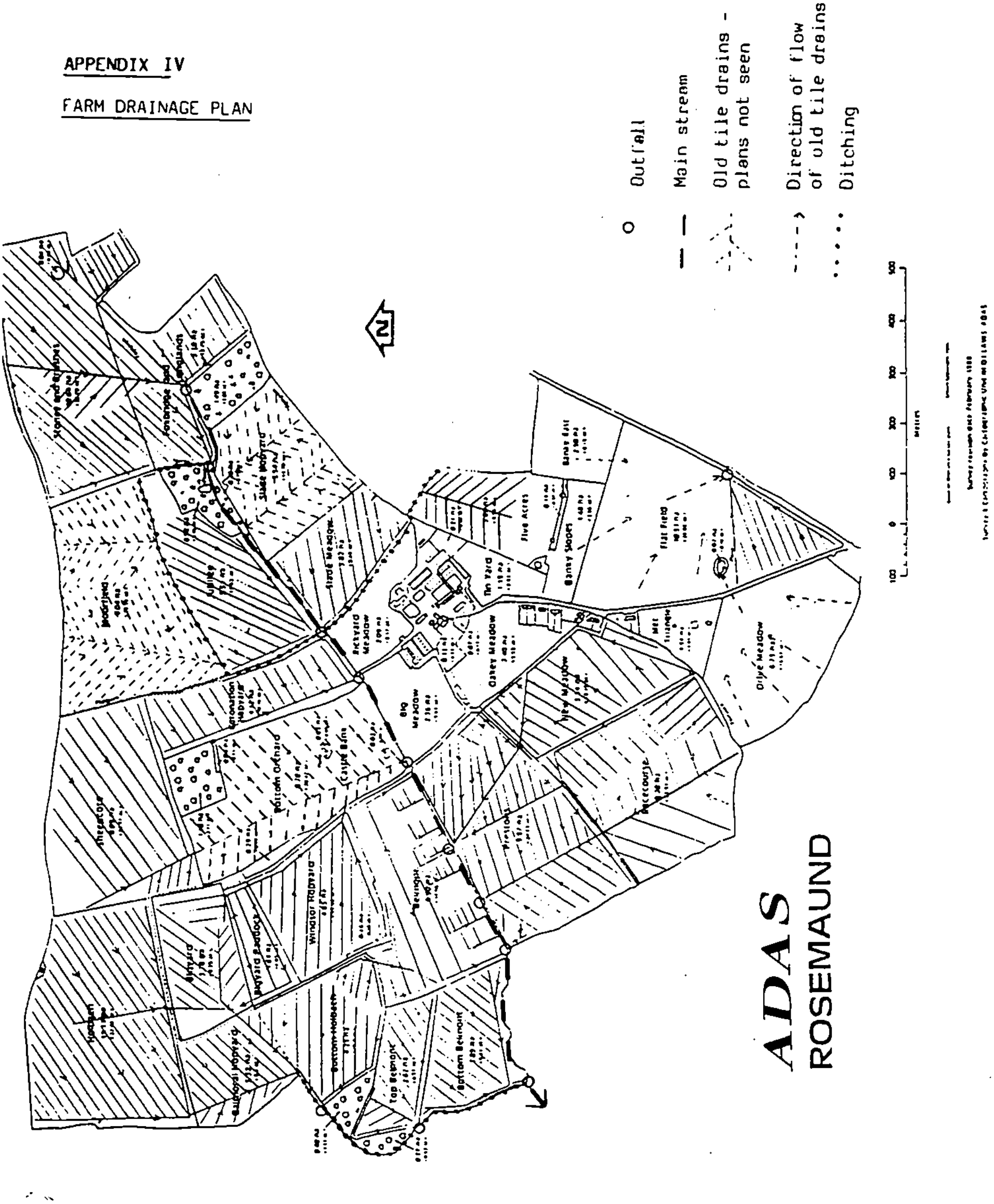
	Rainfall(mm)		Sunshine(hrs)		Mean 10 cm Soil temp °C @ 0900 hrs GMT		No.of days rain(0.1mm or more)	No.of ground frosts	No.of air frosts
	LTM	1991	LTM	1991	LTM	1991	1991	1991	1991
January	61.0	88.7	52.6	67.8	2.73	2.60	18	26	14
February	44.4	24.5	66.5	55.3	2.86	1.81	13	23	19
March	50.9	78.6	105.1	82.4	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 = Longterm 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.

APPENDIX IV

FARM DRAINAGE PLAN



<u>**APPENDIX V**</u>

CROPPING HISTORY OF EACH FIELD 1985-91

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

Abbreviations:				
	BW	Winter beans	P	Peas
	BS	Spring beans	PP	Permanent pasture
	FB	Fodder beet	SB	Spring barley
	FM	Forage maize	SW	Spring wheat
	H	Hops	T	Turnips
	I	Italian ryegrass	WB	Winter barley
	L	Grass ley	WO	Winter oats
	OSR	Oilseed rape	WW	Winter wheat
			LS	Linseed

APPENDIX VI

MAIN PESTICIDES APPLIED TO MAJOR CROPS AT ROSEMAUND 1989-91

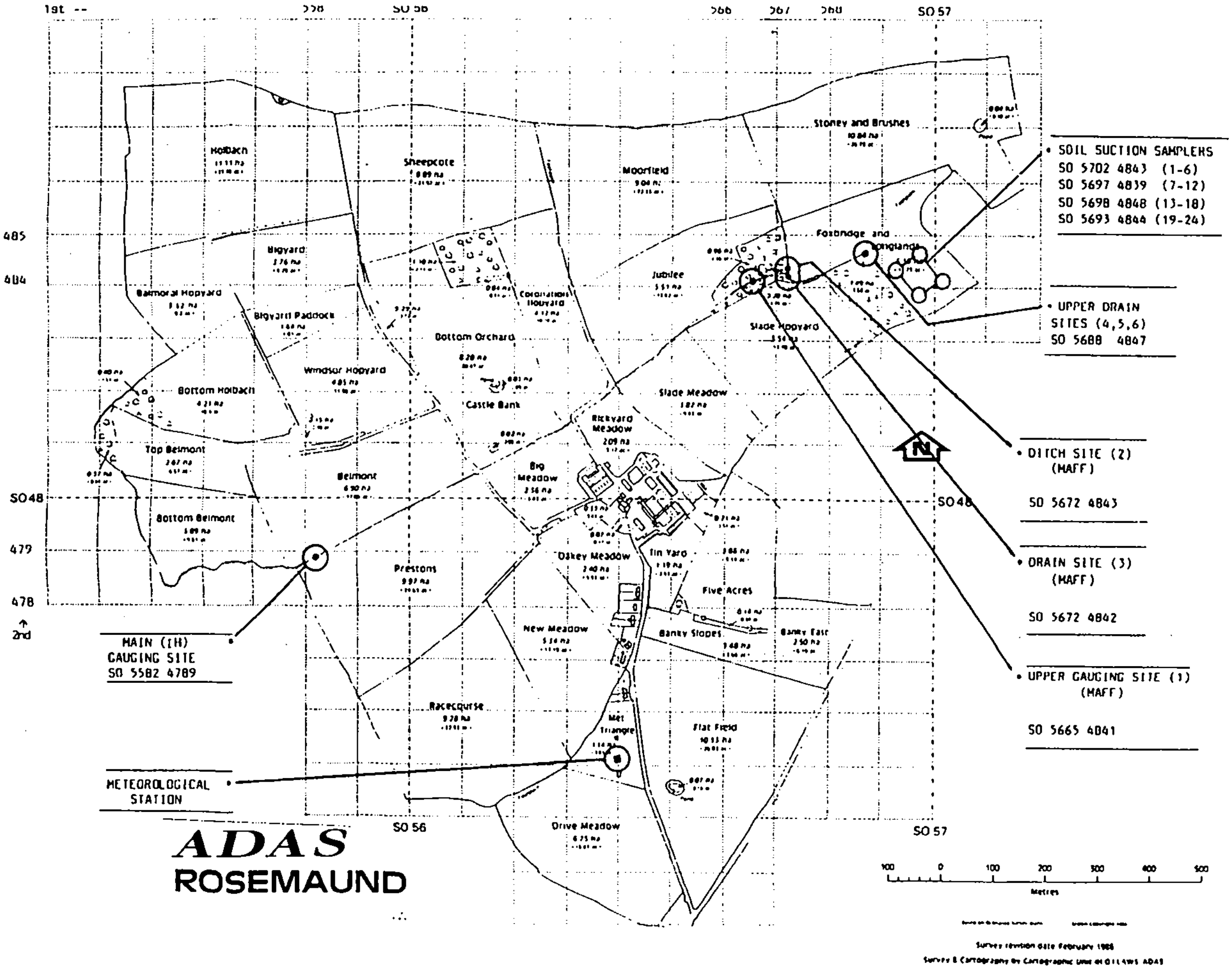
Crop	Pesticide	Application rate/ha	Month
Winter wheat	MECOPROP	2.4 kg	March/April
	FENPROPIDIN	560 g	June
	PROPICONAZOLE	125 g	June
	CARBENDAZIM	250 g	June
	2-CHLOROETHYL PHOSPHONIC ACID	240 g	May
	CHLORMEQUAT)	1.6 kg	April
	CHOLINE CHLORIDE)	80 g	
	BROMOXYNIL)	400 g	April
	IOXYNIL)	400 g	
Winter barley	CHLORPYRIFOS	720 g	November
	MECOPROP	up to 2.4 kg	November, March/April
	CHLORMEQUAT)	1.6 kg	April
	CHOLINE CHLORIDE)	80 g	
	PROCHLORAZ	400 g	April
	PROPICONAZOLE	125 g	April/May
	2-CHLOROETHYL PHOSPHONIC ACID)	230 g	May
	MEPIQUAT CHLORIDE)	450 g	
	BROMOXYNIL)	400 g	March/April
	IOXYNIL)	400 g	
	CARBENDAZIM	250 g	April/May
Hops	SIMAZINE	up to 2250 g	November-March
	BUPIRIMATE	up to 700 g	April-August
	COPPER OXYCHLORIDE	up to 3000 g	April-August
	TRIFORINE	up to 475 g	June-August
	DELTAMETHRIN	up to 40 g	May-August
Grass	MCPA	up to 1.75 kg	

APPENDIX VII - Properties and usage of selected pesticides in England and Wales

Pesticide	Main type/ use	Usage (1980-83) (tonnes p.a)	Solubility in water		Persistence			Drinking water guideline (µg/l)
			(µg/l)	(°C)	Soil	Water	Comments	
Atrazine	Non agricultural herbicide	Several hundred	33	20	Fairly persistent some leaching into water	Fairly persistent	Likely to reach water - has been detected frequently	30
Chlormequat	Growth regulator - cereals	1053	1000×10^3	25	Degraded. Little leaching to lower soil layers	Probably fairly persistent	Unlikely to reach water	10
Chlortoluron	Herbicide - Cereals	1884	70	25	Degraded (no leaching information)	Probably persistent	May reach water	8
MCPA	Herbicide - cereals	981	825	25	Fairly persistent Some leaching into water	Probably persistent	Likely to reach water. Has been detected	10
Mecoprop	Herbicide - cereals	3407	620	25	Degraded No leaching information	Probably persistent	May reach water. Has been detected	7
Simazine	Non agricultural herbicide	Several hundred	5	20	Fairly persistent. Little leaching	Fairly persistent	May reach water Has been detected	30

Note: Taken from R J Williams and S C Bird (1987) Total impact of pollutants in river basins: Phase 2. Progress report on DOE contract 7/7/170, November 1987

APPENDIX VIII



APPENDIX IX

THE SOIL HYDROLOGY OF 'LONGLANDS' ROSEMAUND EHF, HEREFORDSHIRE

SECOND INTERIM REPORT - CROP YEAR 1990/91

by

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Oxfordshire OX10 8BB

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4 March 1992

CONTENTS

EXECUTIVE SUMMARY

This report presents the results of the Soil Hydrological component of The Institute of Hydrology's research program at Rosemaund Experimental Husbandry Farm, Hereford, for crop year 1990/91, conducted within the field named 'Longlands'. The results of a pilot study carried out in the previous year were presented in the First Interim Report.

The main objectives of the soil hydrology process studies were:

(i) to gain insight into the physical processes controlling the movement and storage of soil water in and over the under-drained Bromyard Series soils of Rosemaund;

(ii) from this to provide the basis for physically realistic modelling of the water (and solute) inputs by various pathways to the surface water channels, and

(iii) to aid the interpretation of chemical data.

(iv) to provide pointers to alternative agro-management strategies which might lead to reduced pollution of surface waters by agro-chemicals.

The soil hydrology experimental programme comprised two components:

1. A study of the dynamic behaviour of the soil water reservoir in relation to the effects of a representative field drain throughout the crop cycle. Soil water potentials were monitored within a 1.5 m deep vertical plane containing six profiles, each of six manometer tensiometers, extending on either side of a field drain to the mid-drain position.

2. A preliminary, semi-quantitative study of surface runoff to assess its importance and relationships with antecedent surface soil water content and short-term rainfall intensity and amount.

Results

Several aspects of the results will be relevant to modelling the system:

(i) Four, fairly distinct, hydrological stages of the crop year were identified. These stages, in some form, should be taken account of in the modelling.

(ii) The area can be represented as alternately parallel strips of land which, hydrologically, behave quite differently.

(iii) The profile can be represented in simplified form as three layers, with different properties - topsoil (0-50 cm), subsoil (50-100 cm) and geological formation (below 100 cm).

This information should enable greater physical reality to be achieved in models and also provide pointers to the design of chemical process studies.

Perhaps the most important of the four hydrological stages is the autumn re-wetting of the soil. It seems that two entirely different soil hydrological situations may be established in different years, according to the intensity of autumn rainfall and the timing of cultivation.

(i) If rainfall intensities and amounts in autumn are low, the large macropores created by summer shrinkage cracks in the upper 0.5-1.0 m tend to be closed off by slow soil re-wetting and re-swelling. Cultivation also destroys these shrinkage macropores, at least to the base of the plough layer and, in addition, the worm hole macropores which unlike the shrinkage macropores, remain viable in spite of re-swelling. Thus, a very wet topsoil layer is produced, overlying a very dry subsoil layer remaining from the summer. The water table is not able to be recharged and remains well below the drains, at its summer level, so that significant drain flow is impossible. This situation can persist for weeks or months, as the very low matrix (non-macropore) conductivity of these soils inhibits the wetting front from advancing quickly downwards. The result is a much wetter topsoil condition and late onset of drain flow, as occurred in the autumn/winter of 1990/91.

(ii) Conversely, if the start of autumn is marked by early heavy rains prior to cultivation, water is able to penetrate rapidly to the base of the shrinkage cracks, and quickly to migrate sideways, into the peds, thus allowing the profile to become wet throughout. Hydraulic continuity to the drains and to the underlying geological pathways to the groundwater is established, so that further rain causes the water table to rise quickly to 1 m, allowing drains to start flowing. This seemed to have been the situation in the autumn/winter of 1989/90, although at that time instrumentation was insufficient to provide more than a general indication of what happened.

Surface runoff. The surface runoff ('overland flow') plots showed that surface runoff amounts following most rainfall events are either small and relatively localised, or non-existent; antecedent surface soil moisture appears to be a significant factor in these small events. Larger rainstorms may lead to the combination of these small localised flows, producing sheet overland flow which can be expected to reach the valley bottom and enter the surface water system. This seems to depend mainly on duration and intensity of the rain, although soil surface conditions must also play a major part, particularly in determining the trigger thresholds for such events to start. Current data suggest that events with less than 15-20 mm of rain are unlikely to produce sheet flow. Such storms probably occur only once or twice per winter, but may be important in translocating pesticides under certain conditions.

Further Work

The soil hydrological studies should be continued into the 1991/92 crop year, attempting to confirm some of the results, to assess the effects of winter fallow treatments and to examine the functioning of soil water suction samplers.

The implications of the hydrological understanding gained need to be considered in relation to the movement and degradation of pesticides, the timing of cultivations and chemical applications and antecedent soil conditions and predicted weather systems.

Thus, more effort is called for to gain a parallel understanding of the chemical processes in the soil system and their relationship to the physical (hydrological) processes. Chemical analysis of surface and soil water alone is limited in the extent to which it can explain the system responsible, and thus limits the predictive value of models so derived.

I. INTRODUCTION

For the past few years a major study of pesticides in runoff from an agricultural catchment has been conducted at Rosemaund Experimental Husbandry Farm, some 8 km to the north-east of Hereford. The catchment is an area of 1.8 square kilometres which mostly coincides with the boundaries of the Rosemaund Farm.

A number of organisations have participated in loose coordination, including MAFF, SSLRC, ADAS, BRE and IH, with inputs by NRA (Welsh Region) and FDEU. The overall objective is to develop a generally applicable model relating agricultural pesticide practice, climate, catchment characteristics and operational factors to concentrations of these chemicals in surface water and groundwater.

The main objectives of the soil hydrology studies are:

(i) to gain insight into the physical processes controlling the movement and storage of soil water in and over the under-drained Bromyard Series soils of Rosemaund;

(ii) from this to provide the basis for physically realistic modelling of the water (and solute) inputs by various pathways to the surface water channels, and

(iii) to aid the interpretation of chemical data.

(iv) to provide pointers to alternative agro-management strategies which might lead to reduced pollution of surface waters by agro-chemicals.

The experimental programme this year comprised two components sited within the field named 'Longlands' (see sketch map - Fig. 1):

1. A study of the dynamic behaviour of the soil water reservoir in relation to the effects of a representative field drain throughout the crop cycle. Soil water potentials were monitored within a vertical plane extending 10 m on either side of the line of a field drain to the mid-drain position (Fig. 2). An array of 36 porous pot mercury manometer tensiometers, was set out as six profiles each of six tensiometers at depths 10, 30, 60, 90, 120, and 150 cm. The data were analysed by means of software written to plot 2-dimensional potential diagrams and potential profiles.

2. Preliminary study of surface runoff to assess its importance and to provide preliminary correlations between it and such factors as antecedent surface soil water content and short-term rainfall intensity. This was intended to provide the basis for assessing the possibilities of modelling surface runoff and thus its potential effects on translocation of pesticides in relation to agro-practice, climate, soil surface and slope characteristics.

The report is divided into two parts, dealing with each component separately. It is assumed that the reader is familiar with the context of the soil hydrology experiments within the overall pesticide project at Rosemaund.

II. THE TENSIOMETER ARRAY

Soil Hydrological Stages through the crop year

The tensiometer data are presented in two diagrammatic forms:

a. As a vertical cross section extending from one mid-drain position to the next, showing the distribution of total soil water potential in the upper 1.5 m. Potentials are designated by alphabetic characters, defining zones of different potential. The borders of these zones correspond to isopotential lines, which can be drawn-in by hand. The direction of soil water flux is normal to these lines.

b. As profiles of total potential for each of the six profiles of tensiometers, A to F. Where the profile is becoming more negative upwards, the flux is upwards, and vice versa. The position where the gradient is zero defines the zero flux plane, which is normally present during the summer, separating upward from downward flux.

The data showed that the crop year 1990/91 can usefully be divided into four stages, each distinct in terms of soil water conditions and processes.

Stage 1 - the latter part of the summer dry soil phase until October 1990

This account starts when the previous cereal crop had been harvested and the field was under stubble. The soil was very extensively cracked due to shrinkage, these cracks being typically 5 cm wide at the surface and extending visibly down to 80 to 100 cm (confirmed by excavation). The entire profile was very dry indeed, particularly at the soil surface.

As hydraulic conductivity is extremely low in these conditions, any water transfer, in absence of vegetation, could only be vapour movement to atmosphere via the shrinkage cracks.

The field was prepared for sowing during late September and sown to winter wheat. The instrumentation was installed during October and first data were obtained on 30 October.

Stage 2 - the re-wetting of the soil profile, leading to early stages of drain flow

November/December

By the end of October, rainfall had been sufficient only to re-wet the upper 30 cm or so of the soil, and even here water contents were low, potentials typically being of the order of -60 kPa or less (Fig. 3). Below about 45 cm the soil was too dry for tensiometers to operate, ie. below -80 kPa. The 'wet-over-dry' situation persisted until late December, and although the upper layer became wetter during this time and progressed down to about 55 cm, the zone below remained very dry (Fig. 4). The reason that the wetting front progressed so slowly was partly because of the "conductivity barrier" at the base of the wetted layer and partly to the effective rainfall being insufficient to create saturated conditions at the wetting front.

January-February

A period of heavier rainfall during the last days of December and early January overcame the conductivity barrier and the lower part of the profile started to re-wet. Water distribution in this period was quite irregular, with ephemeral patches of saturation appearing and disappearing in the upper profile. This is exemplified by Figure 5 - the 2-D diagram for 9 January.

A notable feature here is the transitory presence of a bulbous zone of saturation, extending above the drain almost to the surface and down to 1.5 m and below. This extends laterally only about 2.5 m on either side of the drain, the entire mid-drain area beyond remaining unsaturated.

The most probable explanation of this is that acceptance rate of the soil in the mid-drain position is less, causing localised overland flow and/or interflow via macropores which feeds the more open textured and therefore more conductive soil in the region of the drain. Once there, this could briefly remain in the soil above the drain if the slots in the drain pipe had become partly obstructed and, also, if the conductivity of the geological formation below drain level (1 m) was too low to accept this water input rate from the soil above.

By 22 January a water table had appeared at the bottom of the 1.5 m measured profile, and thereafter rose slowly. In the vicinity of the drain this rise occurred much quicker, soon intermittently reaching to well above the drain. In the mid-drain regions the water table remained below drain level at this time (Fig. 6) ie. the reverse of the normal operation of a field drain. The isopotential lines show that the drain (together with the aggregate backfill above it) provided a by-pass flow route which was probably the main recharge path to the aquifer, feeding the zone beneath the drain and spreading out laterally beneath the measured profile.

It is probable that during this time most of the drains sited within the Bromyard Series, ie. other than those close to the valley bottom, acted likewise and contributed little to discharge at the drainage outfall.

It is concluded from this that the mechanical disturbance caused by installing the drain and its backfill, coupled with more subtle subsequent changes to the soil structure due to the proximity of the drain (more soil fauna and flora plus more air = more structure), created improved infiltration conditions within a zone extending to 2 or 3 m on either side.

In soils of the mid-drain zone during this period, potential gradients were downward, not only in the unsaturated zone but also in the saturated zone, (see Fig. 7). There must therefore also have been some groundwater recharge in the mid-drain zone. After 22 February (see below), gradients below the water table, and hence further inputs to the aquifer, tended to zero.

The foregoing interpretations are supported by the time-series graph of water table depths (Fig. 8) for the mid-drain and over-drain positions. These show that prior to 22 February the the mid-drain water table level was below the 'at-drain' water table level.

The situation was reversed around 22 February, following a very heavy rainfall. This rain caused the water table in the vicinity of the drain once more to rise to the surface, possibly fed by localised surface runoff. This provided the head to drive a further large input of water into the aquifer, causing a general rise above drain level, including the mid-drain position. Once the surplus had exited via the drain, a normal draining situation was initiated for the first time, ie. with the water table sloping down towards the drain from either side - stage 3.

Stage 3 - established drainage via field drains

March to mid-April

Following a short transitional stage during late February/early-March, the water table started to slope perceptibly down towards the drain from either side, in the traditional way (eg. the 2-D diagram of 18 March - Fig. 9). From this time onwards, the profiles of total soil water potential show two common features, typified by the data for 18 March - Fig. 10.

1. For any given day, the six profiles comprising the array are all quite similar, ie. in contrast to the previous stage, there was little distinction between the near-drain zone and the mid-drain zone.

2. in the unsaturated zone the gradients of total potential were close to unity and also the soil was very nearly saturated. Below the water table the gradients of total potential are very close to zero. This indicates that downward flux below the water table had ceased, implying not only that all aquifer capacity had been filled but that there was little lateral loss from the aquifer.

The interpretation of this presents something of a problem because the conditions in the unsaturated zone clearly were very favourable for drainage ie. unit potential gradient and near-saturated conditions, whereas the zero potential gradient below the water table suggests that there is little or no vertical downward flow below the water table. Where was the water going, and in what quantity? Two alternative explanations are offered:

1. That throughout the profile there is a system of relatively well-conducting macropores (eg. shrinkage cracks and root channels in the soil, joints in the semi-consolidated geology below) which are sufficiently large that they can only hold water at saturation or near-saturated potentials, ie. close to zero. If so, they would be empty in the unsaturated topsoil and thus not contributing to conductivity above the water table, which therefore would have the low unsaturated conductivity of the soil matrix.

Below the water table however, they would be completely filled and highly conductive, requiring only a very small potential gradient to accommodate the small inputs from the saturated zone above. This therefore would suggest that the soil has a reasonably high saturated conductivity but that this reverts abruptly to the low values of the matrix as soon as the pore water pressure becomes negative (unsaturated).

It must be remembered that below the water table, there may be a lateral hydraulic gradient, driving a lateral component of movement. This, depending on the gradients and conductivities concerned, may be significant (or may not). This is considered further in the discussion.

2. That the topsoil layer down to about 50 cm has good lateral interconnection of worm-hole and root hole macropores, allowing lateral 'interflow' while the water table is in this layer. In contrast, the subsoil between depth 50 and 100 cm has fewer and less well-connected macropores of this type. Hence, once the soil has re-swelled and closed the shrinkage crack macropores the conductivity of this layer becomes very low indeed and little further water movement takes place prior to resumption of uptake by a crop in the spring.

Further work may clarify this.

The water table at the drain position fell below the drain in mid-April, thus concluding the drainage phase.

Towards the end of Stage 2, upward potential gradients started to appear in the upper profile, indicating the onset of crop abstraction. Upward gradients appeared for the first time on 28 March and developed to reach a typical form by 17 April (Fig. 11).

Stage 4 - resumption of crop abstraction and start of depletion of soil reservoir

Mid-April to mid-May

Heavy rain at the end of April temporarily cancelled out the upward gradient and returned the profile briefly to a draining condition, but very soon the increasing water abstraction by the crop roots led to the appearance of a zero flux plane, which became well-established by 8 May. This is shown by Figures 12 and 13; the potential profiles and

2-D diagrams, respectively, for 13 May. Once a zero flux plane becomes established in these soils, any further drain flow becomes extremely unlikely.

Below drain level, the water table continued to fall, finally disappearing below 150 cm in mid-May. An interesting feature of this stage is that the 'gull-wing' shaped water table profile persisted even though the water table was below the actual drain (eg. the 2-d diagram of 7 May (Fig. 14). An explanation for this would be that we are seeing a cross-section of a 'cone of depression' of the water table, centred on a position lower down the drain where (by implication) the water table was still at or above drain level - ie. the lower extent of each drain was still draining. Thus we can envisage a drainage fringe receding laterally (westward) across the field towards the outfall of the drains.

By mid-May the crop was growing strongly and transpiration was outpacing what little rain there was in that period, hence shrinkage cracks were beginning to develop.

By June the upper metre of the profile was drying beyond tensiometer range and an upward gradient had become established throughout the measured depth (1.5 m). The very wet June probably caused transient wetting of the 20-40 cm. but the tensiometers in this zone had by that time been de-commissioned.

This stage leads back into Stage 1 - the late summer condition with maximum soil moisture deficit and maximum soil cracking.

Discussion

Macropores

The hydrological role of macropores in these soils is crucial. Because the conductivity of the soil matrix is so low, it is the macropores that form the dominant flow pathways within the soil.

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

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

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

Summary of the annual cycle

For simplicity, stages 1 and 4 together will be referred to as 'the summer phase', stage 2 as 'the soil re-wetting phase', stage 3 as 'the drainage phase'.

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

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

The soil re-wetting phase

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

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

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

These concepts should be incorporated into models if at all possible.

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

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

The crop abstraction phase In most years, by early April, the water demand of the crop starts to exceed to average rain input rate, so the root zone starts to become drier and a zero flux plane develops beneath it. This zone of upward fluxing water encroaches downwards into the zone beneath as the roots advance and deplete the water reserves of the upper layers. This 'soil moisture deficit' acts as a barrier to further inputs of rain to the lower profile, with the result that the water table recedes to below the drains level into the geological formation. Drainflow is impossible under these conditions and will not start again until the next winter. Progressive abstraction of water by the crop causes the development of shrinkage cracks, in dry years to depths of 1 m or more. At the surface these commonly attain a width of 5 cm.

Downslope saturated flow through the aquifer

Much of the saturated flow beneath the water table, as shown by the 2-D diagrams, converges on the drain and soon exits at the outfall. However, it must be remembered that there is a topographic effect which has not yet been discussed. The field has an average slope of about 6% which, for simplicity, is ignored in the 2-D diagrams. The water table overall can be expected to conform to this gradient, subject to localised troughs corresponding to the lines of the field drains. This implies that there will be an unquantified but fairly constant lateral flow below drain level within the geological formation, presumably to exit as 'base flow' at the valley bottom.

While it seems that most of the conductivity of these soils and the underlying geology is derived from the cracks and joints, it must be noted that the water holding capacity of these pathways is very small - probably much less than 1% of the soil volume. This is clear from the soil water content data of 1989/90, which show a marked difference between the soil of the upper metre and the geological material below 1 m (Fig. 15). Thus, the velocity of the water passing through these pathways must be relatively high. Suppose the lateral saturated conductivity (transmissivity) to be 1.0 m per day, the conductive pathway to have a fractional volume of 0.001 and the gradient is 0.06, then the particle velocity would be (1/0.001)*0.06 = 60 metres/day. These figures are guesswork, but probably not too far out.

Water release characteristics

Figure 18 shows water release characteristics derived from simultaneous measurements of water content made with manometer tensiometers and a neutron probe, respectively, over a range of soil water contents at the top 4 tensiometer depths: 10, 30, 60 and 90 cm.

The moisture changes at each depth corresponding to changes in the matric potential range of 0 to -70 kPa are 0.20, 0.17, 0.10 and 0.03, respectively. This reflects the decrease in larger pores with depth and results in a 'flattening' of the curves - a reduction in specific retention.

This is entirely compatible with the soil structures observed in a large soil pit dug on the site to a depth of 2 m.

It is of particular interest that these curves are compatible with another set produced the previous season, for which 'tensimeter' tensiometers had been used rather than manometer tensiometers. Tensimeters employ a pressure transducer system which is introduced into the tensiometer water column by means of a hypodermic needle inserted through a septum stopper. There had been some doubt as to the veracity of this method for a number of reasons, and these doubts must remain for data relating to soils drier than about -30 kPa.

However, the range of the tensimeter data used to derive the water release curves was above this, and the general correspondence of the two data sets support the conclusions expressed in the first interim report on the autumn wetting up process of 1989. It supports the view that there are indeed two distinct modes of autumn re-wetting, illustrated by the datasets of 1989 and 1990, respectively. In the autumn of 1989, early heavy rain prior to cultivation enabled the entire soil profile to

1 m depth to re-wet via the shrinkage cracks within only a few days. This contrasts with autumn of 1990, when the 'wet-over-dry' situation persisted until the end of December.

The need for more information on transient processes and on conductivity. Much has been learnt from this year's experiment and much can be deduced indirectly, with fair confidence. Additional inputs next year will confirm and refine the findings and, hopefully, make them more quantitative. However, it should be kept in mind that it is pointless to seek very high accuracies as the unpredictable element of spatial variability would render this meaningless.

Two main deficiencies must be dealt with next year. The first of these is the need for profiles of pressure transducer tensiometers, which can be logged frequently to reveal transient processes during and following heavy rainfall. For example, how does the partition of rainfall between overland flow and infiltration vary during a storm event as the surface soil water content changes? Such events may last only a few minutes or hours, but might account for significant movement of solutes.

Secondly, it is not possible to quantify or even realistically to estimate the soil water fluxes at different times and depths without a good idea of the hydraulic conductivity characteristics of the three layers 0 to 50 cm, 50 to 100 cm and 100 to 150 cm, particularly for saturated and near-saturated conditions. Several possible approaches to this are envisaged, including the use of a tension permeameter.

Determination of the full, unsaturated hydraulic conductivity characteristic of these soils is likely to be extremely difficult. With regard to the conductivity of the matrix, it seems that values are so low that conventional techniques may be unable to measure the changes in water content and potential accurately enough. Perhaps this is not particularly serious as large errors in very small numbers will make little difference to estimation of such low fluxes.

The all important role of the macropores is even more problematical.

The saturated conductivity provided by shrinkage crack will can range between close to infinity to close to zero within a relatively short period, depending on the degree of re-swelling. The conductivity of the geological formation below 1m. will be spatially variable depending on the nature of the sub-outcrop from place to place, and will thus be very difficult to estimate on an a real basis from point measurements.

The structure, porosity and pore interconnectivity of the root zone (ie. the top 50 cm) may be expected to change continually with the creation of worm holes, root holes, settlement after cultivation, crop development and freeze-thaw. Thus it is difficult to contemplate undertaking field measurements which will have any real validity. It seems that a modelling approach may be called for here.

It is therefore necessary to treat the present interpretation with caution.

III. THE SURFACE RUNOFF STUDY

Introduction

The aim of this preliminary study was to assess the importance of runoff as a component of the hydrology of Longlands (and therefore of other drained fields sited on the Bromyard soil series) at Rosemaund.

In the literature it is common for the term 'runoff' to encompass sub-surface 'interflow' and groundwater flow, as well as runoff directly over the soil surface, but the 'runoff' is defined here specifically as the flow of water over the surface of the ground.

Surface runoff may provide the most rapid medium for transport of solutes including pesticides. It provides, in principle, the most immediate means by which pesticides can reach watercourses. The study in Longlands set out to observe surface runoff and to assess its importance in a semi-quantitative way, relating it to antecedent soil moisture conditions and to the intensity, volume and duration of rainfall.

Instrumentation

Two runoff plots, with 2 m runoff interception troughs at their downslope ends, were installed (Fig. 1) in October 1989.

1. A 2 m x 2 m area closed against external ingress on all sides - the 'closed plot', and

2. A similar plot which was allowed to remain open at its top end to admit all water from a 2 m wide strip of the field upslope - the 'open plot'.

The 'open plot' was discredited half way through the winter due to rodent excavations, so comments herein are based on the 'closed plot'.

The interception troughs were connected via sections of pipe to tipping bucket flowmeters, data being collected automatically by a Campbell logger. A 0.5 mm bucket rain gauge was also connected to the logger. The normal logging interval was hourly, but a single tip of the raingauge triggered the system into 2-minute logging, which continued until a complete hour passed with no tips of the raingauge, after which hourly logging was resumed.

A prototype capacitance soil water content sensor was installed close to the runoff plots (Fig. 1) at a depth of 5 cm and attached to an automatic logger. This instrument measures the dielectric constant of the soil and hence the soil moisture content. At a depth of only 5 cm it provides a 'surface' soil moisture content measurement every 15 minutes.

Results

Runoff data were collected from 28 November 1990. Before 22 March one flowmeter tip equalled 1.3 litre. After this date, more sensitive tipping buckets were installed with a tip-volume of 16.2 ml.

Because frozen water has a very low dielectic constant compared with that of liquid water, frozen topsoil is indicated as very dry, which may be regarded as anomalous for some purposes, but not necessarily for all. This applied for most of the period from 12 January until the capacitance probe failed electronically. It was inoperative from 1 February to 11 March, after which there was a continuous set of good data into June and beyond.

The equation used to convert raw capacitance probe data - ie. frequency - to soil moisture content - is given below:

$$M = (30438/(F-4946))2$$

where M = volumetric soil moisture content %
F = capacitance probe frequency (reading x 10000)

This calibration was obtained from a site similar to Rosemaund so the water content data should not be taken as absolutes, but rather as indicators of the trends.

Data from the tipping buckets and capacitance probe were combined in time-series diagrams, such as the one in Figure 16. This shows hourly rainfall, runoff and soil moisture content obtained from the capacitance probe for the period 22 February to 9 April. From this, three distinct rainfall events are identified, labelled 1, 2 and 3. The rapid response of the surface soil layers to rainfall input should be noted, and also the fact that only the second rainfall event caused the tipping bucket to start tipping.

These time-series plots enabled 18 distinct rainfall events to be identified. Eleven of these produced surface runoff and seven did not. The events are listed in Table 1, together with antecedent soil moisture content and an indication of whether or not runoff occurred.

Total rainfall for each event was plotted against the antecedent soil moisture content in Figure 17.

Discussion

According to the normally accepted theory, surface runoff only occurs when the so-called 'infiltration capacity' of the soil (the upper limit of the acceptance rate of the soil surface to rain) is exceeded. This is a simplistic approach which takes no account of factors such as hydraulic conductivity, which will change with soil moisture content, the crop and stage of growth and the antecedent condition of the soil surface - is it cracked or capped or frozen? In this study it was notable that heavy rainfall events sometimes produced surface runoff and sometimes failed to do so - see Table 1.

Table 1. Identified Rainfall Events

Event date	Total rainfall mm	Runoff	Antecedent surface water content v/v
			%
19/11/90	6.5	YES	33.0
23/11/90	9.5	YES	34.1
24/11/90	4.0	YES	36.0
09/12/90	3.0	YES	35.8
20/12/90	5.5	YES	33.5
25/12/90	17.5	YES	35.1
05/01/91	6.0	YES	35.7
08/01/91	17.5	YES	36.0
09/01/91	6.0	YES	35.7
15/03/91	1.0	NO	35.8
16/03/91	9.0	YES	35.8
17/03/91	5.0	NO	37.0
18/03/91	5.0	NO	37.5
20/03/91	3.5	NO	37.2
22/03/91	0.5	NO	37.3
02/04/91	7.0	NO	37.8
04/04/91	9.5	YES	40.1
06/04/91	4.5	NO	40.7

What then is the explanation for this? There are two possible fundamental controls of initiation of surface runoff:

1. Antecedent soil moisture deficit of the topsoil. In this case, the wetter the antecedent soil condition, the less the storage capacity to be satisfied and the more likely is runoff to occur ie. wet soil = more runoff.

2. The alternative is control due to the unsaturated hydraulic conductivity of the topsoil, which differs greatly from soil to soil, but which always is greater the wetter the soil. In this case, the wetter the antecedent soil water condition, the easier the soil will accept the rain and hence the less likely is runoff to occur, ie. wet soil = less runoff.

Figure 17 supports the second of these alternatives. Runoff and non-runoff rainfall events are indicated by different symbols. It can be seen that the events fall broadly into two distinct fields, which can be separated by a straight line. This is a boundary condition for the collected data set which can be expressed (tentatively) as:

$$y = 1.3x - 43.0$$

where y = total rainfall in event mm

x = volumetric soil moisture content (%) at 5cm depth measured with the capacitance probe

Therefore:

$y > 1.3x - 43.0$ => surface runoff occurs

$y < 1.3x - 43.0$ => no surface runoff occurs

This boundary condition thus can provide the basis for a simple model of direct surface runoff with total rainfall in event and antecedent soil moisture content as variables. It should however be borne in mind that subsequent data may alter this - it has been calculated from this year's data set only. Because the data set was incomplete for this year due to changes in instrumentation and several week's breakdown of the capacitance probe, the analysis was unable to include short-term rainfall intensity, but this may well be an important factor, which it is intended to address next year.

The amounts of surface runoff generated by this small plot cannot be regarded with a great deal of confidence in the quantitative sense, as the plot was too small to be representative. However, there are some points of interest:

1. The volumes of runoff in relation to total input per rainfall event were largest during January and the first half of February, when volumes of up to nearly 3 litres from the 4 metre^2 plot (= 0.75 mm) per event were common. After that they dropped to little more than 0.3 litres per event maximum. The change coincides with the date of 22 February mentioned in Part I, when the drains started to operate conventionally.

2. After the end of March, as the crop started to develop, little further runoff occurred, in spite of the dryness of the topsoil and some heavy rainfall events. This is thought to be due to the introduction of a new factor - the development of small shrinkage cracks which could intercept the runoff.

3. 0.75 mm of runoff, accumulated along a length of 100 m of valley bottom and an upslope distance of 170 m (to the field boundary) should yield about 12,500 litres of water. This illustrates the possible importance of this process.

IV. SOME INDICATIONS OF PESTICIDE PATHWAYS

A number of implications can be drawn from the soil hydrology concerning the possible pathways taken by dissolved pesticides under the influence of the changing hydrological regime.

Stage 1 - late summer and early autumn period, 1990

It is probable that direct evaporation from the surfaces of the shrinkage cracks, which penetrate as deep as 1 m, would have caused solutes to move from the fine pores within the peds towards the faces of the cracks, there to increase in concentration, but also to be exposed to the atmosphere and to possible oxidation and degradation. These solutes would be readily available for re-mobilisation in the event of an autumn flush of macropore flow in the upper metre.

In 1990 this did not happen, for reasons discussed above. However, in other years such as 1989, and particularly if the field is left fallow, an entirely different set of soil water and solute transport processes might occur, with (hypothetical) mobilised concentrates from the ped faces being flushed down into the groundwater instead of remaining in the soil or being lost to surface runoff.

Applications of pesticide made during the late spring-summer-early autumn period, when a zero flux plane would be present, would be unlikely to penetrate the soil (as solute) below the upper 5-10 cm, other than in conditions of exceptionally heavy summer rain. These chemicals would either be taken up by the crop, become adsorbed onto the clay minerals or move into the smaller pores of the soil matrix. Their fate thereafter is a matter of speculation and should be studied in detail.

Stage 2 - November to December, 1990

This was characterised by a wet upper 40-50 cm, overlaying the very dry soil beneath, remaining from the summer. Operation of the field drains (at 1 m) was impossible under these conditions, nor was interflow along the impeding horizon likely (because no sustained saturation occurred).

However, in other years, if macropore flow were initiated during stage 1, the soil profile could have re-wetted very quickly to the base of the shrinkage crack system and stage 2 would not have happened. Mobilisation of pollutants would probably have differed. More consideration of this is required from the pollution standpoint.

Stage 2 - The soil re-wetting phase

During this period in autumn 1990, the soil zone close to the field drain and the backfill above, provided a preferential (unsaturated) flow path for soil water and soluble pesticides into the aquifer, which was mainly recharged via this route. The drain was not acting as a drain because the water table was higher at the drain than on either side. Here, during the autumn/early winter period, pesticides applied to the crop would be expected to move rapidly down to join the groundwater.

In contrast, in the mid-drain zone, the bulk of those pesticides recently applied, together with remnants from the previous season, would have moved slowly down through the unsaturated soil by piston flow.

Below the water table of the mid-drain region, the presence of small but definite downward potential gradients points to the possibility of downward movement of water and solutes within the saturated zone during this stage, but better knowledge of the saturated conductivity is necessary to quantify this.

Stage 3 - The normal drainage phase

The data suggest that during this period there was continuous but slow drainage through the unsaturated zone down to the water table, which by now was sloping towards the drain in the conventional manner and supplying the effluent from the field drains. In the lower, saturated part of the soil profile beneath the water table, potential gradients were close to zero. This strongly supports the view that there was no further significant vertical downward movement below the water table.

However, as discussed above, there is an overall hydraulic gradient downslope of the order of 6% and it is likely that there is some, but probably small, base flow component moving downslope beneath the depth of the drains. Were this flow to be large it would necessitate there being inputs from the soil above to sustain it. The absence of observable downward potential gradients in the saturated lower soil profile suggests that this is unlikely.

Stage 4 - Period of water abstraction by the crop

Once temperatures rise and the crop starts to grow vigorously, evapotranspiration soon begins to outpace rainfall. From this time onwards there could be little further entry of pesticides into the soil, other than into the top 10 cm or so. The establishment of a zero flux plane precludes progressive downward movement of water or solute. The upward potential gradient would tend to create a concentration of solutes in the topsoil. The subsequent fate of these during the summer period needs to be examined. Are they taken up by the crop along with the water, and if so, what then happens to them then? If they stay and concentrate in the topsoil, is this degraded or left to be re-mobilised next autumn or is it locked in the smallest of the soil pores? These questions need to be answered.

During summer the water table falls below the measured upper 1.5 m to a depth as yet not determined, taking with it any dissolved pesticides.

The volumes of water involved are probably very small indeed, in line with the very small specific retention of this material (shown by the neutron probe data of 1989/90). However, we do not know where this water is issuing - it must be going somewhere and presumably represents a base flow which emerges somewhere in the catchment.

Overland flow

The study of surface runoff (= overland flow) suggests so far that the amounts derived from the cropped areas are fairly small, and it is yet to be established whether this flow accumulates down the slope as sheet runoff or whether it is relatively localised, possibly infiltrating elsewhere, possibly when it encounters the zone over a drain. It is possible however, that significant quantities of chemicals could be available for translocation by overland flow if recently applied. Again more work is needed to assess this properly.

Another aspect of this is the effect of the tramlines, which undoubtedly create considerable runoff downslope due to the compression of the soil by the wheels of the spray machinery. At Rosemaund, or at least in the "Longlands" study area, not only are the tramlines aligned normal to the contours but herbicides are specifically applied to mark them clearly. There is potential for considerable pollution due to these areas, which represent about 5% of the soil area. Thus, 5% of every pesticide application falls onto the tramlines and is available for rapid mobilisation each time it rains. This aspect of agricultural practice deserves more attention, as it is potentially amenable to modification to reduce pollution.

V. RECOMMENDATIONS FOR FURTHER WORK

The following recommendations for further work are made irrespective of funding considerations. They can be carried out properly only if sufficient funding and appropriate staff are available. If not, priority decisions will be called for to draw up a realistic programme for 1991/92.

1. The basic philosophy of the chemical studies should be re-assessed. Insufficient attention is being given to scientific study of the chemical processes, work so far being dominated by chemical analysis, which taken alone is able to provide little understanding of the processes involved, which inevitably must limit the wider applicability of any models developed on this basis.

Coordinated studies are called for to identify the chemical and biochemical processes involved in the dynamic interactions between chemicals and their mineral, biological and hydrological environment.

2. The soil hydrological studies should be pursued at Rosemaund for a further crop season, with a number of refinements. In particular:

(i) The tensiometer array should be maintained and read throughout crop year 1991/92. This will be facilitated by the declared intention of the farm, after 1990 harvest to leave the field fallow, followed by a spring crop of maize or rape in 1992. This will provide the ideal situation to examine the effects of not cultivating the soil in autumn.

(ii) Additionally, two profiles of pressure transducer tensiometers should be installed to monitor transient effects.

(iii) More work should be done to establish the saturated and unsaturated conductivity to enable quantification of water fluxes. Possible techniques would include the CSIRO Tension Permeameter and the 'Instantaneous Profile Method'.

(iv) A wider runoff gully should be installed to replace the present small plots, representing the full width of crop area between two sets of tramlines, sited near to the valley bottom to catch cumulative runoff from the entire upslope area.

(v) More attention should be given to studying the partition of rainfall between infiltration and overland flow on a 'within-event' time scale, using 15 minute or even 2 minute data.

(vi) Wider use should be made of the capacitance probe, particularly to monitor soil water content of the surface layers.

3. Further research is needed into the methodology of obtaining the large soil water samples necessary for pesticide analysis and, if possible, to validate and compare existing methods in the light of knowledge of the soil hydraulic properties.

ACKNOWLEDGEMENTS

We would like to thank the Director of ADAS Rosemaund, Mr Rob Clare and Mr Peter Glendinning, Agricultural Adviser for their continued interest and support in this project. In particular, we would like to record our appreciation of the efforts of John Spink, David Richards, Anthony Wade and Rob Edwards for reading and maintaining the tensiometers and sending the data so promptly to IH. Our thanks also to the Farm Manager, Mr Des Price, for his co-operation and for making the experimental site available, and not hitting our instruments with the spray boom!

Longlands field site 1989 - 1992

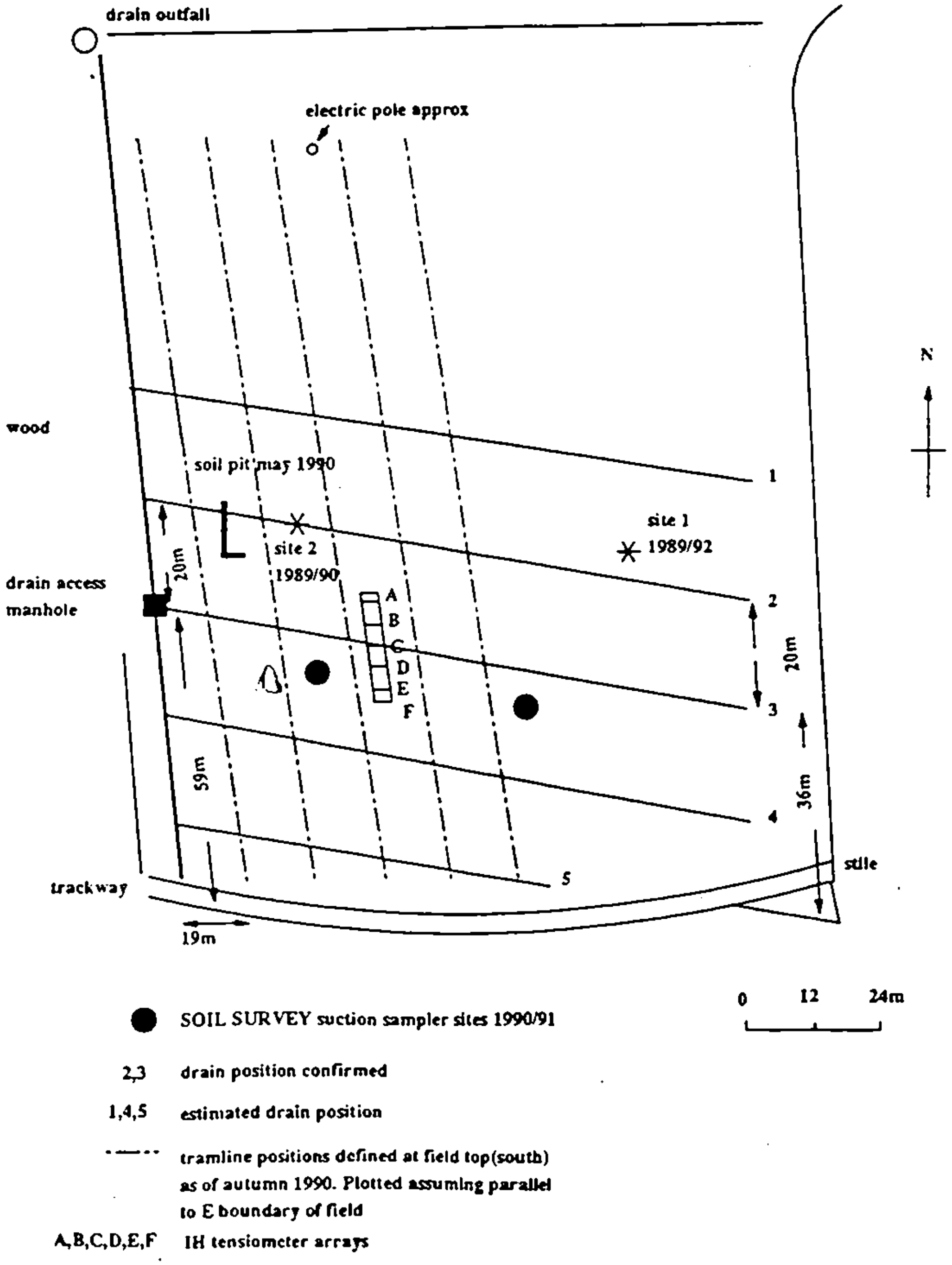


Figure 1. Sketch map of ' Longlands' showing site locations, 1989 - 1992

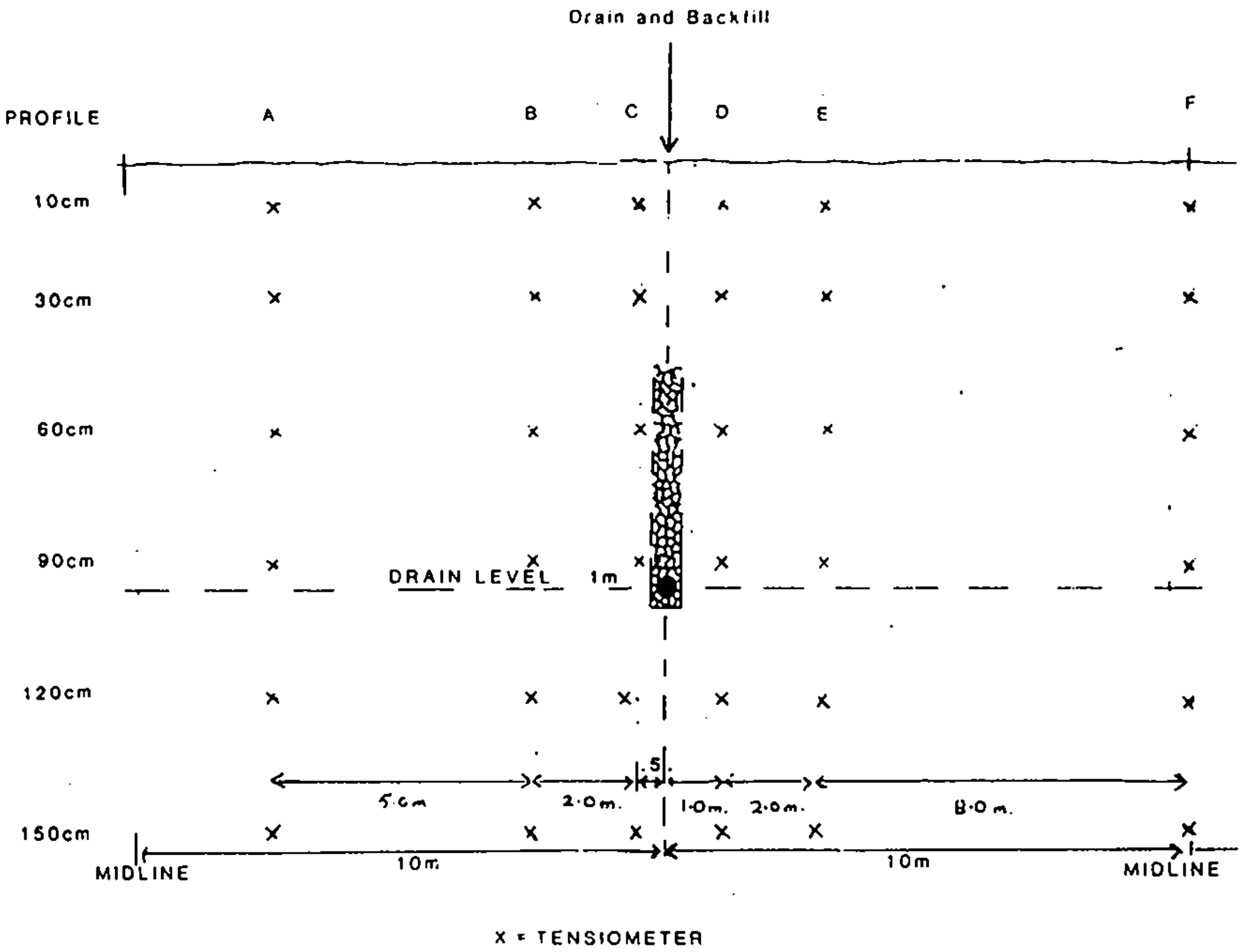
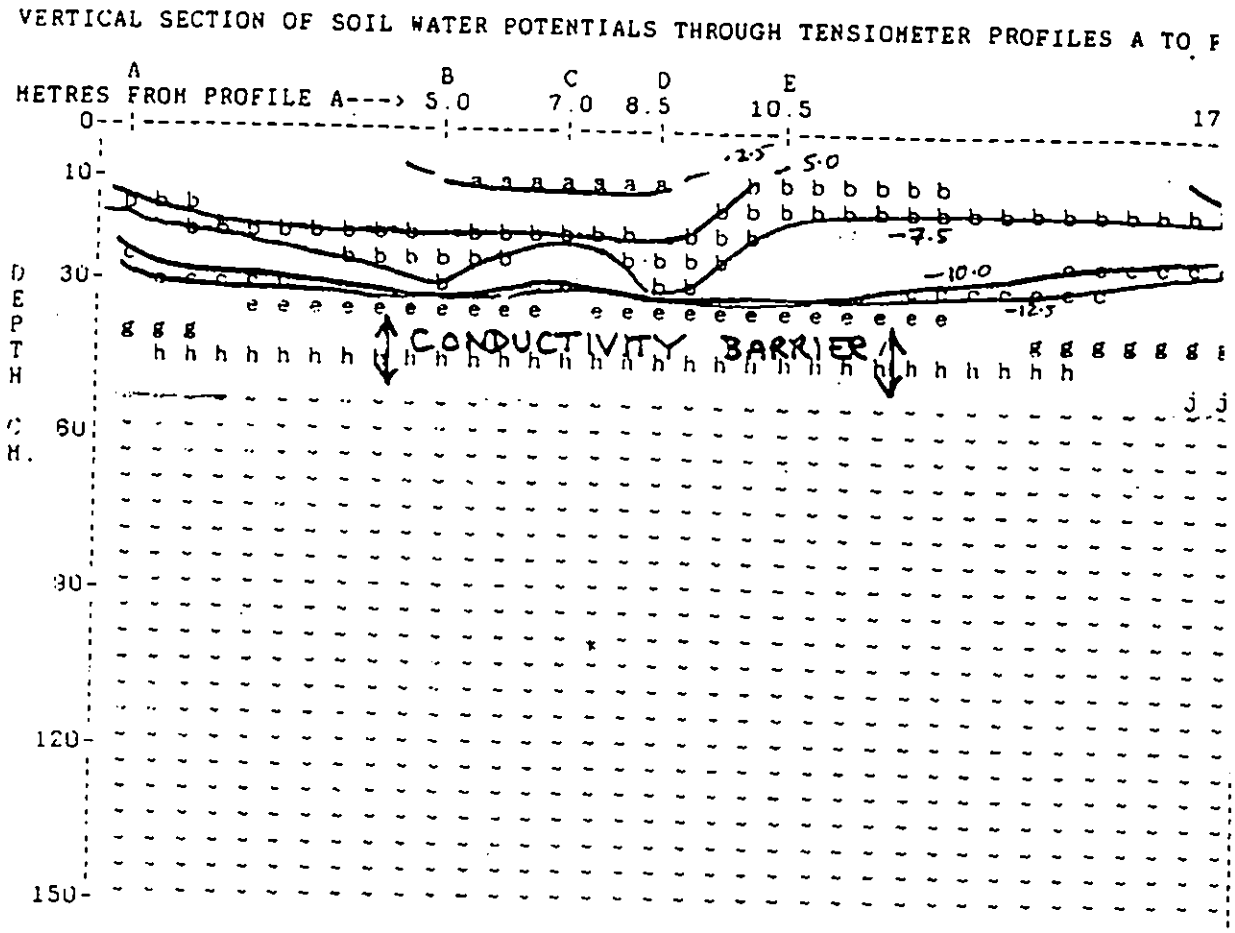


FIGURE 2. Diagram of the layout of the tensiometer array



KEY TO SYMBOLS:-

UNITS: KILOPASCALS (kPa)

. = >0.0
a = 0.0 TO -2.5
b = -5.0 to -7.5
c = -10.0 to -12.5
d = -15.0 to -17.5
e = -20.0 to -25.0
f = -30.0 to -35.0
g = -40.0 to -45.0
h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
~ = <-75.0

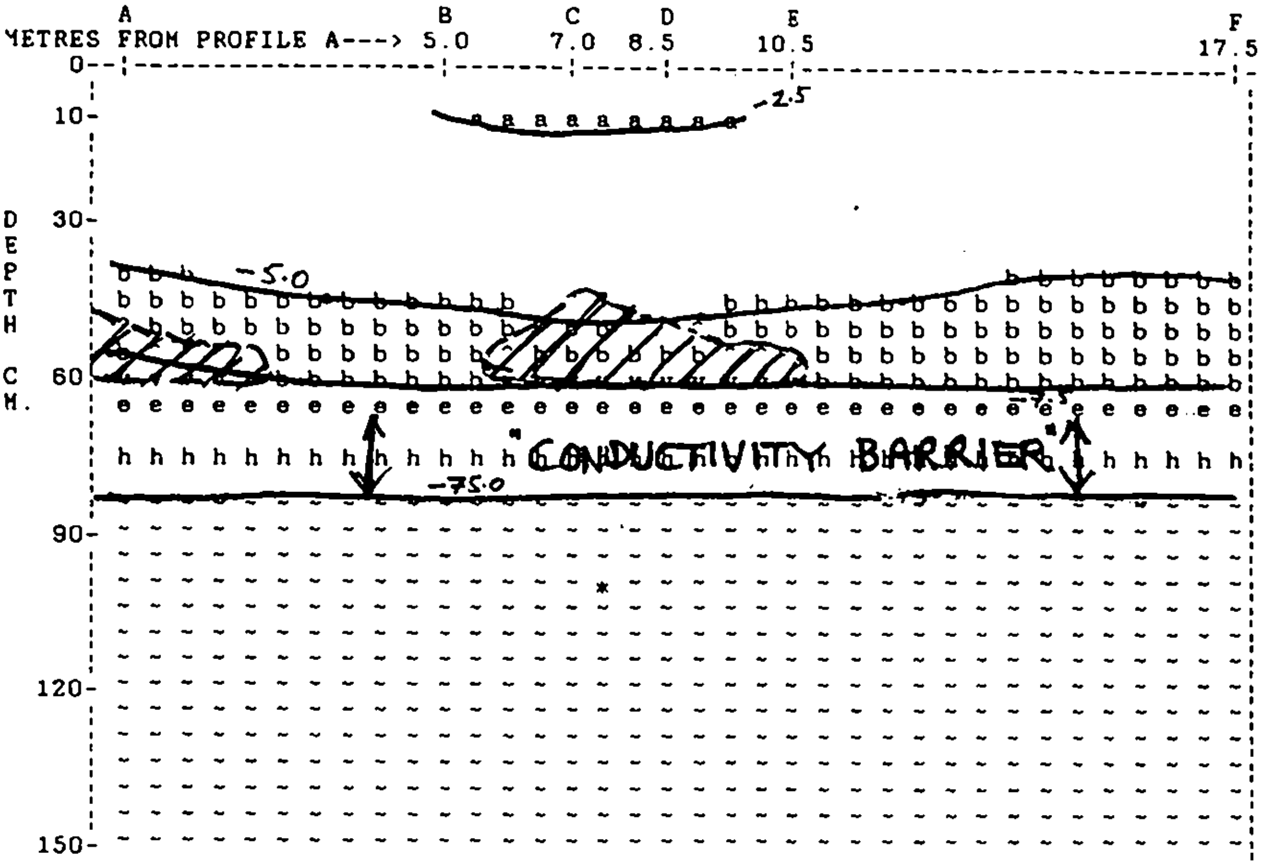
` = WATER TABLE

v = SATURATION FRONT

* = POSITION OF FIELD DRAIN

FIGURE 3. The 2-dimensional diagram for 31/10/90, showing the early appearance of the wetting front in the upper 50 cm., overlying the dry zone remaining from the summer. Tensiometer profiles are marked A to F. Tensiometer depths 10, 30, 60, 90, 120, 150 cm. Linear interpolation by computer. Symbols denote ranges of total potential as indicated in the key.

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:-
UNITS: KILOPASCALS (kPa)

. = >0.0
a = 0.0 TO -2.5
b = -5.0 to -7.5
c = -10.0 to -12.5
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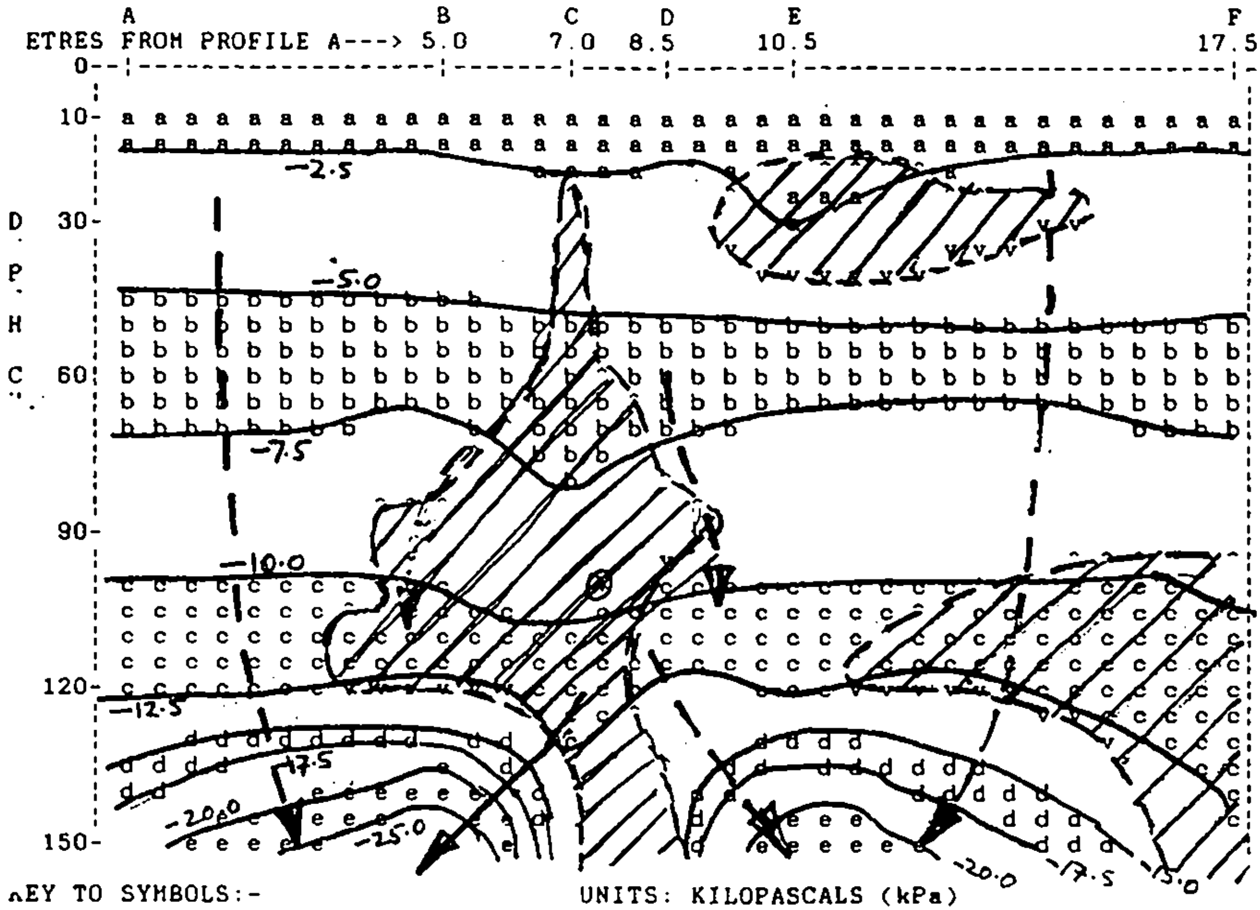
e = -20.0 to -25.0
f = -30.0 to -35.0
g = -40.0 to -45.0
h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
~ = <-75.0

^ = WATER TABLE
v = SATURATION FRONT
▨ = SATURATED

* = POSITION OF FIELD DRAIN

FIGURE 4. The 2-dimensional diagram for 27/12/90 showing the same wet zone 2 months after FIG. 3. The top zone now has higher potentials (i.e. is wetter) but below 80 cm. the soil remains dry.

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:-

UNITS: KILOPASCALS (kPa)

= >0.0
a = 0.0 TO -2.5
b = -5.0 to -7.5
c = -10.0 to -12.5

d = -15.0 to -17.5
e = -20.0 to -25.0
f = -30.0 to -35.0
g = -40.0 to -45.0

h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
˜ = <-75.0

= WATER TABLE v = WETTING FRONT (TOTAL POTENTIAL DIAGRAMS ONLY)

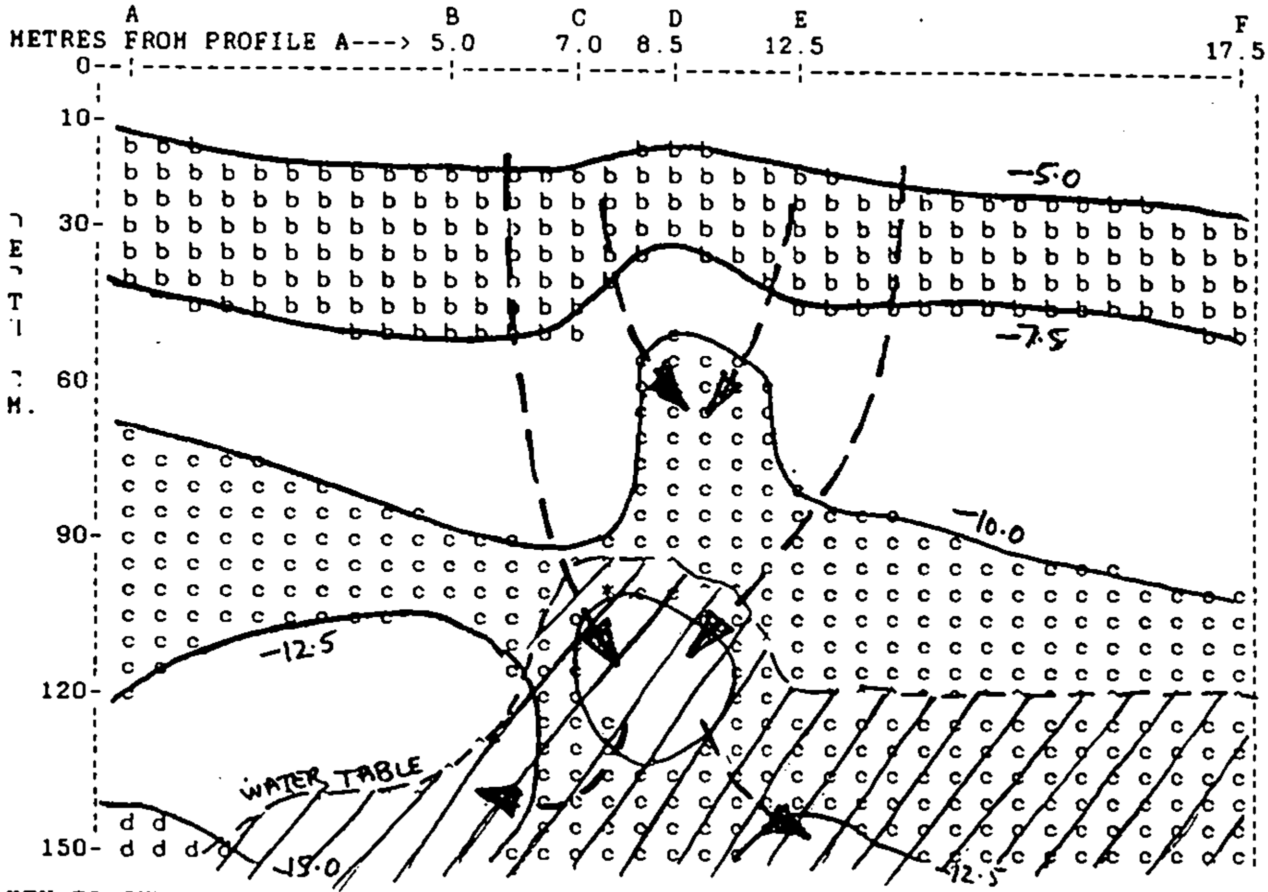
= POSITION OF FIELD DRAIN

▨ = SATURATION

— — → = Flux

FIGURE 5. The 2-dimensional diagram for 9/01/81 showing the profile after entry of water into the lower zone. Note the irregular distribution and lack of water table.

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:- UNITS: KILOPASCALS (kPa)

. = >0.0   d = -15.0 to -17.5   h = -50.0 to -55.0

a = 0.0 TO -2.5   e = -20.0 to -25.0   i = -60.o to -65.0

b = -5.0 to -7.5   f = -30.0 to -35.0   j = -77.0 to -75.0

c = -10.0 to -12.5   g = -40.0 to -45.0   ~ = <-75.0

-^-= WATER TABLE   v = WETTING FRONT (TOTAL POTENTIAL DIAGRAMS ONLY)

* = POSITION OF FIELD DRAIN   — — ➤ = Flux   (▨) = SATURATED

FIGURE 6. The 2-dimensional diagram for 22/01/91, showing a water table soon after it appeared in the profile. Note that it is higher at the drain than on either side, and that the fluxes (normal to the isopotential lines) are converging on the drain from above but diverging below, indicating that the drain is recharging the groundwater, not draining the zone above.

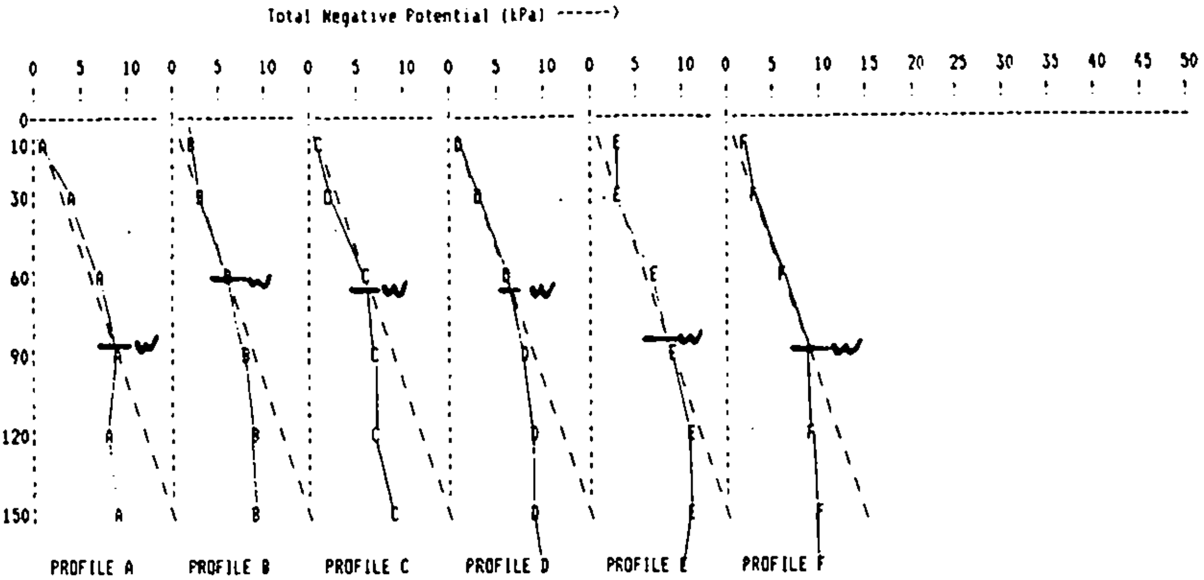


FIGURE 7. Profiles of total potential for profiles A to F on 21/02/81. Note that the gradients below the water table tend to be downwards also, indicating onward downward movement below the water table; this occurred from end January to third week in February only, after which saturated gradients tended to zero.

w = water table

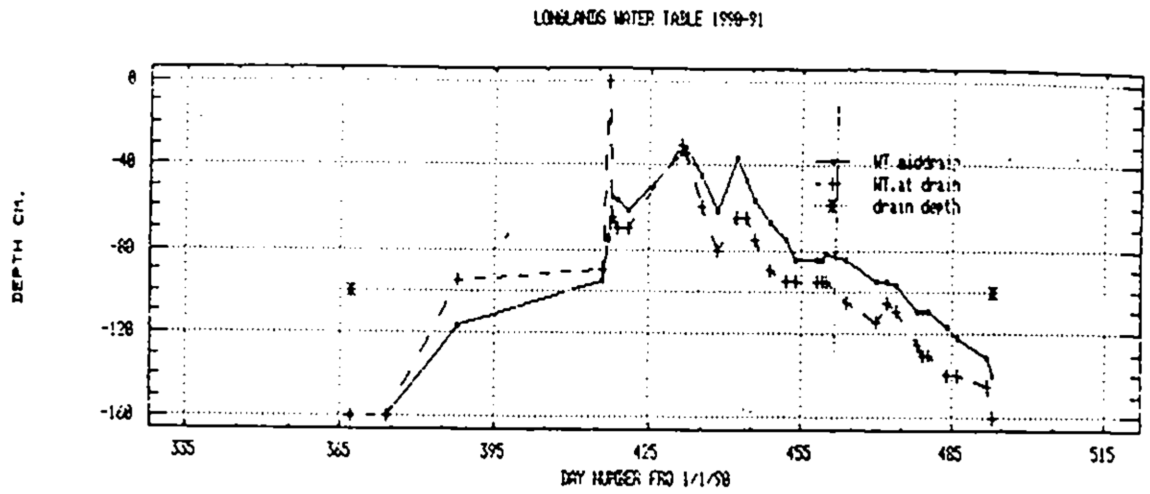
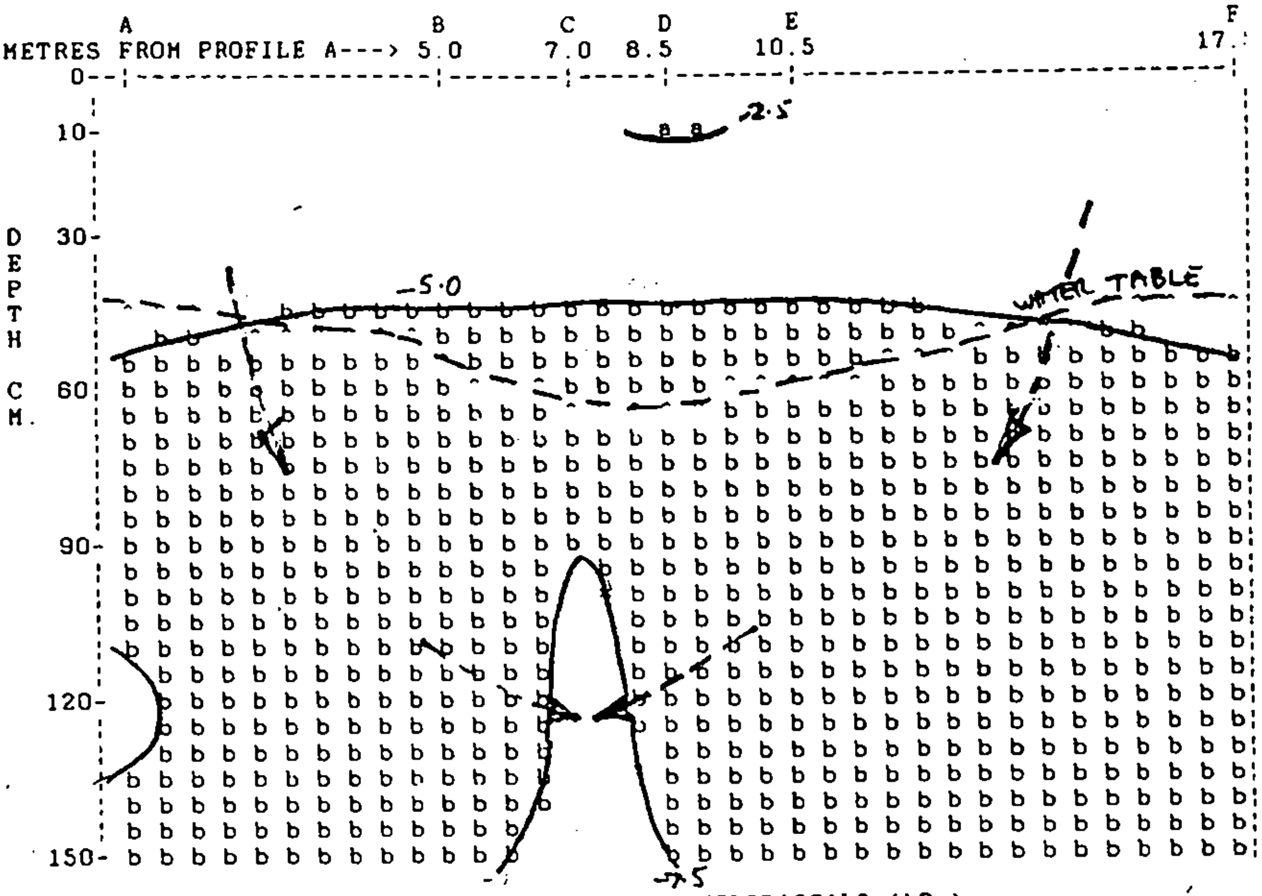


FIGURE 8. Time series graph of water table depth. The full line represents the mean of the levels at the mid-drain position, the dashed line the water level at the drain position. Note the lines cross at the end of February when the normal drainage condition started - minimum level at drain position. Note also when the lines cross the depth of the drain - 1 m.

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:-

UNITS: KILOPASCALS (kPa)

. = >0.0
a = 0.0 TO -2.5
b = -5.0 to -7.5
c = -10.0 to -12.5

d = -15.0 to -17.5
e = -20.0 to -25.0
f = -30.0 to -35.0
g = -40.0 to -45.0

h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
˜ = <-75.0

^ = WATER TABLE V = WETTING FRONT (TOTAL POTENTIAL DIAGRAMS ONLY)

* = POSITION OF FIELD DRAIN

— — ➤ = Flux

FIGURE 9. The 2-dimensional diagram for 18/03/91. Following a 3-week transitional period, normal drainage has now begun, with the water table clearly sloping down to the drain from either side.

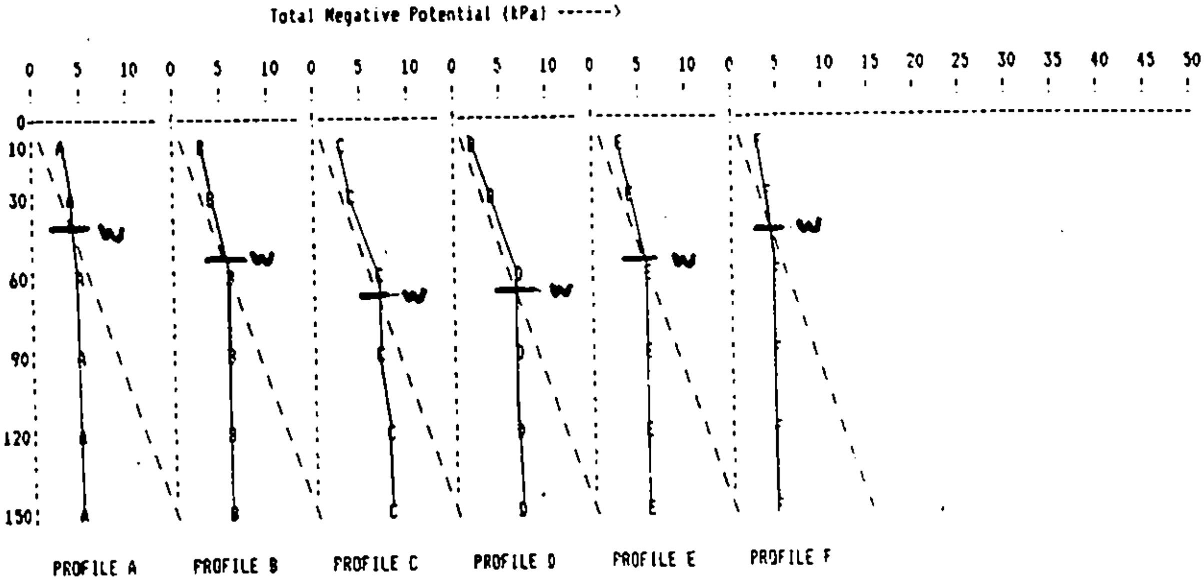


FIGURE 10. Profiles of total potential for 18/03/91, typical of stage 4, showing potential gradients close to unity in the unsaturated zone, but gradients close to zero in the saturated zone.

w = water table

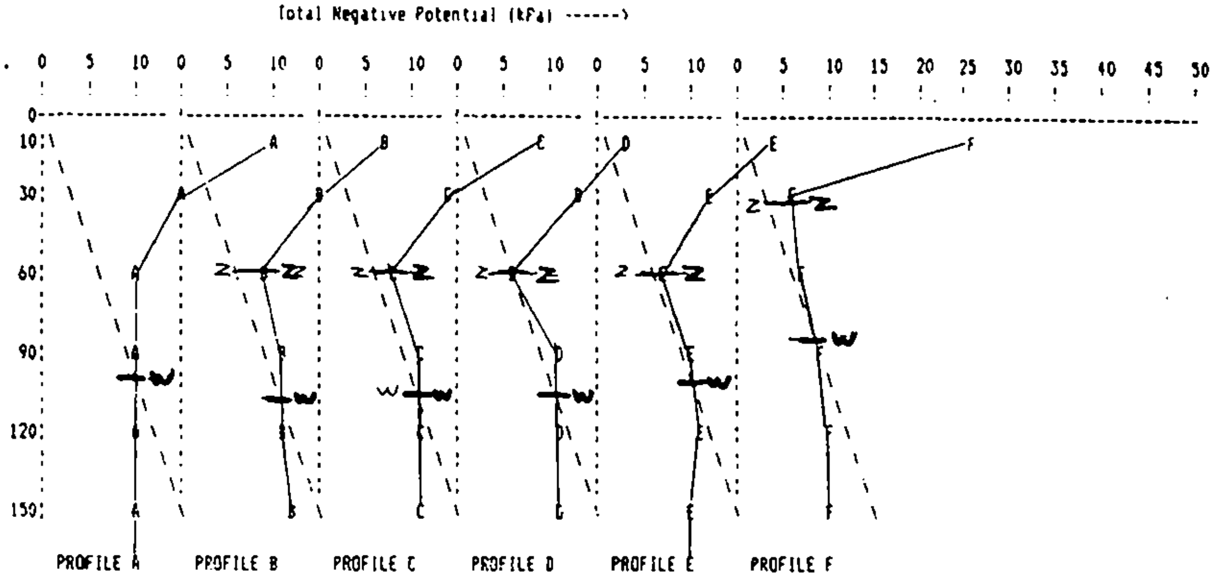


FIGURE 11. Profiles of total potential for 17/04/91. Well developed upward potential gradients are now established in the topsoil.

— Z = zero flux plane
— w: water table

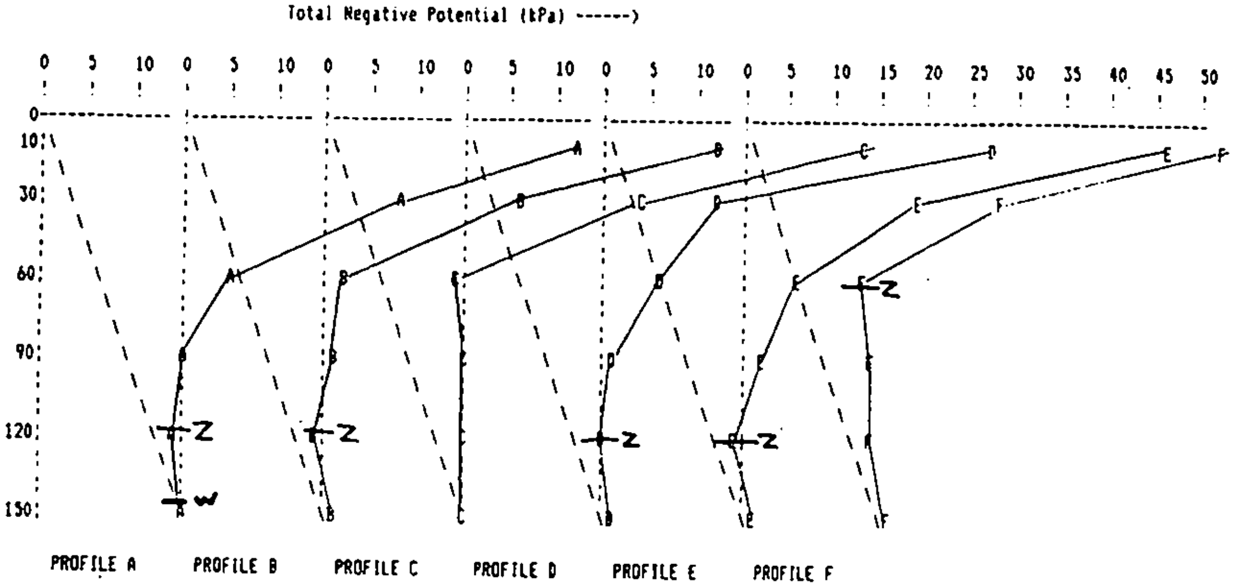
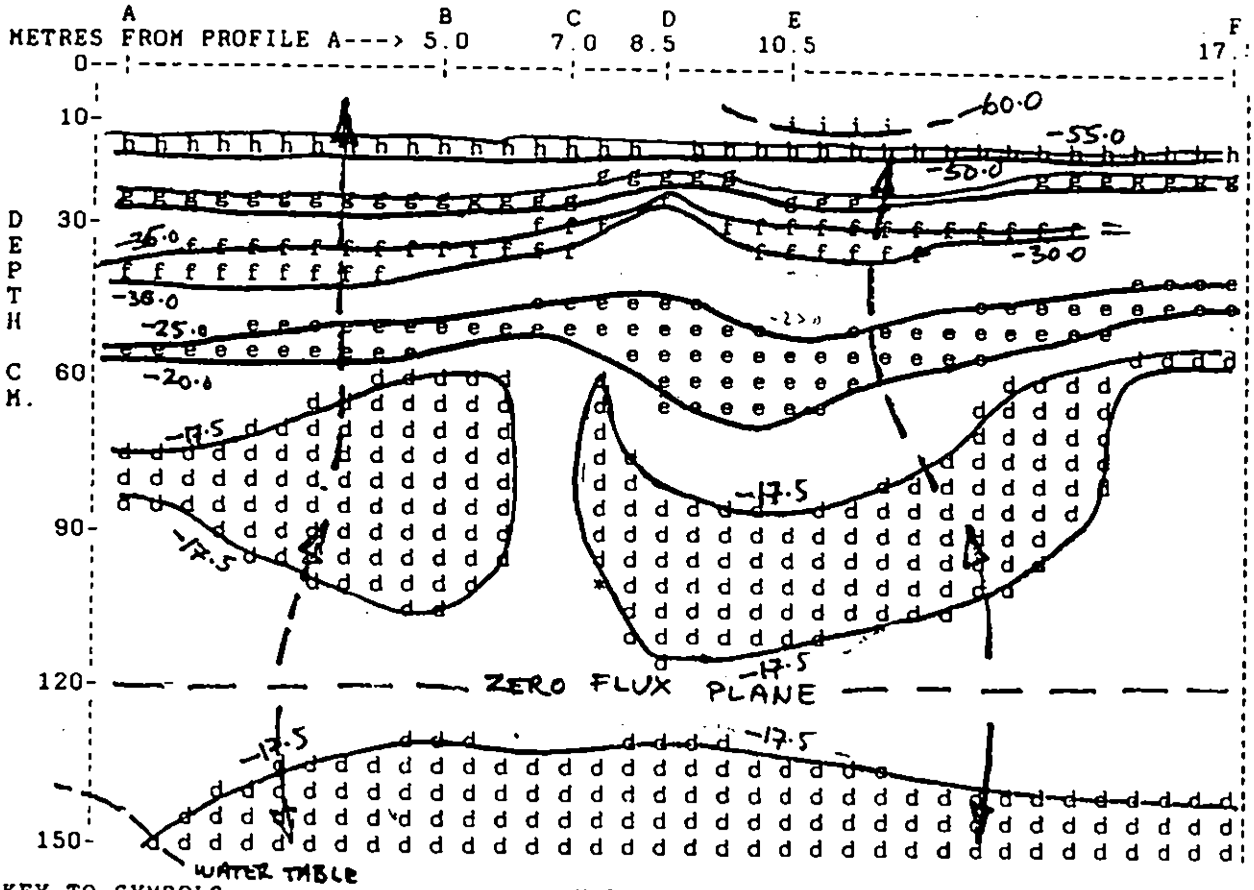


FIGURE 12. Potential profiles for 13/05/91 showing zero flux plane at 120 cm. and steep upward potential gradients in upper 60 cm. of the profile at all points.

—Z = zero flux plane

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:-

UNITS: KILOPASCALS (kPa)

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a = 0.0 TO -2.5
b = -5.0 to -7.5
c = -10.0 to -12.5

d = -15.0 to -17.5
e = -20.0 to -25.0
f = -30.0 to -35.0
g = -40.0 to -45.0

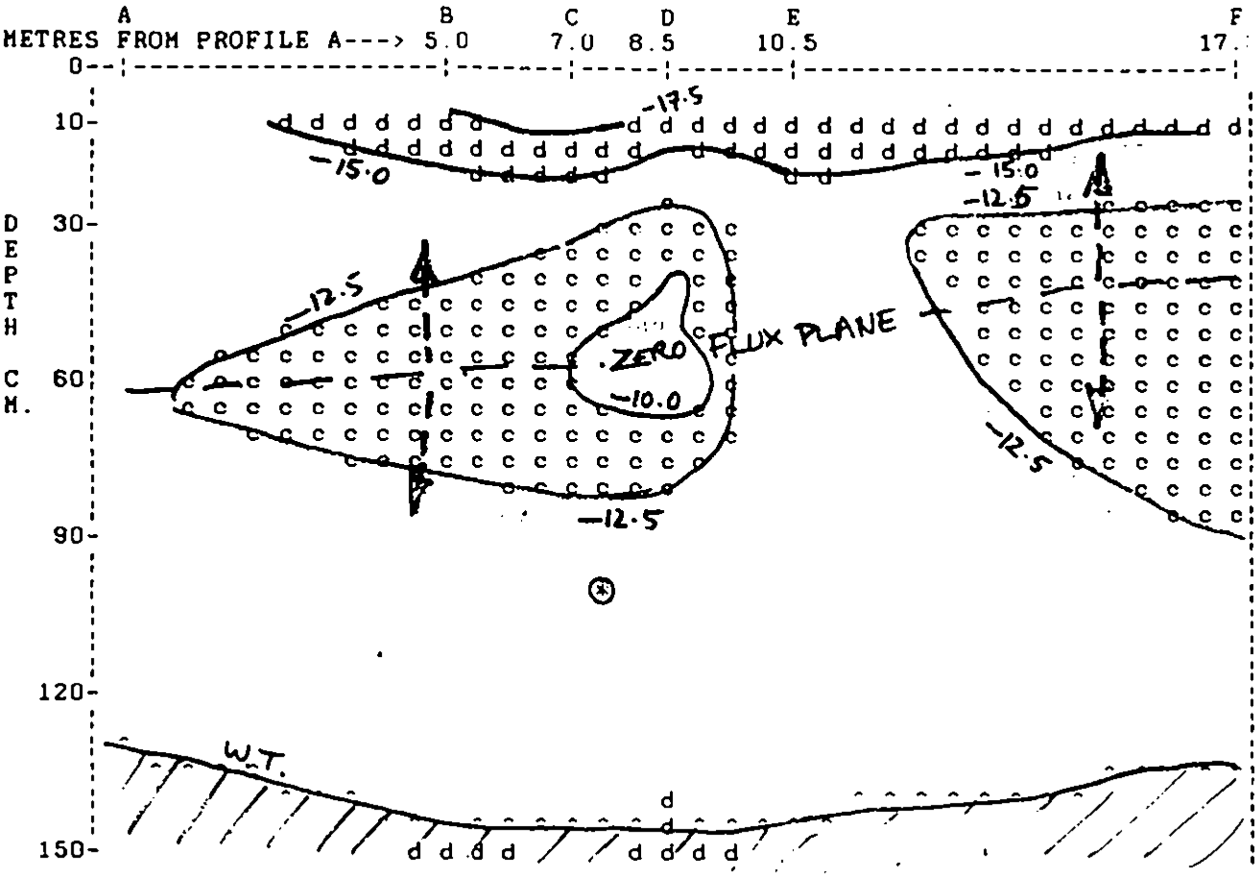
h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
~ = <-75.0

^ = WATER TABLE   V = WETTING FRONT (TOTAL POTENTIAL DIAGRAMS ONLY)

* = POSITION OF FIELD DRAIN   — — ▶ = Flux

FIGURE 13. The 2-dimensional diagram for 13/05/91, showing well developed zero flux plane at and the final disappearance of the water table below the measured, 150 cm. profile.

VERTICAL SECTION OF SOIL WATER POTENTIALS THROUGH TENSIOMETER PROFILES A TO F



KEY TO SYMBOLS:-

UNITS: KILOPASCALS (kPa)

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f = -30.0 to -35.0
g = -40.0 to -45.0
h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
˜ = <-75.0

^ = WATER TABLE V = WETTING FRONT (TOTAL POTENTIAL DIAGRAMS ONLY)

⊛ = POSITION OF FIELD DRAIN — — → = Flux ▨ = SATURATION

FIGURE 14. The 2-dimensional diagram for 07/05/91, showing the water table now below drain level, but still retaining its "gull" shape.

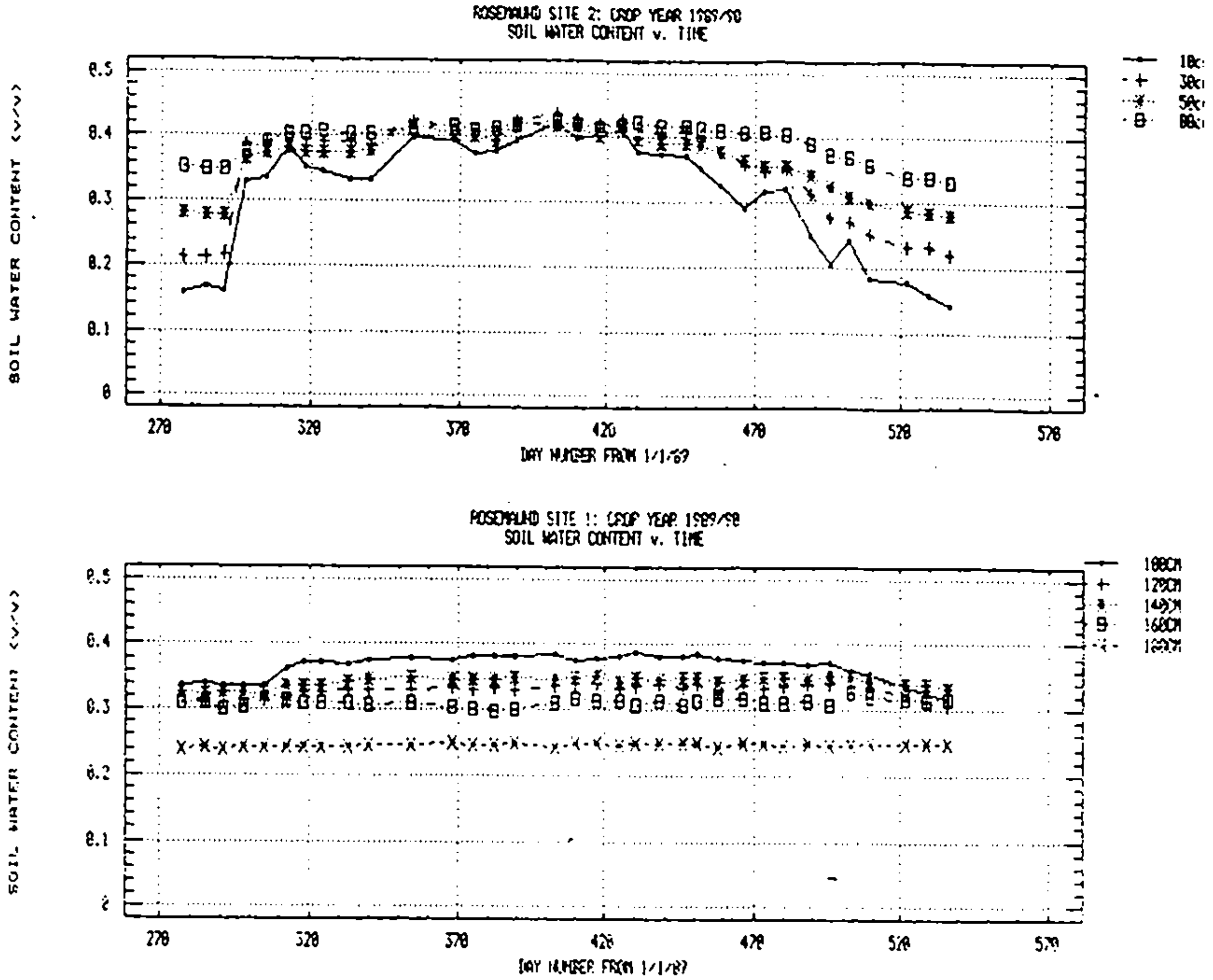


FIGURE 15. Soil water content variation, 1989/90, for the soil layer (0 to 80 cm.) and the geological parent material beneath (100 to 180 cm.)

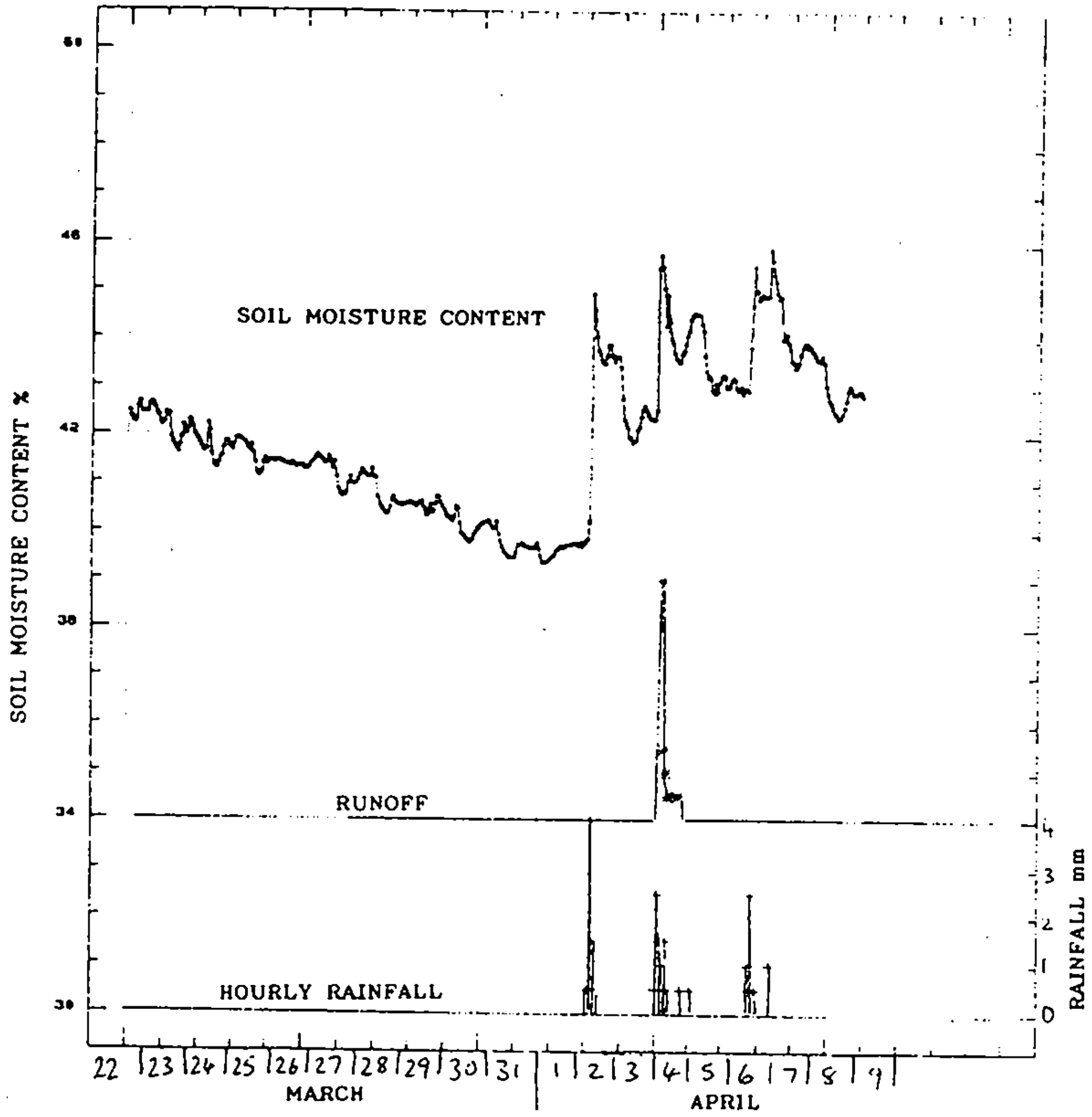
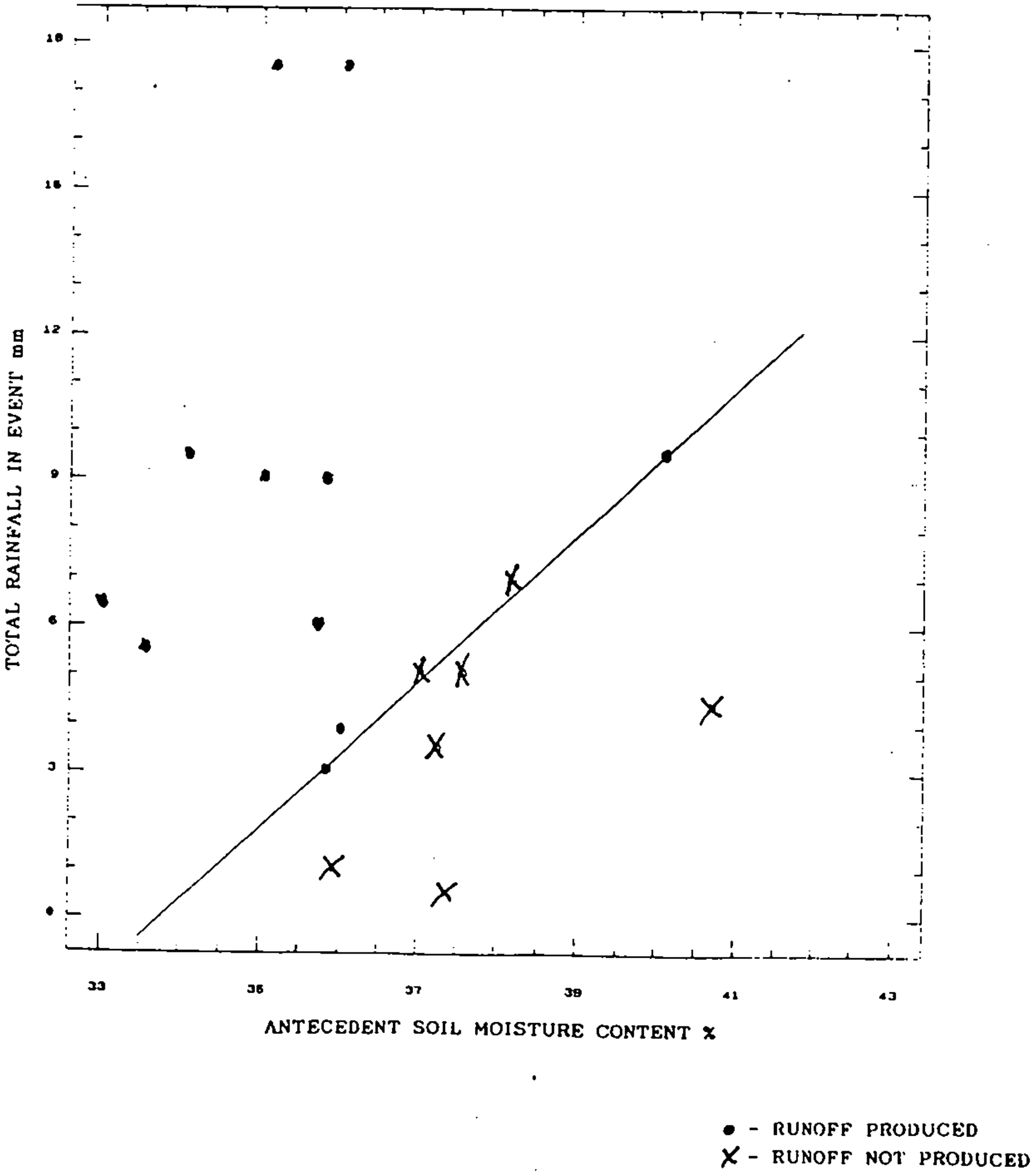


FIGURE 16. Time series plot of hourly rainfall, surface runoff and soil water content at depth 5 cm., 22nd. March -9th. May, 1991. Three rainfall events are shown, labelled 1, 2 and 3.

FIGURE 17. The 18 identified rainfall events plotted as total per event against antecedent soil water content at depth 5 cm. Events producing runoff and events not producing runoff are separated by a linear boundary condition, shown by the line.



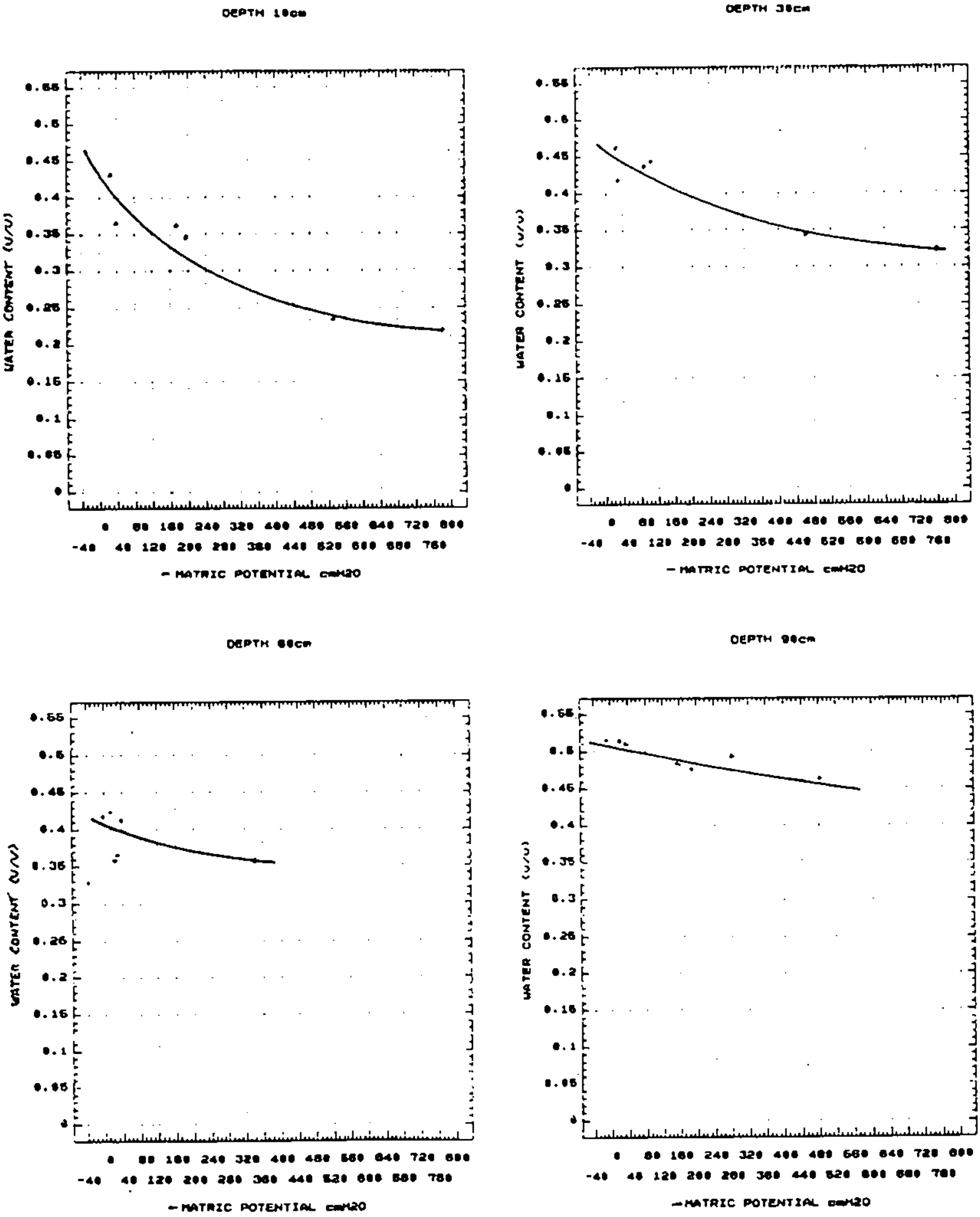


FIGURE 18. Water release characteristics at four depths derived from in-situ matric potential and soil water content measurements in Longlands over crop year 1990/91.

APPENDIX X

Soil Water Samples, Spring 1990 - Mecoprop (2) and dichlorprop (3)

Sample number	Soil[1] type	Sample depth	Volume (ml) and Concentration (ppb)								
			20 3 90			18 4 90			22 5 90		
			vol.	conc. (2)	(3)	vol.	conc. (2)	(3)	vol.	conc. (2)	(3)
1	shallow	50	100			410	nd	nd	0		
4	shallow	50	0			290	0.42	0.72	0		
19	shallow	50	*400			0			0		
22	shallow	50	0			0			0		
7	normal	50	420	0.27	nd	-			0		
10	normal	50	0			0			0		
13	normal	50	0			-			0		
16	normal	50	0			0			0		
	mean			0.27	0		0.21	0.36			
2	shallow	100	*930			900	nd	nd	0		
5	shallow	100	940	0.13	0.22	-			0		
20	shallow	100	400	nd	0.26	-			90	0.74	0.37
23	shallow	100	*610			490	nd	nd	0		
8	normal	100	*920			850	0.10	0.14	trace}		
11	normal	100	960	nd	0.72	-			400	} nd	nd
14	normal	100	*820			600	nd	1.10	0		
17	normal	100	900	nd	nd	-			0		
	mean			0.03	0.3		0.02	0.31		0.37	0.19
3	shallow	150	1000	0.12	0.25	-			610		
6	shallow	150	*1000			795	nd	nd	0		
21	shallow	150	*1000			1000	0.24	nd	620	nd	0.50
24	shallow	150	1000	0.22	0.17	-			510	int	int
9	normal	150	-			-			-		
12	normal	150	*1000			980	nd	nd	25		
15	normal	150	1000			-			550	nd	0.25
18	normal	150	*1000			-			470	nd	1.10
	mean			0.17	0.21		0.08	0.00		0.00	0.62

---

[1] indicates with 'normal' phase Bromyard or 'shallow' phase Bromyard

nd indicates that no pesticide concentration was detected

int - analytical interference

* - samples for isoproturon taken from 9 sites

APPENDIX XI

MANUAL WATER SAMPLES

Table W1. Winter 1989/90 Isoproturon/lindane experiment

Date	Time	Stream*	(Site 1)		Ditch*	(Site 2)		Drain	(Site 3)		Left drain*		(Site 4)	Middle drain*		(Site 6)	Right drain*		(Site 5)
		Flow rate (l/s)	IPU conc. (µg/l)	lindane conc. (µg/l)	Flow rate (l/s)	IPU conc. (µg/l)	lindane conc. (µg/l)	Flow rate (l/s)	IPU conc. (µg/l)	lindane conc. (µg/l)	Flow rate (l/s)	IPU conc. (µg/l)	lindane conc. (µg/l)	Flow rate (l/s)	IPU conc. (µg/l)	lindane conc. (µg/l)	Flow rate (l/s)	IPU conc. (µ/g)	lindane conc. (µg/l)
3.11.89	15.00 -16.00	0.27	0.2	0.003	-	0.6	0.020	slight	0.9	0.010	zero	-	0.012	zero	-	-	slight	0.2	-
8.11.89	09.40	-	-	-	-	-	-	AUTOSAMPLER			-	-	-	-	-	-	-	-	-
9.11.89	09.30 -12.30	0.80	0.4	0.113	-	-	0.031	0.07	1.5	0.173	0.002	-	0.333	zero	-	0.301	0.017	0.3	0.019
10.11.89	00.10	-	-	-	-	-	-	AUTOSAMPLER			-	-	-	-	-	-	-	-	-
27.11.89	16.30	0.27	0.2	-	-	-	-	zero	-	-	zero	-	-	zero	-	-	zero	-	-
13.12.89	14.00	AUTOSAMPLER			-	-	-	AUTOSAMPLER			-	-	-	-	-	-	-	-	-
18.12.89	15.30	17.87	3.0	0.070	-	-	0.043	4.5	3.2	0.390	7.0	1.9	0.278	3.5	-	-	3 approx	0.5	0.211
24.01.90	14.45	>4.0	-	0.001	-	-	0.027	1.3	-	0.037	2.1	-	0.028	-	-	0.038	0.38	-	-
16.02.90	12.00 -13.00	>3.3	-	0.002	-	-	0.005	0.67	-	0.002	2.0	-	0.004	-	-	0.003	0.17	-	0.003
06.03.90	16.00	>2.0	-	0.002	-	-	0.006	0.25	-	0.002	0.33	-	0.002	-	-	0.004	0.07	-	0.002
19.03.90	15.00	AUTOSAMPLER			-	-	-	AUTOSAMPLER			-	-	-	-	-	-	-	-	-
20.03.90				-			0.001			0.006			0.001			nd			-

AUTOMATIC WATER SAMPLES

Table W2. Winter 1989/90: Isoproturon/lindane experiment
Field drain at grid ref: SO 5672 4842 (Site 3)

Date	Time	Rainfall (mm)	Drain flowrate (1/sec)	Isoproturon concentration in drain water (µg/l)	Lindane concentration in drain water (µg/l)
	21.40	0	0		
	22.40	0	0		
	23.40	0	0		
8.11.89	00.40	0	0		
	01.40	0.5	0		
	02.40	0.5	0		
	03.40	0.5	0		
	04.40	2.5	0		
	05.40	4.5	0		
	06.40	3.5	0.017		
	07.40	3.5	0.337		
	08.40	2.0	0.614		
	09.40	2.5	1.264	Sampler triggered	
	10.40	3.5	1.055	-	-
	11.40	2.5	1.669	-	4.46
	12.40	2.5	2.084	-	-
	13.40	0	2.328	-	0.33
	14.40	0	2.292	-	-
	15.40	0	1.835	-	0.16
	16.40	0	1.361	8.4	-
	17.40	0	0.968	-	-
	18.40	0	0.768	2.5	-
	19.40	0	0.608	-	0.18
	20.40	0	0.470	2.4	-
	21.40	0	0.352	-	0.23
	22.40	0	0.288	1.8	-
	23.40	0	0.237	-	0.094
9.11.89	00.40	0	0.198	1.6	-
	01.40	0	0.176	-	0.12
	02.40	0	0.155	1.8	-
	03.40	0	0.136	-	0.17
	04.40	0	0.120	1.5	-
	05.40	0	0.109	-	0.041
	06.40	0	0.098	1.5	-
	07.40	0	0.088	-	1.31
	08.40	0	0.080	1.2	-

Total = 28.5 mm

AUTOMATIC WATER SAMPLES

Table W3. Winter 1989/90: Isoproturon/lindane experiment
Field drain at grid ref: SO 5672 4842 (Site 3)

Date	Time	Rainfall (mm)	Drain flowrate (l/sec)	Isoproturon concentration in drain water (µg/l)	Lindane concentration in drain water (µg/l)
9.11.89	15.10	0	0.039		
	16.10	0	0.036		
	17.10	1.0	0.034		
	18.10	3.0	0.031		
	19.10	3.5	0.035		
	20.10	0	0.478		
	21.10	0.5	0.365		
	22.10	1.0	0.385		
	23.10	1.5	0.349		
10.11.89	00.10	0	0.657	Sampler triggered	
	01.10	0	0.677	-	4.14
	02.10	0	0.626	13.7	-
	03.10	0	0.548	-	0.59
	04.10	0	0.494	9.7	-
	05.10	0.5	0.443	-	1.16
	06.10	0	0.394	8.9	-
	07.10	0	0.344	-	0.1
	08.10	0	0.298	2.2	-
	09.10	0	0.257	-	0.16
	10.10	0	0.225	2.6	-
	11.10	0	0.195	-	0.12
	12.10	0	0.180	2.3	-
	13.10	0	0.168	-	0.10
	14.10	0	0.157	2.3	-
	15.10	0	0.146	-	0.06
	16.10	0	0.135	2.5	-
	17.10	0.5	0.122	-	0.12
	18.10	0	0.181	2.2	-
	19.10	0	0.187	-	0.13
	20.10	0	0.18	1.9	-
	21.10	0	0.172	-	0.16
	22.00	0	0.164	1.8	-
					0.15

Total = 11.5 mm

AUTOMATIC WATER SAMPLES

Table W4. Winter 1989/90: Isoproturon/lindane experiment
Field drain at grid ref: SO 5672 4842 (Site 3) and Stream at SO 5665 4841 (Site 1)

Date	Time	Rainfall (mm)	Drain flowrate (l/sec)	Isoproturon concentration in drain water (µg/l)	Lindane concentration in drain water (µg/l)	Stream flowrate (l/sec)	Isoproturon concentration in stream water	Lindane concentration in stream water (µg/l)
13.12.89	04.00	0	0			1.4		
	05.00	2.0	0			1.4		
	06.00	3.5	0			1.9		
	07.00	3.0	0			2.8		
	08.00	2.0	0			3.5		
	09.00	4.0	0			3.5		
	10.00	2.0	0.031			4.8		
	11.00	1.5	0.159			6.8		
	12.00	4.0	0.357			7.4		
	13.00	1.0	0.481			8.0		
	14.00	0	1.618	Sampler triggered		10.8	Sampler triggered	Sampler triggered
	15.00	1.0	1.387	-	0.45	11.6	-	-
	16.00	0	1.130	8.8	-	9.4	-	-
	17.00	2.0	3.007	-	0.22	7.4	-	0.27
	18.00	1.5	2.683	4.3	-	7.4	5.0	-
	19.00	0.5	1.879	-	0.16	7.4	-	0.24
	20.00	0.5	1.401	3.6	-	8.0	5.4	-
	21.00	1.0	1.274	-	0.07	8.0	-	-
	22.00	1.5	1.335	1.6	-	8.0	3.5	-
	23.00	0	1.648	-	0.016	8.7	-	0.06
14.12.89	00.00	0	1.722	3.3	-	9.4	2.9	-
	01.00	0	1.705	-	-	9.4	-	0.10
	02.00	0	1.740	2.5	-	8.7	4.9	-
	03.00	0	1.926	-	0.09	8.7	-	0.09
	04.00	2.0	1.917	2.1	-	8.7	3.6	-
	05.00	3.0	1.769	-	0.19	8.7	-	0.08

Table W4 continued. Winter 1989/90: Isoproturon/lindane experiment
Field drain at grid ref: SO 5672 4842 (Site 3) and Stream at SO 5665 4841 (Site 1)

Date	Time	Rainfall (mm)	Drain flowrate (l/sec)	Isoproturon concentration in drain water (µg/l)	Lindane concentration in drain water (µg/l)	Stream flowrate (l/sec)	Isoproturon concentration in stream water	Lindane concentration in stream water (µg/l)
14.12.89	06.00	6.0	1.629	2.00	-	10.8	4.5	-
	07.00	2.0	1.484	-	0.05	17.9	-	0.09
	08.00	2.0	1.44	1.2	-	35.6	2.9	-
	09.00	1.0	2.493	-	-	35.6	-	0.04
	10.00	0	8.520	1.1	-	34.1	2.1	-
	11.00	2.0	10.893	-	0.04	32.6	-	0.05
	12.00	1.0	9.268	5.2	-	31.2	3.2	-
	13.00	1.5	9.223	-	0.23	28.4	-	0.29
	14.00	0.5	7.789	-	-	28.4	-	-
	15.00	0	6.949	-	-	29.8	-	-
	16.00	0	8.295	-	-	28.4	-	-
	17.00	0.5	8.382	-	-	25.8	-	-

Total rainfall = 52.5 mm

AUTOMATIC WATER SAMPLES

Table W5. Winter 1989/90 Isoproturon/lindane Experiment
Field drain at grid ref: SO 5672 4842 (Site 3) and
Stream at grid ref: SO 5665 4841 (Site 1)

Date	Time	Rainfall (mm)	Drain flowrate (l/sec)	Lindane concentration in drain water (µg/l)	Stream flowrate -estimated* (l/sec)	Lindane concentration in stream water (µg/l)
19.3.90	12.00	0	0.036		0.7	
	13.00	2.0	0.036		0.7	
	14.00	3.5	0.036		1.3	
	15.00	2.0	0.036		2.0	Sampler triggered
	16.00	1.0	0.036		1.9	0.009
	17.00	0.5	0.040	0.027	1.5	-
	18.00	0	0.185	-	1.1	0.021
	19.00	0	0.530	0.008	0.9	-
	20.00	0	0.394	-	0.9	0.007
	21.00	0	0.239	0.002	0.9	-
	22.00	0	0.243	-	1.0	0.010
	23.00	0	0.131	0.010	0.8	-
20.3.90	00.00	0	0.097	-	0.7	0.008
	01.00	0	0.076	0.019	0.7	-
	02.00	0	0.062	-	0.7	0.008
	03.00	0	0.059	0.001	0.7	-
	04.00	0	0.057	-	0.7	0.008
	05.00	0	0.056	0.004	0.7	-
	06.00	0	0.054	-	0.7	0.005
	07.00	0	0.053	0.003	0.7	-
	08.00	0	0.053	-	0.7	0.004
	09.00	0	0.053	0.003	0.7	-
	10.00	0	0.054	-	0.7	0.030
	11.00	0	0.054	0.003	0.7	-
	12.00	0	0.054	-	1.2	0.011
	13.00	0	0.055	0.004	1.0	-
	14.00	0	0.054	-	0.7	0.005
	15.00	0	0.054	0.005	0.8	-

Total rainfall = 9.0 mm

+ Note: concentrations of mecoprop and dichlorprop (sprayed on 20.3.90) were all below 0.2 µg/l in stream and drain water during this rainfall event.

* Estimated stream flow data derived from the flow gauge at SO 5582 4789 - shifted back 1 hour and divided by 10. The flow gauge at SO 5665 4841 had been damaged by flooding

MANUAL WATER SAMPLES

Table W6. Autumn 1990. Isoproturon/dimethoate experiment
Isoproturon concentrations

		Site Number											
		1		2		3		4		5		6	
Date	Time	Flow rate (1/s)	Concentration (µg/1)	Flow rate (1/s)	Concentration (µg/1)	Flow rate (1/s)	Concentration (µg/1)	Flow rate (1/s)	Concentration (µg/1)	Flow rate (1/s)	Concentration (µg/1)	Flow rate (1/s)	Concentration (µg/1)
31.10.90	14.30	0.30	0.04	-	0.03	d	0.03	nil	-	nil	-	nil	-
16.11.90	09.15	0.17	0.22	-	-	d	nd	nil	-	nil	-	nil	-
29.11.90	-	0.15	1.50	-	0.43	d	26.20	nil	-	nil	-	nil	-
14.12.90	11.15	0.14	0.57	-	0.08	d	7.65	nil	-	nil	-	nil	-
03.01.91	14.30	0.60	0.95	-	0.26	0.005	8.77	nil	-	nil	-	nil	-
09.01.91	12.00	3.33	-	-	0.83	1.43	-	nil	15.70	0.005	6.40	nil	-
15.01.91	10.45	1.67	0.46	-	0.13	0.033	1.72	2.0	0.78	0.25	4.57	1.25	2.05
								d	-	0.030	1.20	0.083	0.22

Note: nd = < 0.01 µg/1
d = dripping

MANUAL WATER SAMPLES

Table W7. Autumn 1990 Isoproturon/dimethoate experiment
Dimethoate concentrations

		Site Number											
		1		2		3		4		5		6	
Date	Time	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)
31.10.90	14.30	0.30	nd	-	nd	d	nd	nil	-	nil	-	nil	-
16.11.90	09.15	0.17	nd	-	nd	d	nd	nil	-	nil	-	nil	-
29.11.90	-	0.15	0.02	-	nd	d	-	nil	-	nil	-	nil	-
14.12.90	11.15	0.14	-	-	0.05	d	2.85 nil	nil	-	nil	-	nil	-
03.01.91	14.30	0.60	0.10	-	0.30	0.005	1.60	nil	1.25	0.005	1.10	nil	-
09.01.91	12.00	3.33	-	-	0.05	1.43	-	2.00	0.08	0.25	0.15	1.25	0.06
15.01.91	10.45	1.67	nd	-	nd	0.033	0.45	d	-	0.030	0.03	0.083	0.02

Note: nd = <0.01-0.05 µg/l
d = dripping

Table W8. Autumn 1990. Isoproturon/dimethoate experiment Site 1 (stream)

Date	Time	Rainfall (mm)	Flow rate (l/sec)	Isoproturon concentration (µg/l)	Dimethoate concentration (µg/l).
25.12.90	03.00	0	0.34	-	-
	04.00	1.0	0.34	-	-
	05.00	1.0	0.34	-	-
	06.00	2.5	0.34	-	-
	07.00	2.5	0.68	-	-
	08.00	5.0	0.68	-	-
	09.00	5.5	1.70	-	0.12
	10.00	0	* 3.40	17.20	-
	11.00	0	2.38	-	3.05
	12.00	0	1.70	10.30	-
	13.00	0	1.19	-	2.37
	14.00	0	1.19	13.60	-
	15.00	0	1.19	-	1.47
	16.00	0	1.19	16.80	-
	17.00	0	0.68	-	1.18
	18.00	0	0.68	11.60	-
	19.00	0	0.68	-	0.81
	20.00	0	0.68	7.90	-
	21.00	0	0.68	-	0.15
	22.00	0	0.68	3.95	-
	23.00	0	0.68	-	0.52
26.12.90	00.00	0	0.68	3.16	-
	01.00	0	0.68	-	0.38
	02.00	0	0.68	2.77	-
	03.00	0	0.68	-	0.33
	04.00	0	0.68	2.37	-
	05.00	0	0.68	-	0.28
	06.00	0.5	0.68	1.92	-
	07.00	1.0	0.68	-	0.28
	08.00	0	0.68	1.92	-
	09.00	0	0.68	-	-

Note 1: * = Point at which conductivity of stream water dropped from the background level (approximately 600 u S) to lower level (approximately 450 u S)

Note 2: The autosampler at Site 3 malfunctioned. Samples taken at 09.00 and 14.00 on 25.12.90 contained 9.95 and 4.95 µg/l isoproturon respectively

AUTOMATIC WATER SAMPLES

Table W9. Spring 1991. Isoproturon/dimethoate experiment
Site 1 (stream)

Date	Time	Rainfall (mm)	Flow rate (l/sec)	Isoproturon concentration (µg/l)	Dimethoate concentration (µg/l)
8.1.91	00.00	0	-	-	-
	01.00	1.0	1.70	-	-
	02.00	0	1.19	-	-
	03.00	2.0	1.19	-	-
	04.00	0	0.17	-	-
	05.00	0	0.17	-	-
	06.00	0	0.17	-	-
	07.00	0	2.38	-	-
	08.00	0	2.38	-	-
	09.00	0	1.70	-	-
	10.00	0.5	1.70	-	-
	11.00	1.5	1.70	-	-
	12.00	4.5	2.38	-	-
	13.00	3.0	3.40	-	-
	14.00	2.5	5.61	-	0.16
	15.00	2.0	* 8.50	2.62	-
	16.00	1.0	10.21	-	-
	17.00	0	12.08	1.46	-
	18.00	0	10.21	-	0.04
	19.00	0	8.50	-	-
	20.00	0	6.80	-	0.02
	21.00	0	6.80	1.12	-
	22.00	0	5.61	-	nd
	23.00	0	4.42	0.56	-
09.01.91	00.00	0	4.42	-	0.01
	01.00	0	4.42	0.06	-
	02.00	0	3.40	-	nd
	03.00	0	3.40	0.13	-
	04.00	0	3.40	-	nd
	05.00	0	3.40	0.42	-
	06.00	0	3.40	-	nd
	07.00	0	2.38	0.10	-
	08.00	0	3.40	-	nd
	09.00	1.0	2.38	0.32	-
	10.00	2.5	2.38	-	0.03
	11.00	0	4.42	0.60	0.03
	12.00	0	6.80	-	-
	13.00	0	5.61	0.75	0.22

Note: * = point at which conductivity dropped from its background value of approximately 530 u S to <400 u S

AUTOMATIC WATER SAMPLES

Table W10. Spring 1991. Isoproturon/dimethoate experiment
Site 3 (drain)

Date	Time	Rainfall (m)	Flow rate* (l/sec)	Isoproturon + concentration	Dimethoate + concentration
08.01.91	09.00	0	-	-	-
	10.00	0.5	-	-	-
	11.00	1.5	-	-	-
	12.00	4.5	approx 1.4	-	-
	13.00	3.0	-	12.10	-
	14.00	2.5	-	-	-
	15.00	2.0	-	-	0.58
	16.00	1.0	-	3.82	-
	17.00	0	-	-	0.10
	18.00	0	-	2.80	-
	NO SAMPLES TAKEN OVERNIGHT				
9.1.91	09.00	1.0	-	-	-
	10.00	2.5	-	1.83	-
	11.00	0	-	4.36	0.30
	12.00	0	-	2.15	0.16
	13.00	0	-	0.71	0.13
	14.00	0	-	0.56	0.05

* No flow rate data were recorded automatically. The flow rate at 12.00 on 08.01.91 was measured manually.

" + The autosampler failed to trigger,and samples were taken after it was triggered" manually.

AUTOMATIC WATER SAMPLES

Table W11. Spring 1991. Isoproturon/dimethoate experiment
Site 1 (stream)

Date	Time	Rainfall (mm)	Flow rate* (l/sec)	Isoproturon concentration (µg/l)
21.2.91	06.00	0	1.4	-
	07.00	0.5	1.4	-
	08.00	0.5	1.5	-
	09.00	1.0	1.5	-
	10.00	0.5	1.7	-
	11.00	1.0	1.8	-
	12.00	1.0	1.9	-
	13.00	1.0	2.4	-
	14.00	0.5	2.8	-
	15.00	3.0	3.1	-
	16.00	1.5	4.8	-
	17.00	0.5	6.8	-
	18.00	0	8.2	2.07
	19.00	0	9.1	-
	20.00	0	8.7	-
	21.00	0.5	8.2	1.52
	22.00	0	7.4	1.16
	23.00	0	6.7	1.25
22.2.91	00.00	0	6.2	0.70
	01.00	0	5.9	0.72
	02.00	0	5.5	0.43
	03.00	0	4.9	0.86
	04.00	0	4.8	0.79
	05.00	0	4.4	0.63
	06.00	0	4.2	0.26
	07.00	0	4.1	0.49
	08.00	0	3.9	0.47
	09.00	0	3.9	0.65
	10.00	0	3.7	0.44
	11.00	0	3.6	0.38
	12.00	0	3.5	-
	13.00	0	3.4	-
	14.00	0.5	3.3	-
	15.00	0	3.3	-
	16.00	1.0	3.3	-

* Calculated values based on 0.1 of the flow rate at the main gauging site.

SOIL WATER SAMPLES

Table W12. Winter 1990. Isoproturon/dimethoate experiment in Foxbridge and Longlands
Soil water taken by suction samplers

a) Isoproturon (µg/l) - sprayed 23.11.90

		Date			
Depth (cm)	Site No.	12.12.90	4.1.91	15.1.91	21.2.91
50	1	1.03	-	-	0.89
50	4	-	0.83	-	-
50	7	0.06	0.20	0.18	0.09
50	10	-	-	-	-
50	13	-	12.45	-	-
50	16	-	-	-	-
50	19	-	1.00	1.19	-
50	22	-	-	-	-
50	25	-	0.39	1.27	-
100	2	-	-	0.03	0.01
100	5	-	0.03	-	-
100	8	-	6.00	18.20	2.93
100	11	-	-	0.57	-
100	14	-	-	-	-
100	17	-	-	-	0.01
100	20	-	0.07	0.11	-
100	23	-	-	-	0.04
100	26	-	nd	-	-
150	3	-	-	0.36	0.08
150	6	-	-	9.43	-
150	9	-	-	10.60	5.14
150	12	-	-	-	-
150	15	-	-	1.55	1.37
150	18	-	-	-	0.03
150	21	-	-	-	-
150	24	-	-	-	0.05
150	27	-	-	-	-

Note: nd = <0.01 µgl/1

SOIL WATER SAMPLES

Table W13. Winter 1990. Isoproturon/dimethoate experiment Soil water taken by suction samplers in Foxbridge and Longlands;

b) Dimethoate (µg/l) - sprayed 28.11.90

Depth (cm)	Site No.	Date 12.12.90	04.01.91	15.01.91	21.02.91
50	1	-	nd	-	-
50	4	nd	-	0.05	nd
50	7	-	-	-	-
50	10	-	-	0.12	nd
50	13	-	-	-	-
50	16	-	nd	-	-
50	19	-	-	-	nd
50	22	-	0.25	-	-
50	25	nd	-	-	nd
100	2	-	0.15	-	-
100	5	-	-	0.02	nd
100	8	-	-	-	-
100	11	-	0.25	-	nd
100	14	-	-	-	-
100	17	-	-	-	-
100	20	-	-	-	nd
100	23	-	-	-	-
100	26	-	-	0.05	nd
150	3	-	-	-	-
150	6	-	-	-	nd
150	9	-	-	-	-
150	12	-	-	0.05	nd
150	15	-	-	-	-
150	18	-	-	0.04	-
150	21	-	-	0.04	nd
150	24	-	-	0.16	-
150	27	-	-	0.16	nd

Note: nd = <0.01 µg l-1

MANUAL WATER SAMPLES

Table W14. Spring 1991. MCPA/oxydemeton-methyl experiment*

		Site number											
		1		2		3		4		5		6	
Date	Time	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)	Flow rate (l/s)	Concentration (µg/l)
07.03.91	16.00	60.11	0.54	-	0.09	5.00	1.38	-	1.43	2.5	0.47	-	-
14.03.91	11.15	3.33	0.40	-	0.02	2.00	0.02	1.00	1.42	0.18	4.75	0.47	-
20.03.91	10.30	10.00	0.03	-	0.02	1.00	0.02	2.5	0.07	0.37	0.05	1.0	0.12

* The concentrations shown above are for MCPA. Considerable difficulties were experienced with oxydemeton analysis and only results for 20.03.91 are available at present. These show that oxydemeton-methyl concentrations were below the detection limit (0.2 µg/l) on that date.

AUTOMATIC WATER SAMPLES

Table W15. Spring 1991. MCPA/oxydemeton-methyl experiment
Sites 1 (stream) and 3 (drain)

Date	Time	Rainfall (mm)	Drain flow rate (l/sec)	DRAIN MCPA concentration (µg/l)	DRAIN Oxydemeton concentration (µg/l)	Stream * flow rate (l/s)	STREAM MCPA concentration (µg/l)	STREAM Oxydemeton concentration (µg/l)
4.3.91	08.00	0	0.01			0.03		
	09.00	1.0	0.01			0.03		
	10.00	2.0	0.01			0.04		
	11.00	1.0	0.01			0.03		
	12.00	1.5	0.01			0.07		
	13.00	0.5	0.02			0.13		
	14.00	0	0.02			0.06		
	15.00	0.5	0.02			0.09		
	16.00	0.5	0.02			0.09		
	17.00	2.0	0.02			0.11		
	18.00	2.0	0.02			0.15		
	19.00	1.0	0.03			0.30		
	20.00	0	0.04			0.46		
	21.00	0	0.05			0.45		
	22.00	0	0.05			0.45		
	23.00	0	0.06			0.49		
5.3.91	00.00	0	0.07			0.42		
	01.00	0	0.08			0.43		
	02.00	0	0.15			0.36		
	03.00	0	0.27			0.30		
	04.00	0	0.42			0.28		
	05.00	0	0.62	-	-	0.30	-	0.76
	06.00	0.5	0.88	-	-	0.30	12.44	-
	07.00	0	1.19	-	-	0.29	-	0.52

Table W15 continued. Spring 1991. MCPA/oxydemeton-methyl experiment
Sites 1 (stream) and 3 (drain)

Date	Time	Rainfall (mm)	Drain flow rate (l/sec)	DRAIN MCPA concentration (µg/l)	Oxydemeton concentration (µg/l)	Stream * flow rate (l/s)	STREAM MCPA concentration (µg/l)	Oxydemeton concentration (µg/l)
5.3.91	08.00	0	1.22	18.80	-	0.29	7.76	-
	09.00	0	1.16	-	-	0.27	-	0.24
	10.00	0.5	1.09	10.80	-	0.59	0.98	-
	11.00	0	1.02	-	-	0.67	-	nd
	12.00	0	0.95	3.72	-	0.73	1.28	-
	13.00	0	0.88	-	-	0.74	-	nd
	14.00	0	0.82	1.69	-	0.76	1.13	-
	15.00	0	0.76	-	-	0.69	-	nd
	16.00	0	0.74	0.90	-	0.66	-	-
	17.00	0	0.72	-	-	0.66	-	nd
	18.00	0	0.68	2.47	-	0.64	0.28	-
	19.00	0	0.65	-	-	0.67	-	0.20
	20.00	0	0.61	2.93	-	0.66	1.13	-
	21.00	0	0.58	-	-	0.67	-	0.19
	22.00	0	0.56	1.17	-	0.67	3.12	-
	23.00	0	0.54	-	-	0.71	-	nd
6.3.91	00.00	0.5	0.53	-	-	0.62	0.69	-
	01.00	1.0	0.52	-	-	0.66	-	nd
	02.00	0	0.50	0.88	-	0.61	0.34	-
	03.00	0	0.49	-	-	0.66	-	-
	04.00	0	0.48	0.38	-	0.62	0.57	-
	05.00	0	0.47			0.67		
	06.00	0	0.46			0.69		
	07.00	0.5	0.45			0.64		
	08.00	0.5	0.45			0.62		

Table W15 (continued). Spring 1991. MCPA/oxydemeton-methyl experiment
Sites 1 (stream) and 3 (drain)

Date	Time	Rainfall (mm)	Drain flow rate (l/sec)	DRAIN		Stream * flow rate (l/s)	STREAM	
				MCPA concentration (µg/l)	Oxydemeton concentration (µg/l)		MCPA concentration (µg/l)	Oxydemeton concentration (µg/l)
6.3.91	09.00	0.5	0.44			0.62		
	10.00	0	0.43			0.62		
	11.00	0	0.42			0.64		
	12.00	0	0.42			0.64		
	13.00	0	0.42			0.67		
	14.00	0	0.41			0.69		
	15.00	0	0.41			0.69		
	16.00	0	0.41			0.73		
	17.00	0	0.41			0.71		
	18.00	0	0.41			0.67		
	19.00	0.5	0.40			0.67		
	20.00	0.5	0.40			0.66		
	21.00	0	0.40			0.62		
	22.00	0	0.40			0.66		
	23.00	0	0.40			0.71		
7.3.91	00.00	0	0.41			0.71		
	01.00	1.5	0.43			0.64		
	02.00	3.0	0.44			0.69		
	03.00	1.5	0.46			0.95		
	04.00	1.5	0.47			1.15		
	05.00	2.5	0.48			1.44		
	06.00	2.5	0.48			1.96		
	07.00	2.0	0.48			4.51		
	08.00	2.0	0.49			4.91		
	09.00	2.5	0.49			5.60		
	10.00	0.5	0.48	-	-	6.40	-	nd

Table W15 (continued). Spring 1991. MCPA/oxydemeton-methyl experiment
Sites 1 (stream) and 3 (drain)

Date	Time	Rainfall (mm)	Drain flow rate (1/sec)	DRAIN MCPA concentration (µg/1)	Oxydemeton concentration (µg/1)	Stream * flow rate (1/s)	STREAM MCPA concentration (µg/1)	Oxydemeton concentration (µg/1)
7.3.91	11.00	0	0.48	6.96	-	6.58	1.23	-
	12.00	0	0.48	-	-	6.07	-	-
	13.00	0	0.48	6.96	-	5.29	1.98	-
	14.00	0	0.47	-	-	4.32	-	-
	15.00	0	0.46	-	-	3.75	0.67	-
	16.00	0	0.46	-	-	3.17	-	-
	17.00	0	0.50	-	-	2.75	0.81	-
	18.00	0	0.66	-	-	2.45	-	-
	19.00	0	1.35	-	-	2.13	0.34	-
	20.00	0	2.36	-	-	1.98	-	-
	21.00	0	3.72	-	-	1.81	1.25	-
	22.00	0	5.50	-	-	1.67	-	-
	23.00	0	7.82	-	-	1.50	0.68	-
8.3.91	00.00	0	10.67	-	-	1.48	-	-
	01.00	0.5	13.72	-	-	1.39	0.87	-
	02.00	0.5	15.49	-	-	1.37	-	-
	03.00	3.0	15.33	-	-	1.37	0.85	-
	04.00	2.0	13.40	-	-	1.46	-	-
	05.00	1.0	11.62	-	-	2.08	1.30	-
	06.00	0	9.99	-	-	2.42	-	-
	07.00	0	8.58	-	-	2.53	1.34	-
	08.00	0	7.33	-	-	2.50	-	-
	09.00	0	6.75	-	-	2.13	2.23	-
	10.00	0	5.67	-	-	2.03	-	-

* The stream flow rate was estimated by multiplying the flowrate at the main gauging site by 0.1. This may underestimate the true flow rate at certain times because the drain flow rate at Site 3 occasionally appears to exceed that at Site 1 downstream.
nd = <0.15 µg 1-1 oxydemeton methyl

AUTOMATIC WATER SAMPLES

Table W16. Spring 1991. MCPA/oxydemeton-methyl experiment
Site 1 (stream)

Date	Time	Rainfall (mm)	Stream * flowrate (l/s)	MCPA concentration (µg/l)	Oxydemeton concentration (µg/l)
16.3.91	08.00	0	1.7		
	09.00	0.5	1.8		
	10.00	0.5	1.7		
	11.00	1.0	1.8		
	12.00	0	2.0		
	13.00	2.5	2.0		
	14.00	1.5	2.0		
	15.00	4.0	3.5		
	16.00	0	5.7	-	nd
	17.00	0	6.0	12.68	-
	18.00	0	5.2	-	nd
	19.00	0	4.9	0.84	-
	20.00	0	4.6	-	nd
	21.00	0	4.4	0.49	-
	22.00	0	4.4	-	-
	23.00	0	4.4	0.95	-
17.3.91	00.00	0.5	4.4	-	-
	01.00	0	4.3	0.52	-
	02.00	0	4.2	-	-
	03.00	0	4.1	0.69	-
	04.00	0	4.1	-	-
	05.00	0.5	4.1	0.37	-
	06.00	0	3.9	-	-
	07.00	0	3.9	0.32	-
	08.00	0	3.9	-	-
	09.00	0	3.9	0.51	-
	10.00	0	3.9	-	-
	11.00	0	3.9	0.27	-
	12.00	0	3.7	-	-
	13.00	0	3.7	0.30	-
	14.00	2.5	3.5	-	-
	15.00	3.5	3.6	0.31	-
	16.00	0	5.3	-	-
	17.00	0	5.7	-	-

* Flow rate estimated by multiplying flowrate at main gauging site by 0.1

nd = <0.15 µg/l oxydemeton-methyl

AUTOMATIC WATER SAMPLES

Table W17. Spring 1991. MCPA/oxydemeton methyl experiment
Site 3 (drain) *

Date	Time	Rainfall (mm)	Drain flow rate (l/s)	MCPA concentration (µg/l)
19.3.91	10.00	0	0.9	
	11.00	0	0.9	46.80
	12.00	0	0.9	-
	13.00	0	0.8	14.70
	14.00	0	0.8	-
	15.00	0	0.8	25.90
	16.00	0	0.7	-
	17.00	0	0.7	6.74
	18.00	0	0.7	-
	19.00	0	0.7	3.66
	20.00	0	0.6	-
	21.00	0	0.6	3.00
	22.00	0	0.6	-
	23.00	0	0.6	8.20
20.3.91	00.00	0	0.5	-
	01.00	0	0.5	5.42
	02.00	0	0.5	-
	03.00	0	0.5	2.32
	04.00	0	0.5	-
	05.00	0	0.5	7.97
	06.00	0	0.5	-
	07.00	0	0.5	-
	08.00	0	0.5	-
	09.00	0.5	0.5	-
	10.00	0.5	0.5	-
	11.00	1.5	0.5	-

* The sampler was triggered manually at 10.00 on 19.3.91.

SOIL WATER SAMPLES

Table W18. Spring 1991. MCPA/oxydemeton-methyl experiment. Foxbridge and Longlands. MCPA concentrations (µg/l). sprayed 28.2.91

Depth (cm)	Site No.	Date 21.3.91	23.4.91	9.5.91
50	1	4.24	-	-
50	4	0.32	-	-
50	7	0.86	nd	nd
50	10	0.40	-	-
50	13	0.25	-	-
50	16	0.40	-	-
50	19	0.40	-	-
50	22	4.58	-	-
50	25	4.58	0.12	-
100	2	0.05	nd	-
100	5	-	-	-
100	8	nd	0.53	0.71
100	11	0.32	0.18	nd
100	14	-	-	-
100	17	0.33	nd	nd
100	20	0.06	nd	nd
100	23	0.46	nd	nd
100	26	1.26	nd	nd
150	3	nd	-	nd
150	6	0.2	0.12	0.04
150	9	2.58	2.02	2.16
150	12	0.27	nd	0.03
150	15	0.25	-	-
150	18	0.33	nd	nd
150	21	nd	nd	nd
150	24	nd	-	-
150	27	0.27	0.01	0.02

Note: nd = <0.01 µg/l MCPA

Table S1

Results of MCPA analysis

Soil levels of MCPA in Foxbridge and Longlands following Spring 1991 application

Data are ppb (µg/kg) on wet weight basis

Date	1.3.91	5.3.91	14.3.91	26.3.91		10.4.91
	66.3	64.4	8.3	6.5		nd
	101.3	83.9	6.8	3.3		nd
	255.2	94.4	4.0	nd		nd
	192.2	74.8	36.9	1.3		nd
	257.6	152.5	13.3	2.2		nd
	200.3	74.5	31.8	1.1		
	124.2	39.2	5.5	3.2		
	273.9	250.5	12.5	nd		
	220.5	6.3	4.4			
Profile:						
0-25 cm	764	378	8.0	3.8	3.8	1.7
25-50 cm	62.2	14.9	4.7	2.3	nd	nd
50-75 cm	67.7	53.2	2.0	2.8	nd	nd
75-100 cm	14.7	53.2	2.0	2.3	nd	nd

nd: not detected (detection limit 1 µg/kg wet weight)

APPENDIX XII

Table A1. WINTER 1990/91 EVENT: 25 December 1990
MAIN GAUGING SITE @ GRID REF; SO5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Atrazine (µg/l)	Simazine (µg/l)	Isoproturon (µg/l)	Dimethoate (µg/l)
251290	415	1	3.84				
251290	515	1	3.84				
251290	615	2.5	3.84				
251290	715	5	5.01				
251290	815	5.5	13.93	0.62	4.12	0.82	<0.02
251290	915		19.43	0.48	4.12		<0.02
251290	1015		52.29	0.33	1.96	0.18	<0.02
251290	1115		41.82	0.23	1.21	0.2	<0.02
251290	1215		23.44	0.24	1.01	0.32	<0.02
251290	1315		17.53	0.31	1.14	0.25	<0.02
251290	1415		12.24	0.34	1.15	0.52	<0.02
251290	1515		12.24	0.43	1.48	0.87	<0.02
251290	1615		9.09	0.37	1.06	1.14	<0.02
251290	1715		9.09				<0.02
251290	1815		7.64	0.44	1.08	0.89	<0.02
251290	1915		7.64	0.55	1.29	0.4	<0.02
251290	2015		7.64	0.54	1.2	1.76	<0.02
251290	2115		6.28	0.63	1.31	0.55	<0.02
251290	2215		5.01	0.66	1.31	0.89	<0.02
251290	2315		6.28	0.55	1.04	1.02	<0.02
261290	15		6.28	0.75	1.32	0.72	<0.02
261290	115		6.28	0.73	1.43	1.23	<0.02
261290	215		6.28	0.81	1.52	0.45	<0.02
261290	315		6.28	0.81	1.43	0.88	<0.02
261290	415		5.01	0.9	1.49	0.05	<0.02
261290	515		6.28	0.83	1.28	0.84	<0.02
261290	615	0.5	5.01	0.92	1.33	0.98	<0.02
261290	715	1	6.28	0.85	1.24	0.79	<0.02

Table A2. WINTER 1990/91 EVENT: 5 January 1991
MAIN GAUGING SITE @ GRID REF; SO5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Atrazine (µg/l)	Simazine (µg/l)	Isoproturon (µg/l)	Dimethoate (µg/l)
5.1.91	345	1	6.28				
	445	2	6.28				
	545	0.5	10.62	0.56	0.85	0.09	<0.02
	645	3.5	23.44	0.58	0.92	0.08	<0.02
	745	0.5	32.18	0.71	1.07	0.08	<0.02
	845	0	27.69	0.69	1.21	0.02	<0.02
	945	0	23.44				<0.02
	1045	1.5	23.44	0.78	1.05	0.08	<0.02
	1145	0	23.44	0.81	0.94	0.06	<0.02
	1245	0	23.44	0.56	1.25	0.11	<0.02
	1345	0.5	23.44	0.3	1.49	0.14	<0.02
	1445		27.69	0.25	0.86	0.05	<0.02
	1545		25.53	0.25	0.78	0.11	<0.02
	1645		23.44	0.29	0.69	0.08	<0.02
	1745		23.44	0.25	0.59	0.05	<0.02
	1845		21.40	0.18	0.59	0.03	<0.02
	1945		23.44	0.18	0.59	0.03	<0.02
	2045		23.44	0.18	0.59	0.04	<0.02
	2145		17.53	0.18	0.46	0.06	<0.02
	2245		21.40	0.31	0.79	2.46	<0.02
	2345		19.43	0.28	0.66	0.18	<0.02
6.1.91	45		23.44	0.48	0.85	0.17	<0.02
	145		17.53	0.42	0.68	5.19	<0.02
	245		15.69	0.52	0.8	0.12	<0.02
	345		15.69	0.59	0.92	0.13	<0.02
	445		17.53	0.65	1.04	0.05	<0.02

Table A3. WINTER 1990/91 EVENT: 8 January 1991
MAIN GAUGING SITE @ GRID REF; SO5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Atrazine (µg/l)	Simazine (µg/l)	Isoproturon (µg/l)	Dimethoate (µg/l)
8.1.91	1015	0.5					
	1115	1.5					
	1215	4.5					
	1315	3		0.24	0.32	0.02	0.02
	1415	2.5		0.16	0.71		0.02
	1515	2		0.08	0.57	0.02	0.02
	1615	1		0.07	0.5	0.02	0.02
	1715			0.07	0.44	0.02	0.02
	1815			0.08	0.46	0.02	0.02
	1915			0.07	0.45	0.02	0.02
	2015			0.09	0.44	0.02	0.02
	2115			0.13	0.49	0.02	0.02
	2215			0.13	0.56	0.22	0.02
	2315			0.15	0.52	0.16	0.02
9.1.91	15			0.15	0.44	0.1	0.02
	115			0.16	0.49	0.11	0.02
	215			0.14	0.43	0.16	0.02
	315			0.23	0.41	1.31	0.02
	415			0.22	0.48	0.19	0.02
	515			0.17	0.38	1.56	0.02
	615	2		0.19	0.43	1.16	0.02
	715			0.19	0.4	0.02	0.02
	815			0.19	0.35	0.02	0.02
	915	1		0.3	0.83	6.72	0.02
	1015	2.5		0.31	0.84	1.54	0.02
	1115			0.15	0.37	0.06	0.02
	1215			0.11	0.54	0.11	0.02

Table A4. WINTER 1990/91 EVENT: 21 February 1991
MAIN GAUGING SITE @ GRID REF; SO5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Atrazine (µg/l)	Simazine (µg/l)	Isoproturon (µg/l)	Dimethoate (µg/l)
21.2.91	800	0.5	12.24				
	900	0.5	13.93				
	1000	1.0	15.69				
	1100	0.5	15.69				
	1200	1.0	17.53				
	1300	1.0	19.43				
	1400	1.0	25.53				
	1500	0.5	27.69				
	1600	3.0	27.69	0.05	0.22	<0.02	<0.02
	1700	1.5	34.51				
	1800	0.5	57.83	0.06	0.09	<0.02	<0.02
	1900	0.0	75.52				
	2000	0.0	88.18				
	2100	0.0	84.96	0.08	0.36	<0.02	<0.02
	2200	0.5	81.77				
	2300		75.52				
22.2.91	0		69.44				
	100		63.54				
	200		57.83				
	300		52.29				
	400		49.60	0.09	0.22	<0.02	<0.02
	500		46.96				
	600		44.36				
	700		41.82				
	800		39.33				
	900		36.89				
	1000		36.89				
	1100		36.89				
	1200		34.51				
	1300	0.5	34.51				
	1400		32.18	0.12	0.26	<0.02	<0.02
	1500		32.18	0.09	0.24	<0.02	<0.02

Table A5. WINTER 1990/91 EVENT: 16 March 1991
MAIN GAUGING SITE @ GRID REF; SO5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Atrazine (µg/l)	Simazine (µg/l)	Isoproturon (µg/l)	Dimethoate (µg/l)	Oxydemeton µg/l
16.3.91	0915	0.5	17.53					
	1015	0.5	17.53					
	1115	1	15.69					
	1215	0	17.53					
	1315	2.5	19.43					
	1415	1.5	17.53					
	1515	4	34.51	0.96	8.7	2.86	<0.02	<10.0
	1615	0	46.96	1.6	15.3	6.66	<0.02	<10.0
	1715	0	57.83	1	9.9	3.78	<0.02	<10.0
	1815	0	52.29	0.67	5.7	5.24	<0.02	<10.0
	1915	0	46.96	0.48	4	1.96	<0.02	<10.0
	2015	0	44.36	0.42	3.4	4.69	<0.02	<10.0
	2115	0	44.36	0.35	2.4	2.95	<0.02	<10.0
	2215	0	41.82	0.35	2.4	5.01	<0.02	<10.0
	2315	0	41.82	0.34	2.2	3.7	<0.02	<10.0
17.3.91	0015	0.5	41.82	0.24	1.3	0.39	<0.02	<10.0
	0115	0	41.82	0.15	1.7	2.37	<0.02	<10.0
	0215	0	41.82	0.21	1.7	4.43	<0.02	<10.0
	0315	0	39.33	0.29	1.5	16.2	<0.02	<10.0
	0415	0	36.89	0.28	1.7	3.01	<0.02	<10.0
	0515	0.5	39.33	0.16	0.65	2.2	<0.02	<10.0
	0615	0	36.89	0.24	1.4	3.3	<0.02	<10.0
	0715	0	36.89	0.28	1.4	2.04	<0.02	<10.0
	0815	0	36.89	0.28	1.4	3.28	<0.02	<10.0
	0915	0	36.89	0.2	1.6	3.64	<0.02	<10.0
	1015	0	36.89	0.3	1.1	3.01	<0.02	<10.0
	1115	0	36.89	0.21	1.1	6.58	<0.02	<10.0
	1215	0	34.51	0.25	1	12.9	<0.02	<10.0
	1315	0	36.89	0.2	0.95	15	<0.02	<10.0
	1415	2.5	34.51	0.18	0.85	6.01	<0.02	<10.0

Table A6. WINTER 1990/91 EVENT: 8 January 1991
LONGLANDS DRAIN SITE @ GRID REF; SO5688 4849

Date	Time	Rain	Flow	Isoproturon (µg/l)	Dimethoate (µg/l)
8.1.91	1030	0.5	0.01		
	1130	1.5	0.01		
	1230	4.5	0.02		
	1330	3	0.14	0.15	0.02
	1430	2.5	0.32	0.11	0.02
	1530	2	0.42	0.12	0.02
	1630	1	0.48	0.11	0.02
	1730		0.39	0.09	0.02
	1830		0.30	0.38	0.02
	1930		0.23	0.06	0.02
	2030		0.18	0.12	0.02
	2130		0.14	0.18	0.02
	2230		0.12	0.21	0.02
	2330		0.10	0.09	0.02

Table A7. WINTER 1990/91 EVENT: 21 February 1991
LONGLANDS DRAIN SITE @ GRID REF; SO5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Isoproturon (µg/l)	Dimethoate (µg/l)
21.2.91	830	0.5	0.10		
	930	0.5	0.10		
	1030	1.0	0.12		
	1130	0.5	0.15		
	1230	1.0	0.18		
	1330	1.0	0.25	0.03	<0.02
	1430	1.0	0.34	0.06	<0.02
	1530	0.5	0.42	0.02	<0.02
	1630	3.0	0.75	0.02	<0.02
	1730	1.5	1.31	0.02	<0.02
	1830	0.5	1.48	1.88	<0.02
	1930	0.0	1.48	1.38	<0.02
	2030	0.0	1.37	0.05	<0.02
	2130	0.0	1.20	2.59	<0.02
	2230	0.5	1.05	2.5	<0.02
	2330		0.87	2.44	<0.02
22.2.91	30		0.75	2.54	<0.02
	130		0.68	1.94	<0.02
	230		0.61	2.52	<0.02
	330		0.54	1.98	<0.02
	430		0.48	1.69	<0.02
	530		0.42	2.7	<0.02
	630		0.42	1.67	<0.02
	730		0.37	1.42	<0.02
	830		0.34	1.33	<0.02

Table A8. WINTER 1990/91 EVENT: 4 March 1991
LONGLANDS DRAIN SITE @ GRID REF; SO5688 4849

Date	Time	Rain (mm)	Flow (l/s)	Isoproturon (µg/l)	Dimethoate (µg/l)	Oxydemeton (µg/l)
4.3.91	1030	1.0				
	1130	2.0				
	1230	1.0				
	1330	1.5				
	1430	0.5				
	1530	0.0				
	1630	0.5				
	1730	0.5				
	1830	2.0				
	1930	2.0				
	2030	1.0		1.41	0.01	<10.0
	2130			2.25	0.01	<10.0
	2230			1.05	0.01	<10.0
	2330			2.1	0.01	<10.0
5.3.91	0030			1.54	0.01	<10.0
	0130			1.6	0.01	<10.0
	0230			1.48	0.01	<10.0
	030			1.73	0.01	<10.0
	0430			1.59	0.01	<10.0
	0530			1.93	0.01	<10.0
	0630			1.44	0.01	<10.0
	0730			0.07	0.01	<10.0
	0830			1.58	0.01	<10.0
	0930			1.65	0.01	<10.0
	1030			1.66	0.01	<10.0
	1130			2	0.01	<10.0
	1230			2.46	0.01	<10.0
	1330				0.01	<10.0
	1430			2.21	0.01	<10.0
	1530			2.06	0.01	<10.0
	1630			1.59	0.01	<10.0
	1730			1.95	0.01	<10.0
	1830			2.18	0.01	<10.0
	1930			2.19	0.01	<10.0

APPENDIX XIII

ROSEMAUND INTERLABORATORY CALIBRATION EXERCISE, 1991

Introduction

Materials

All pesticides used were purchased from Greyhound Pesticides and were of the following purities.

mecoprop	99.8%
dimethoate	99.9%
isoproturon	99.9%
simazine	99.6%

The acetone used (Analar grade) was purchased from BDH.

Method

Water was collected from the stream by an automatic sampler. In all 48 litres were collected in 1 litre amber jars. The water samples were combined in a large plastic tank. Blank samples (2 litres each) were removed from the tank and stored in sealed amber winchesters. Stock solutions of pesticides were made up in water (dimethoate), water/acetone (mecoprop) or acetone (isoproturon and simazine). Subsamples of the river water (4 x 9 litres) were transferred to glass tanks and the appropriate amount of each pesticide stock solution was added. The solutions were stirred with a large metal spatula and 4 x 2 litre subsamples of each solution were transferred to amber winchesters for analysis. Samples were sent out by overnight courier in order to arrive at the participating laboratories on the same day. The participating laboratories were;

Lab A - MAFF, Pesticide Laboratory, Cambridge
Lab B - University of Birmingham
Lab C - NRA, Welsh Region
Lab D - IoH

Results

The results of the analysis of the 4 spiked solutions and the blank solution are shown in tables 1-5. One of the sample bottles (spiked sample 1) was broken on transit to laboratory A. Laboratory D were unable to analyse for mecoprop, but they did detect atrazine in all samples at a level of 2.7-3.1 µg/l. Laboratory B carried out 2 different methods of analysis for simazine, one by HPLC and one by GC-MS. The GC-MS results indicated that the HPLC analysis contained a co-eluted contaminant and so the GC-MS results are used here in the subsequent statistical analysis (the HPLC results are shown in brackets in tables 1-5).

Tables 6-8 show the mean, standard deviation and range of all determinations for dimethoate, isoproturon and simazine. The data used in tables 6-8 are not corrected for the concentrations found in the blank samples. Tables 9-11 show the mean, standard deviation and range of all determinations for dimethoate, isoproturon and simazine. The data used in tables 9-11 have been corrected for the concentrations found in the blank samples to allow comparison with the spiked concentrations.

Tables 12-15 show the measured results, corrected for the blank values, as a percentage of the spiked concentrations for each laboratory.

Discussion

With the exception of the low concentrations of isoproturon and simazine, the measured levels for dimethoate, isoproturon and simazine were within a factor of 2 of the spiked level (see tables 12-15). Problems occurred with the low concentrations of isoproturon and simazine, and in one laboratory's case dimethoate, due to the high levels of these chemicals found in the blank (frequently higher than the spiked level).

With the exception of mecoprop, the agreement between laboratories was generally good, with the range of values obtained for any given sample typically covering a factor of 3 (see tables 6-8). The mecoprop results from laboratory C were anomalously high. Further investigation by this laboratory has identified a systematic error in the derivitisation procedure used for the quantification of mecoprop. An amended method for analysis of mecoprop has been shown to be satisfactory. Unfortunately, it has not been possible to re-analyse the 1991/91 mecoprop samples using the amended method.

Table 1. Analysis of blank sample

Pesticide	Spiked conc. µg/l	Measured concentrations µg/l			
		A	B	C	D
Mecoprop	/	0.1	nd	3.6	/
Dimethoate	/	0.7	0.10*	<0.10	0.12
Isoproturon	/	1.4	0.51	0.70	1.08
Simazine	/	0.8	0.2 (2.66)	1.68	0.91

* - had correct retention time for dimethoate but did not have the correct spectrum

Table 2. Analysis of spiked sample 1

Pesticide	Spiked conc. µg/l	Measured concentrations µg/l			
		A	B	C	D
Mecoprop	5.17	/	4.60	282	/
Dimethoate	2.00	/	2.96	0.75	2.1
Isoproturon	0.21	/	1.30	0.74	1.29
Simazine	1.05	/	0.6 (2.92)	3.68	1.74

Table 3. Analysis of spiked sample 2

Pesticide	Spiked conc. µg/l	Measured concentrations µg/l			
		A	B	C	D
Mecoprop	2.59	3.7	2.50	328	/
Dimethoate	0.501	1.8	0.78	0.28	0.81
Isoproturon	0.529	1.5	2.28	1.02	1.68
Simazine	0.839	1.3	0.4 (2.88)	3.60	1.52

Table 4. Analysis of spiked sample 3

Pesticide	Spiked conc. µg/l	Measured concentrations µg/l A	B	C	D
Mecoprop	1.03	1.5	1.30	47	/
Dimethoate	5.00	5.7	7.04	2.01	5.1
Isoproturon	9.86	8.7	9.14	4.83	10.2
Simazine	2.62	2.7	1.2 (4.32)	7.11	3.1

Table 5. Analysis of spiked sample 4

Pesticide	Spiked conc. µg/l	Measured concentrations µg/l A	B	C	D
Mecoprop	10.3	12.9	8.56	762	/
Dimethoate	1.00	2.7	1.53	0.37	1.04
Isoproturon	2.96	3.5	3.34	2.48	3.6
Simazine	0.210	0.8	0.3 (2.36)	2.43	1.15

Table 6. Mean, standard deviation and range of measurements for dimethoate

Sample	Mean (µg/l)	σ_{n-1}	Range (µg/l)
Blank	0.23	0.32	<0.1 - 0.7
Sample 1	1.94	1.11	0.75 - 2.96
Sample 2	0.92	0.64	0.28 - 1.8
Sample 3	4.96	2.13	2.01 - 7.04
Sample 4	1.41	0.98	0.37 - 2.7

Table 7. Mean, standard deviation and range of measurements for isoproturon

Sample	Mean (µg/l)	σ_{n-1}	Range (µg/l)
Blank	0.92	0.40	0.51 - 1.4
Sample 1	1.11	0.32	0.74 - 1.29
Sample 2	1.62	0.52	1.02 - 2.28
Sample 3	8.22	2.34	4.83 -10.2
Sample 4	3.23	0.51	2.48 - 3.6

Table 8. Mean standard deviation and range of measurements for simazine

Sample	Mean (µg/l)	σ_{n-1}	Range (µg/l)
Blank	0.90	0.61	0.2 - 1.68
Sample 1	2.01	1.56	0.6 - 3.68
Sample 2	1.71	1.35	0.4 - 3.6
Sample 3	3.53	2.52	1.2 - 7.11
Sample 4	1.17	0.91	0.3 - 2.43

Table 9. Comparison of spiked concentration of dimethoate with the mean, standard deviation and range of measurements corrected for the blank

Spiked conc. (µg/l)	Measured values (µg/l)		
	Mean	σ_{n-1}	Range
0.501	0.69	0.34	0.28 - 1.1
1.00	1.18	0.70	0.37 - 2.0
2.00	1.86	1.06	0.75 - 2.86
5.00	4.73	2.03	2.01 - 6.94

Table 10. Comparison of spiked concentration of isoproturon with the mean, standard deviation and range of measurements corrected for the blank

Spiked conc. (µg/l)	Measured values (µg/l)		
	Mean	σ_{n-1}	Range
0.210	0.35	0.39	0.04 - 0.79
0.529	0.70	0.74	0.1 - 1.77
2.96	2.31	0.46	1.78 - 2.83
9.86	7.30	2.25	4.13 - 9.12

Table 11. Comparison of spiked concentration of simazine with the mean, standard deviation and range of measurements corrected for the blank

Spiked conc. (µg/l)	Measured values (µg/l)		
	Mean	σ_{n-1}	Range
0.210	0.27	0.33	0 - 0.75
0.839	0.81	0.76	0.2 - 1.92
1.05	1.08	0.83	0.4 - 2.0
2.62	2.68	1.91	1.0 - 5.43

Table 12. Measured results, corrected for the blank, expressed as a percentage of the spiked concentration for laboratory A

Mecoprop

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
1.03	1.4	136
2.59	3.6	139
5.17	/	/
10.3	12.8	124

Dimethoate

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.501	1.1	220
1.00	2.0	200
2.00	/	/
5.00	5.0	100

Isoproturon

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	/	/
0.529	0.1	19
2.96	2.1	71
9.86	7.3	74

Simazine

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0	0
0.839	0.5	60
1.05	/	/
2.62	1.9	73

Table 13. Measured results, corrected for the blank, expressed as a percentage of the spiked concentration for laboratory B

Mecoprop

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
1.03	1.30	126
2.59	2.50	97
5.17	4.60	89
10.3	8.56	83

Dimethoate

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.501	0.68	136
1.00	1.43	143
2.00	2.86	143
5.00	6.94	139

Isoproturon

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.79	376
0.529	1.77	335
2.96	2.83	96
9.86	8.63	88

Simazine

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.1	48
0.839	0.2	24
1.05	0.4	38
2.62	1.0	38

Table 14. Measured results, corrected for the blank, expressed as a percentage of the spiked concentration for laboratory C

Mecoprop

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
1.03	43.4	4214
2.59	324.4	12525
5.17	278.4	5385
10.3	758.4	7363

Dimethoate

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.501	0.28	56
1.00	0.37	37
2.00	0.75	38
5.00	2.01	40

Isoproturon

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.04	19
0.529	0.32	60
2.96	1.78	60
9.86	4.13	42

Simazine

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.75	357
0.839	1.92	229
1.05	2.0	190
2.62	5.43	207

Table 15. Measured results, corrected for the blank, expressed as a percentage of the spiked concentration for laboratory D

Mecoprop - No data

Dimethoate

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.501	0.69	138
1.00	0.92	92
2.00	1.98	99
5.00	4.98	100

Isoproturon

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.21	100
0.529	0.60	113
2.96	2.52	85
9.86	9.12	92

Simazine

Spiked concentration (µg/l)	Measured concentration (µg/l)	% (measured/spiked)
0.210	0.24	114
0.839	0.61	73
1.05	0.83	79
2.62	2.19	84

APPENDIX XIV

Table 6.1A. Physico chemical data on pesticides

Property	Isoproturon	Lindane	Mecoprop
Molecular weight	290.85	206.3	214.6
Vapour pressure (mmHg)	9.4×10^{-6}	2.5×10^{-8}	7.5×10^{-7}
Solubility (mg/l)	55.0	17.0	620
Log K_{ow}	2.71	3.72	2.3
Degradation rate in soil (h^{-1})	1.44×10^{-3}	2.06×10^{-4}	3.0×10^{-3}

Table 6.1B. Measured and predicted lindane concentrations in the top 1 m of soil in Foxbridge and Longlands following the Autumn 1989 application (wet weight basis)

Time after application (days	Measured (mg/kg)	Modelled Literature Rate (mg/kg)	Modelled Fitted Rate (mg/kg)
0	-	0.036	0.036
5	0.040	0.035	0.032
21	0.026	0.033	0.022
47	0.015	0.029	0.012
91	<0.002	0.023	0.005

Table 6.1C. Measured and predicted isoproturon concentrations in the top 1 m of the experimental fields following the Autumn 1989 application (wet weight basis)

Time after applications (days)	Foxbridge + Longlands		Stoney + Brushes	
	Measured (mg/kg)	Modelled (mg/kg)	Measured (mg/kg)	Modelled (mg/kg)
0	-	0.065	-	0.025
5	0.1	0.055	0.03	0.021
21	0.05	0.033	-	-
31	-	-	0.01	0.009
47	0.01	0.014	-	-
75	-	-	<0.01	0.002
91	<0.01	0.004	-	-

Table 6.1D. Measured and predicted mecoprop concentrations in the top 1 m of soil in Foxbridge and Longlands following the Spring 1990 application (wet weight basis)

Time after application (days)	Measured (mg/kg)	Modelled (mg/kg)
0	-	0.046
5	0.059	0.040
9	0.033	0.024
15	0.020	0.017
22	0.015	0.011
35	0.011	0.005
62	0.002	0.001