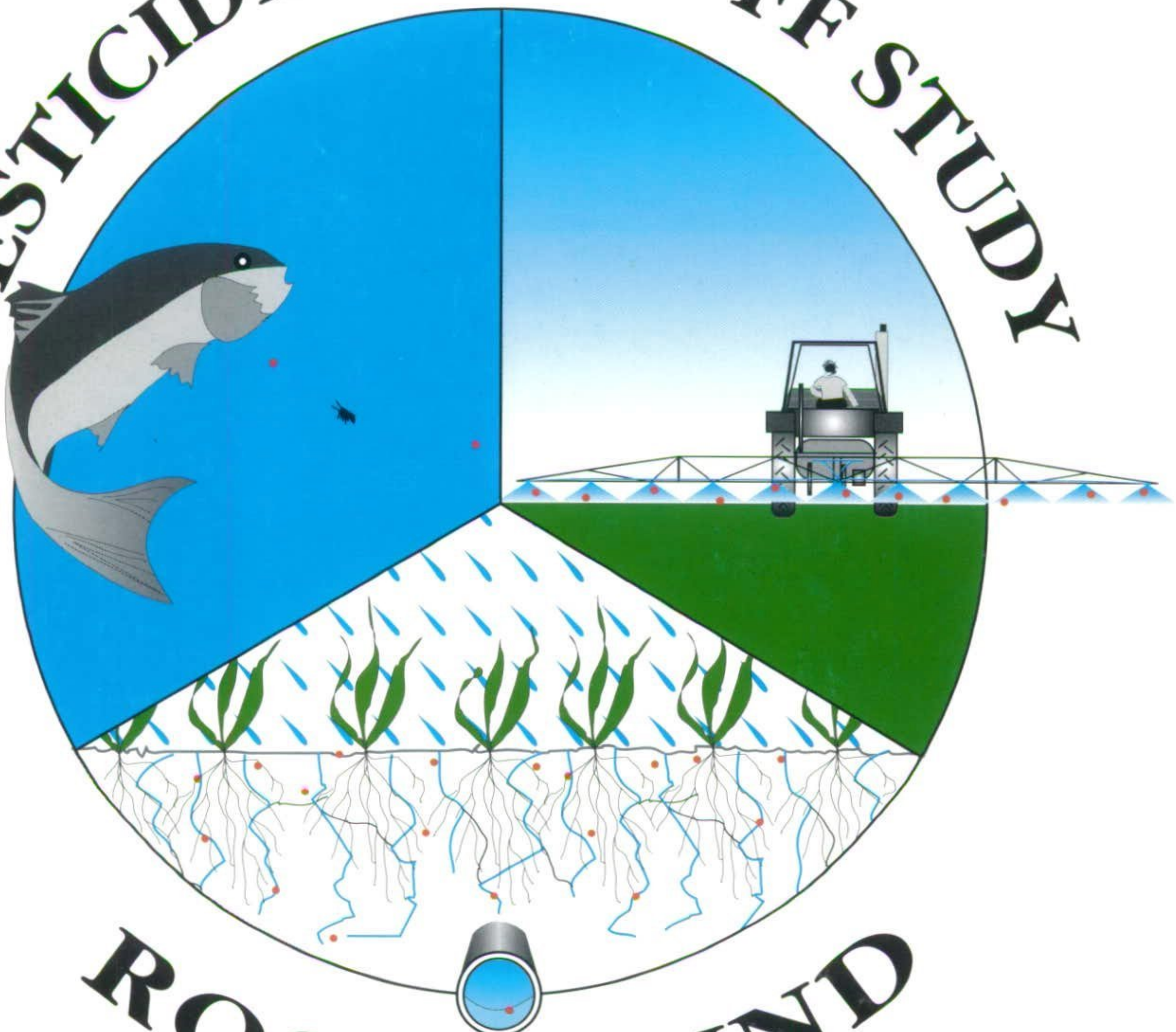
1993/073

PESTICIDE RUN - OFF STUDY



ROSEMAUND

[redacted]

MAFF

ADAS
FOOD, FARMING, LAND & LEISURE

Institute of
Hydrology

NRA

bre

SSLRC

THE UNIVERSITY
OF BIRMINGHAM

PESTICIDE RUN-OFF STUDY
AT ADAS ROSEMAUND

Report of Years 3 to 5
Autumn 1990 to Spring 1992

Editor: C M Hack

This report is confidential: no part of it is to be reproduced or quoted in any way without the prior consent of all the co-operating organisations responsible for the work.

MAJOR CONTRIBUTORS

1. ADAS

Mr R W Clare*
Miss C M Hack*+
Mr R Edwards

ADAS Rosemaund
Preston Wynne
Hereford HR1 3PG

Tel: (0432) 820 444
Fax: (0432) 820 121

Mr G Harris+
Mr T Pepper

ADAS Soil and Water Research Centre
Anstey Hall
Maris Lane, Trumpington
Cambridge CB2 2LF

Tel: (0223) 840 011
Fax: (0223) 814 618

2. MAFF

Dr P Matthiessen*
Mr R Rycroft*
Mr D Sheahan

MAFF Fisheries Laboratory
Remembrance Avenue
Burnham on Crouch
Essex CM0 8HA

Tel: (0621) 782 658
Fax: (0621) 784 989

3. NATIONAL RIVERS AUTHORITY (NRA)

Mr M Mills*+
Mr R West

National Rivers Authority Welsh Region
River House
St Mellons Business Park
St Mellons
Cardiff CF3 OLT

Tel: (0222) 770 088
Fax: (0222) 798 555

4. INSTITUTE OF HYDROLOGY (IH)

Mr R J Williams*+
Mr P C R Volkner+
Mr J Bell+
Dr L Bhardwaj

Institute of Hydrology
Wallingford
Oxford OX10 8BB

Tel: (0491) 838 800
Fax: (0491) 832 256

5. BUILDING RESEARCH ESTABLISHMENT (BRE)

Dr D Brooke*+
Dr M Crookes+

Building Research Establishment
Building Research Station
Bucknall Lane
Garston
Watford WD2 7JR

Tel: (0923) 894 040
Fax: (0923) 664 010

6. SOIL SURVEY AND LAND RESEARCH CENTRE (SSLRC)

Mr G Beard+ Dr A Carter+	Soil Survey and Land Research Centre Shardlow Hall Shardlow Derby DE7 2GN Tel: (0332) 799 000 Fax: (0332) 799 161
Dr J Hollis+	Soil Survey and Land Research Centre Silsoe Campus Silsoe Bedfordshire MK45 4DT Tel: (0525) 860 428 Fax: (0525) 861 147

7. UNIVERSITY OF BIRMINGHAM

Mr A Turnbull+ Prof R M Harrison	University of Birmingham Institute of Public and Environmental Health Edgbaston Birmingham B15 2TT Tel: (021) 414 3493 Fax: (021) 414 5925

COMMITTEE MEMBERSHIP

* Member of Management Steering Group (Chairman - R W Clare)
\+ Member of Technical Group (Chairman - R J Williams)

CONTENTS

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 falling on 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), the second covered Years 2 to 4 (Autumn 1989-Spring 1991; additional data were presented for Years 2 and 3), and this report presents additional data for Autumn 1990, as well as data for Autumn 1991 and Spring 1992. The report is intended to be both a summary of progress and a repository of 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 are conscious that Rosemaund's catchment characteristics and cropping practices are such that pesticide concentrations appearing in the stream probably represent a reasonably 'worst-case'. In particular, the soils are artificially drained and prone to 'by-pass flow' which accelerates the appearance of rainwater and associated pesticides in the drains and minimises the adsorptive potential of the soil. The data are therefore likely to set an upper limit for the pesticidal contamination of UK surface waters. However, it should be borne in mind that soils in which by-pass flow is an important component of the hydrological regime are widespread in the UK (approximately 28% of all soils), so the Rosemaund data are of direct applicability to many agricultural situations.

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. The next report will describe full modelling results, but it is worth indicating here that a catchment-specific model developed by IH and a predictive fugacity model (SoilFug) developed by the University of Milan (DiGuardo *et al.*, 1994) have both been successfully validated using a comprehensive cross-section of data from

Rosemaund. The former gives good estimates of mean and peak pesticide concentrations in Rosemaund stream by combining a hydrological model with a pesticide behaviour model. The latter successfully predicts mean concentrations during each rainfall event (usually slightly overestimating the observed value), and shows promise as a tool for assisting with pesticide risk evaluations because it has few catchment-specific parameters. SoilFug has also been successfully validated with data from two Italian catchments.

1.5 Most of the data presented in this report concern the continuing records of water flows and pesticide concentrations seen in soil, drains and stream at Rosemaund. The data focus on the dynamic situation during rainfall events, although some data are also presented for the 'background' levels seen between events. The main datasets referred to concern isoproturon and dimethoate levels in soil following applications in Autumn 1990, carbofuran and atrazine levels in soil and water in Autumn 1991 and Spring 1992 (as well as some simazine data for water alone), and aldicarb, trietazine and terbutryn levels in water (plus soil levels for aldicarb) in Spring 1992.

1.6 The data reveal similar patterns in space and time to those described in previous reports, again showing that most pesticides can translocate from the fields to the stream within a few hours of rain falling. Peak concentrations are usually coincident with or slightly before peak flow rates, but tend to decline rapidly thereafter. The mechanism which produces this behaviour is likely to be complex, but is intimately connected with the occurrence of by-pass flow and the consequent failure of the pesticide to equilibrate fully with the soil before being partly transferred to the drains and stream. The picture is complicated still further by the fact that some drain and stream flow does not originate directly from rain but from deeper soil water.

1.7 The peak levels seen in the stream and flow-weighted mean levels for the same event were, respectively, as follows:- isoproturon 17.2 and 10.6 µg/l, simazine 15.3 and 3.3 µg/l, dimethoate 3.0 and 1.2 µg/l, atrazine 49.4 and 1.9 µg/l, carbofuran 49.4 and 6.2 µg/l, aldicarb (as sulphone and sulphoxide) 2.8 and 0.9 µg/l. Peak values for trietazine and terbutryn were 3.6 and 0.24 µg/l respectively. In almost all cases, pesticide concentrations returned to background levels within 6-12 hours of peak flow and the maximum amount of pesticide (52.6 g carbofuran) mobilised into the stream during an event was only 0.6% of that applied. The exception in terms of the persistence of elevated concentrations was a 72.5 mm rainfall event on

8/9 January 1992. This event had a return period of 50 years, and elevated concentrations of carbofuran and atrazine persisted in the stream for at least 4 days.

1.8 Unlike most of the pesticides previously tested at Rosemaund, the insecticide and nematicide carbofuran is extremely toxic to crustacea. Biological water quality was therefore measured during the carbofuran experiment from the end of October 1991 to January 1992. A sensitive feeding rate bioassay based on the amphipod crustacean *Gammarus pulex* was continuously deployed in the stream throughout this period, which ended with the large event on 8/9 January. *G. pulex* is a good animal to use for this purpose because it plays a pivotal role as a leaf shredder in many stream ecosystems. This bioassay had been previously deployed at Rosemaund in 1990 during a mecoprop/dichlorprop runoff event, but had not detected any effects due to the low toxicity of these herbicides to crustacea. The results from the carbofuran experiment showed that not only did the *Gammarus* go off their feed during the large rainfall event, but they all subsequently died. Later laboratory experiments confirmed that the carbofuran concentrations seen during the event were acutely toxic to *Gammarus*. Furthermore, a subsequent rainfall event on 25 January (which was not monitored with *Gammarus*) also produced concentrations in the stream which would have been lethal or severely damaging to crustacea and insect larvae. The next report will present results which show that a chlorpyrifos runoff event was also acutely toxic to invertebrates in the stream.

1.9 It has therefore been shown that some of the runoff events seen at Rosemaund are not just of academic interest, but depending on the toxicity of the pesticide concerned, are able to cause significant impacts on stream fauna. This illustrates the importance for the risk evaluation process of developing predictive models of pesticide translocation to headwater streams. It could be argued that significant effects may not be expected further downstream where neat field drainage water will become diluted, and that these results are therefore of little significance. However, it should be remembered that headwater streams are often of considerable conservation significance, so one of the aims of pesticide risk assessments must be to protect these vulnerable habitats in the immediate vicinity of arable fields.

1.10 The final experiments to be presented in this series of reports will concern a range of pesticides which include some that are strongly adsorbed to particulates and are therefore not generally considered to be prone to leaching. The relevant compounds include the insecticides deltamethrin and chlorpyrifos, the herbicide trifluralin, and the fungicide fenpropimorph. It will be demonstrated that two of the strongly adsorbed substances (trifluralin, and especially deltamethrin) do nevertheless appear in the stream at concentrations up to 1.9 µg/l, showing that contaminated soil particles are able to travel down the soil profile and enter the stream via the field drains. Furthermore, peak chlorpyrifos levels in one field drain of 4.3 µg/l, although partly adsorbed on particulates, were able to cause adverse biological effects in the stream.

1.11 In summary, the continuing work at Rosemaund is showing that pesticides with a very wide range of properties are able to translocate rapidly from fields to the stream at concentrations that are sometimes acutely toxic to stream fauna. The final report will show that simple computerised models are able to predict these concentrations with satisfactory accuracy. The mechanism responsible for rapid translocation at Rosemaund is so-called by-pass flow down soil macropores, a phenomenon which dominates the hydrological regime in nearly a third of UK soils and is an important component in many more.

2. INTRODUCTION

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

Reviews of pesticides in drinking waters sources in England and Wales (Lees and McVeigh, 1988: Drinking Water Inspectorate, 1992) have indicated that a number of sources may contain individual pesticide levels greater than the Maximum Acceptable Concentrations (MAC) laid down in the European Community Drinking Water Directive (Council of the European Communities Directive, 1980). This directive stipulates a MAC of any single pesticide in potable waters of 0.1 µg/l and a MAC of 0.5 µg/l for total pesticides. Although these MACs may be over-cautious from the standpoint of human health, the failure of a proportion of samples to comply has caused public concern.

The Water 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 NRA will be responsible for ensuring compliance with these statutory WQOs and the consultation proposals for WQOs include: a new general classification scheme for controlled waters, use related objectives and standards and incorporation of the requirements of relevant EC Directives. It is vital that the movement and fate of pesticides in the aquatic environment is well understood and predictable so that the NRA can seek to control diffuse inputs of such chemicals and ensure compliance with the statutory objectives Without such information it is difficult to envisage how compliance with such standards could be achieved.

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

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

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

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

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

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

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

This report is the third joint summary of progress to date by all of the organisations which have collaborated in the Pesticide Run-Off Study at ADAS Rosemaund between Autumn 1990 to Spring 1992. Joint reports in a similar format to this are and 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 (e.g. *Gammarus* feeding assay).

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

3.2.3 ADAS

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

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

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

4. STUDY SITE

4.1 LOCATION

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

4.2 CLIMATE

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

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

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

4.3 GEOLOGY AND SOILS

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

Table 4.2. Classification of Soils of Rosemaund

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

4.4 AGRICULTURE

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

Table 4.3. Arable Rotation at Rosemaund

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

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

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

4.5 GENERAL PESTICIDE USE AT ROSEMAUND

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

4.6 LEACHING POTENTIAL AND SELECTION OF PESTICIDES FOR STUDY

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

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

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

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

Table 4.4. Pesticides monitored at ADAS Rosemaund

Herbicides	Isoproturon MCPA Mecoprop Dicamba 2,4-D Triclopyr Dichlorprop Trietazine Terbutryne Simazine+ Atrazine+
Insecticides	Aldicarb Carbofuran Dimethoate Lindane+ Deltamethrin Oxydemeton-methyl

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

5. SUMMARY EXPERIMENT REPORTS

5.1 EXPLANATION OF SUMMARY REPORTS

The results from the experiments carried out between Autumn 1991 and Spring 1992 are reported below. They are reported in summary form to present an overall picture of the findings in this study. Surveys of the site carried out by SSLRC and SWRC are reported first followed by the summary reports of pesticide monitoring. The pesticide monitoring summary reports have been placed in chronological order, each covering a season of experiments; autumn 1991 and then spring 1992. The MAFF/BRE sections contain some data from the year 1990-1991 as this was unavailable at the time of writing the previous annual report.

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

5.2 DETAILS OF PESTICIDE APPLICATIONS MONITORED IN THIS STUDY

All of the monitoring in this study concentrated on pesticides applied to fields at the upper end of the catchment. (Foxbridge and Longlands, Stoney). With the exception of atrazine, monitoring followed the normal use of pesticides as per cropping, timing and rates of application. Atrazine was applied on an experimental permit to enable the monitoring of this important pesticide. They were applied using either a self propelled Chaviot dedicated sprayer or granular applicators. Details of the pesticides monitored are given in Table 5.14

Table 5.1. Details of pesticides monitored in each season

Season	Pesticide monitored	Rate applied (kg/ha)	Product name	Fields	Crop	Date
Autumn 91	carbofuran	3.0	Yaltox	S	OSR	03.12.91
	atrazine	5.6	Gesatop	F&L	ST	27.10.91
Spring 92	aldicarb	5.5	Temik	F&L	SB	27.02.92
	trietazine & terbutryne	1.0:1.0	Senate	F&L	SB	05.03.93

S	Stoney	OSR	Oilseed rape	SB	Spring beans
F&L	Foxbridge and Longlands	ST	Stubble		

5.3 MONITORING AND SAMPLING SITES

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

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

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

OS reference numbers	Descriptive name
SO 5582 4789	Main gauging site (IH)
SO 5665 4841	Upper gauging site 1 (MAFF)
SO 5667 4842	Stream Site 1A (MAFF)
SO 5668 4843	Stream Site 1B (MAFF)
SO 5672 4843	Ditch, Site 2 (MAFF)
SO 5672 4842	Ditch, Site 3 (MAFF)
SO 5688 4847	Foxbridge & Longlands drain outfall: Site 4 - left hand drain (MAFF) Site 5 -right hand drain (IH, MAFF) Site 6 - middle drain (MAFF & IH)
SO 5702 4843	Soil suction samplers (SSLRC) (Nos 1-6)
SO 5697 4839	(Nos 7-12)
SO 5698 4848	(Nos 16-21)
SO 5693 4844	(Nos 22-27)

5.4 SOIL AND SOIL HYDROLOGY SURVEYS

Further surveys of the soil and soil hydrology were carried out by SSLRC in 1991-92 to add to information already collected concerning the processes and pathways controlling the movement of soil water (and hence, of dissolved agrochemicals and their derivatives). In addition to this a survey of the drains in Foxbridge and Longlands was carried out in Autumn 1991 by ADAS SWRC.

5.4.1 SSLRC soil water sampling and soil characterisation

5.4.1.1 Introduction

The SSLRC contribution has 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 the Institute of Public and Environmental Health at the University of Birmingham. The project, begun in the autumn of 1989, is ongoing and will continue until the end of Spring 1993. Investigations regarding the saturated hydraulic conductivity of the soil were made on the Middleton series (Keyworth, 1992).

5.4.1.2 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. A detailed description of the installation and sampling procedures are described by Carter and Cope (1990). For the 1991/92 monitoring season the method of installation was modified slightly by the introduction of bentonite clay to seal the sampler into its hole and prevent possible preferential flow. Water samples were transported to Institute of Public and Environmental Health at the University of Birmingham immediately after collection. Daily rainfall data was obtained from the ADAS Rosemaund meteorological station.

Autumn 1991

Soil water suction samplers removed from the Foxbridge and Longlands field at the end of the spring 1991 season were returned to the SSLRC laboratory for cleaning and repair. Each sampler was cleaned externally with clean deionised water. The interiors were flushed with acetone followed by hexane. Each tube was sheathed in foil, transported to Foxbridge and Longlands and reinstalled during the period 23-24 September. Tubes 13, 14 and 15, installed in the 1990 to 1991 season were not replaced. However, for continuity the 1990/91 numbering of the samplers was retained. The suction samplers were relocated to their previous positions (Figure 1)

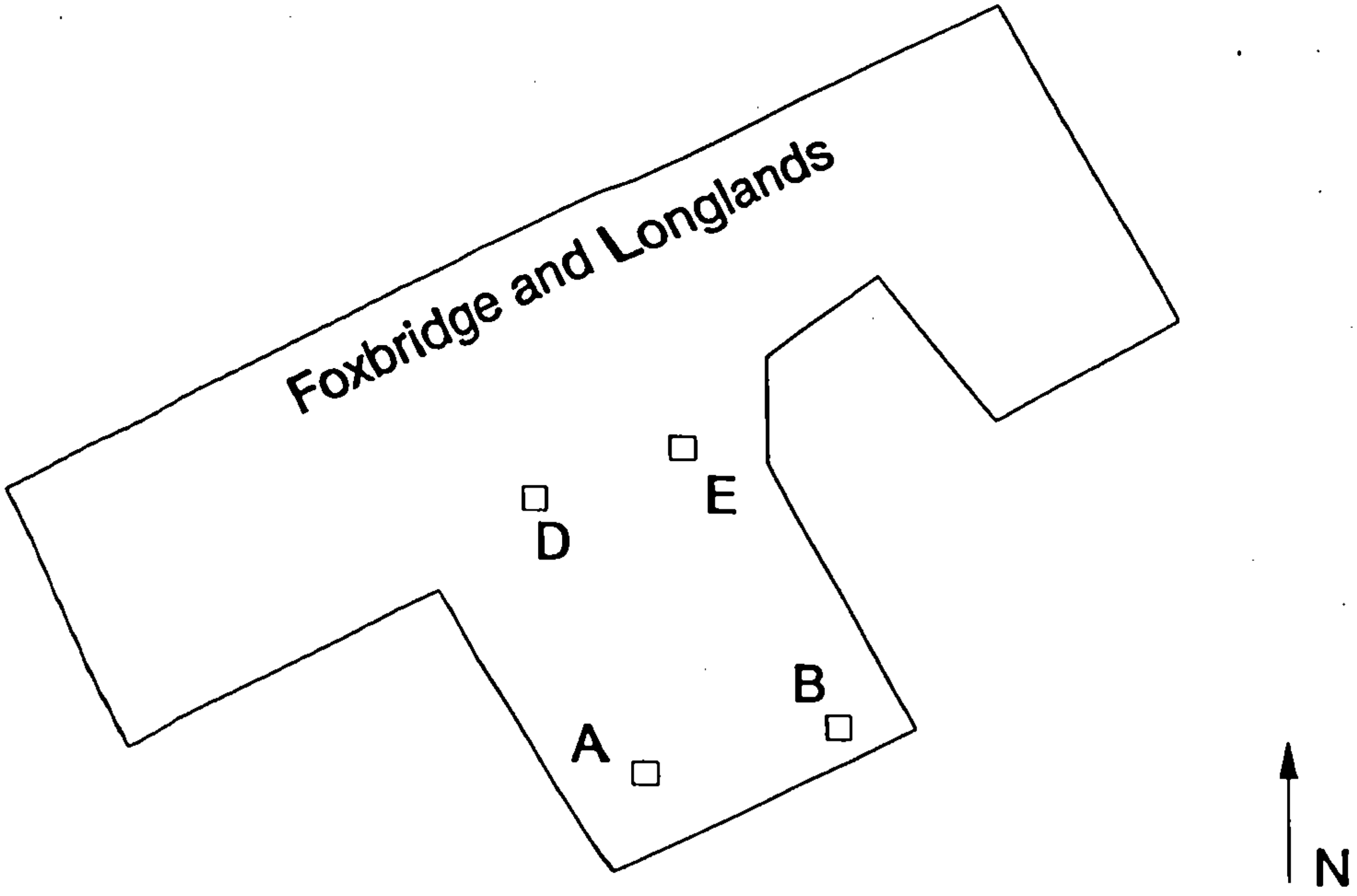


Figure 1. Soil Water Sampling Sites, Autumn 1991-Spring 1992

and each was reinstalled into its original hole following the method outlined in Carter and Cope (1990).

A pre-spray sample was taken on 24 October 1991. However, a soil moisture deficit of approximately 70 mm was still present and only three samplers yielded. Slight soil shrinkage around the samplers was evident so it was expected that early flushes may move rapidly to sampler pot depth. Three samplers, numbers 4,5 and 26, malfunctioned and were replaced on 7 November.

The first sampling after atrazine application occurred on 6 November in response to a rainfall event of 17.1 mm. Water samples were obtained mainly from the Middleton soil (Fig 1, sites D and E). On 6 December the soils had completely rewetted and nearly all samplers yielded a reasonable quantity of liquid.

Further sampling continued at regular intervals (7.1.92 and 6.2.92) and in response to events (14.1.92) until the end of the spring 1992 season. Sampling dates and volume of liquid obtained is given in Table G1 (Appendix VII) for 1991/92 autumn/spring season. Soil water concentrations for atrazine are given in Table W15 (Appendix XII).

Spring 1992

Soil samplers remained *in situ* and sampling continued following cultivation of the field, sowing of beans and spraying with aldicarb. The field was cultivated by traditional methods, avoiding each group of samplers. The soil surrounding the samplers was cultivated and sown by hand. Sampling for aldicarb was continued up to 13 May 1992. The volume of sample obtained is given in Table G1 (Appendix VII) and the aldicarb concentrations in Table W19 (Appendix XII).

5.4.1.3 Soil water regimes

Dipwells installed for the autumn 1990-spring 1991 sampling season (Carter and Beard, 1992) were retained. The depth to water-table for each hole was recorded on each site visit (Table G2, Appendix VII) and the data plotted in figures 2 and 3.

Figure 2 Water Table Depth at Site D

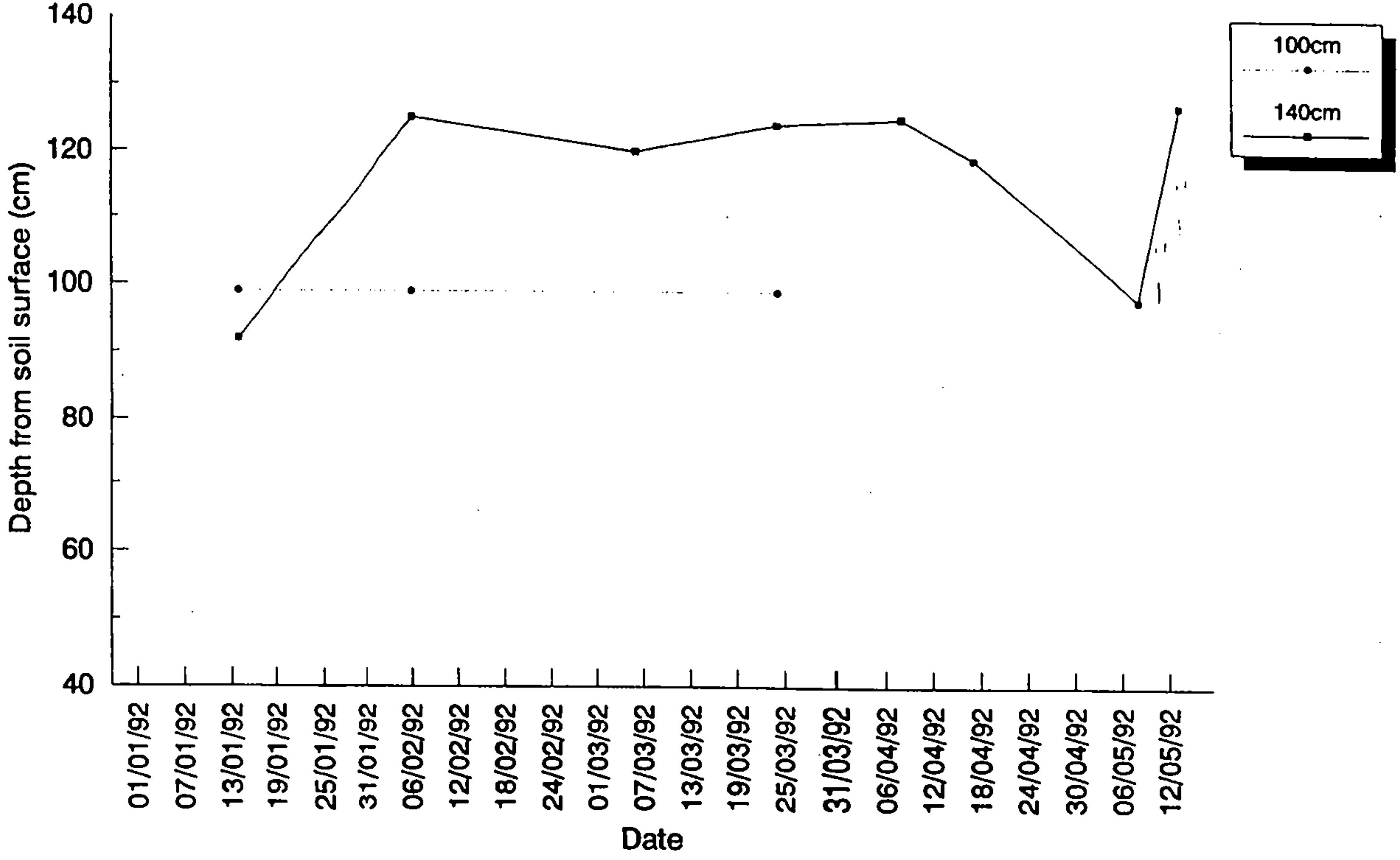
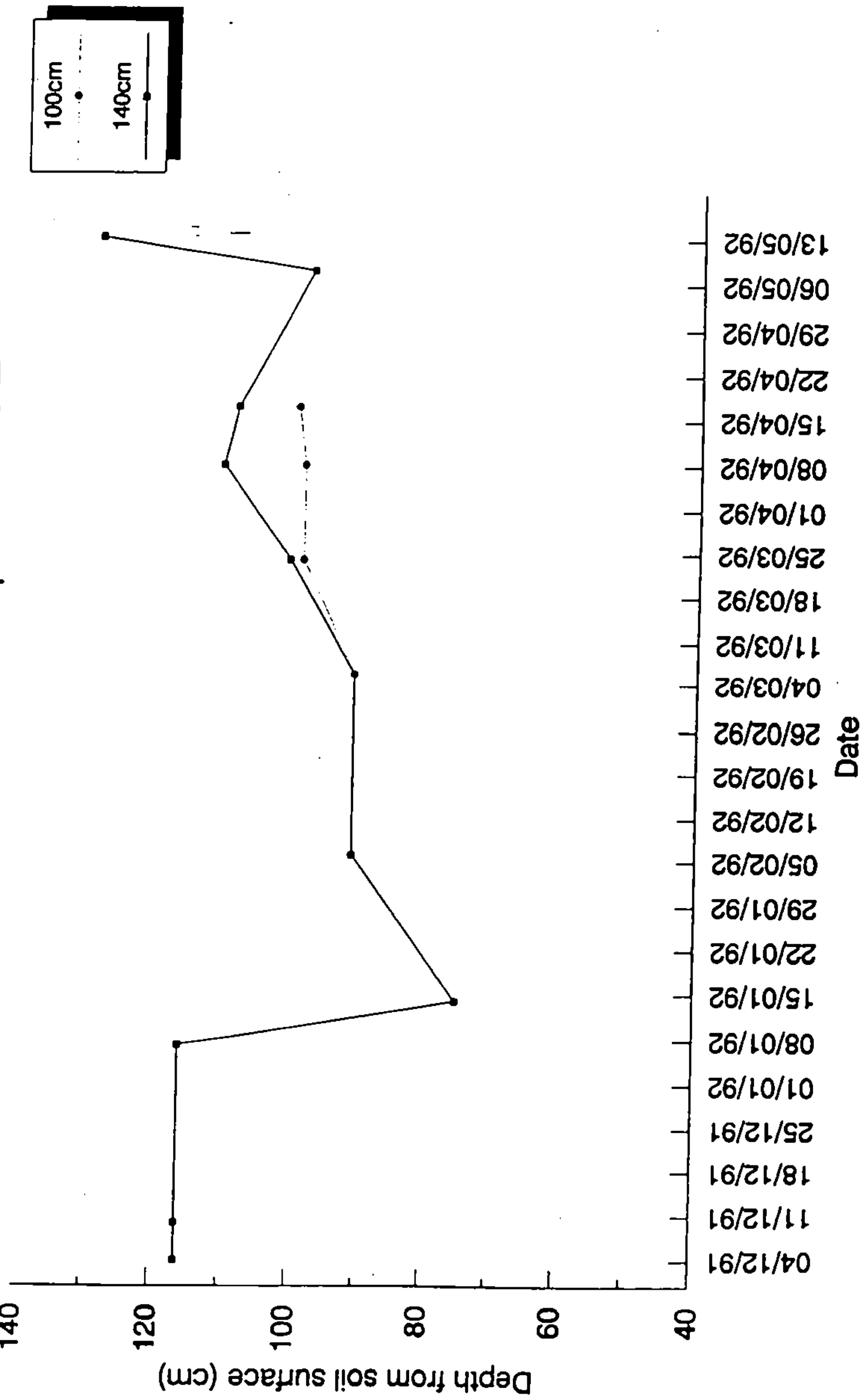


Figure 3 Water Table Depth at Site E



5.4.1.4 Hydraulic Conductivity Measurements

Saturated hydraulic conductivity measurements using the Guelph Permeameter were made on top soils (Ap horizons) of the Middleton series. The Middleton series was chosen over the Bromyard series because it develops large cracks as it dries and was considered very susceptible to bypass flow, particularly when in deficit. The work was carried out in July.

5.4.1.5 Suction samplers and Flow regimes

Following on from the work carried out by the SSLRC to assess the nature and volume of the supply zone around the porous sampler pot, a sampler of 100 cm length was installed in the vicinity of location A (Fig 1). The Institute of Hydrology subsequently investigated the influence of suction sampling on the surrounding hydrology. This work is still continuing and suction sampling at 50 cm depth has been added to the study. Suction around the samplers after evacuation is recorded using a pressure transducer tensiometer system.

5.4.1.6 Results and Discussion

Soil water sampling
Autumn 1991-Spring 1992 Atrazine

No results were available for the pre-spray sampling obtained in October due to the insufficient sample from the majority of porous pots. From the succeeding eleven samples the results indicated that atrazine moved in different quantities in the different soils. The quality of sample obtained at each site depended on rainfall and water movement through the soil. Occasionally where volumes were low samples from a similar depth on the same soil type were bulked. At times even this provided insufficient sample for analysis

The first sampling in response to an event occurred on 14 January 1992 and resulted in increased levels of atrazine in the samplers (Table W15, Appendix XII). Subsequent samplings also gave reasonably high concentrations in both routine and event situations. It was notable that atrazine concentrations were substantially higher from sampler tubes 16-27 (Sites D and E, Fig. 1). Without further work it is not possible to assess the reason for this, though the cracks and macropores at these two sites described in a previous report (Carter and Beard, 1990) are substantial.

Methylene blue studies also show penetration along cracks and faunal channels occurs to depth (>75 cm) at sites D and E, but is far less at sites A and B.

Only levels of atrazine above 0.1 µg/l in suction samplers are likely to breach accepted levels in soil drainage waters and affect stream quality.

Water sampling in May ceased for two reasons:

1. The start of a soil moisture deficit was reflected in the reduction of sample volume.
2. The available analytical capacity at Birmingham University had been exceeded at this time.

Autumn 1991-Spring 1992 - Carbofuran

Levels of carbofuran obtained from soil suction samples were all low but occurring in identifiable quantities in a surprising number of samples. More surprising is the fact that carbofuran was not applied to Foxbridge and Longlands, the fields with the suction samples. It is possible that subsurface lateral flow may have carried carbofuran into the sphere of influence of the suction samplers but how this occurred is not understood.

Spring 1991 - Aldicarb

All the results for aldicarb (and its products) are presented elsewhere in this report (Section 5.5). The results for soil water show no parent aldicarb was detected. Aldicarb readily degrades from aldicarb to 'sulphoxide' and 'sulphone' and these two degradation products were occasionally detected, usually in a 1:1 ratio. The analysis for aldicarb and major degradation products was lengthy and complicated (Section 5.7) Due to this, primary screening of samples was undertaken. Therefore where it was considered no aldicarb was likely to be present in the light of sampling date and parallel samples already analysed, the samples were discarded at the laboratory such samples are indicated by 'x' in Table W19 (Appendix XII).

Hydraulic conductivity measurements

Four measurements of hydraulic conductivity were made as part of an MSc thesis (Keyworth, 1992) and the results (Table 5.3) show considerable variability. Methylene blue dye was introduced into the auger hole in the topsoil in an attempt to trace pathways of flow. Excavation of each auger hole revealed a bulb of saturated soil up to 0.3 m in diameter. However, the dye used in the permeameter appeared to have only infiltrated along fine cracks and biopores. Excavation of the highest conductivity auger hole revealed a dyed vertical worm channel 5 mm in diameter penetrating to 80 cm depth. This was the main pathway conducting water to depth.

Table 5.3. Saturated hydraulic conductivity measurements

Soil series	Ksat (cmd^{-1})
Middleton	127
	39
	25
	30

This limited work shows that low conductivities are mainly attributable to water flow in the soil matrix and minor pores and fissures and high conductivities are likely to result from both matrix and macropore flow.

On relatively clayey soils there are some problems associated with smearing of the permeameter during excavation. Although care was taken to avoid this, sealing of macropores may have occurred in some cases, leading to a lower macropore flow than would normally be the case.

5.4.2 SOIL MOISTURE STATUS - DRAINAGE INVESTIGATION (FOXBRIDGE AND LONGLANDS)

5.4.2.1 Background

Tensiometric investigations by John Bell (Institute of Hydrology) suggested that a problem may exist with the effectiveness of the study drain in Foxbridge and Longlands. To determine whether problems were likely to arise with the carrying capacity of the target drain, ADAS undertook a field investigation of the drain in

October 1991 together with a subsequent computer simulation of the hydraulic performance.

5.4.2.2 Procedure

(i) Field:

(1) The field location of the lateral drainage pipe involved was confirmed and an excavation undertaken by ADAS Rosemaund at the entry point of the lateral to the field main.

(2) The dimensions of the excavation were determined from the specification of the video-camera system identified. Limitations in the length of drainage run that could be surveyed from the access point confirmed that a second access point at the top end of the drain would be subsequently required.

(3) Site investigation:

- (a) Camera investigation of drainage pipe including video (VHS) and written report.
- (b) Endoscopic examination of drainage pipe entry points.
- (c) Examination of permeable fill, including cleanliness and trench width.
- (d) Determination of drainage pipe depth, type, internal diameter, and gradient.

(ii) Laboratory investigation:

(1) Determination of porosity of permeable fill.

(2) Determination of hydraulic capacity of pipe drainage system
- Computer test of drainage potential using FDEU HYDINT model.

(3) Report of findings.

5.4.2.3 Results

(i) Field surveys

The video camera and drainage condition investigation was carried out in three parts:-

- Lateral drain, from major excavation, 97 m eastwards.

- Main drain, from major excavation, 98.4 m north.
- Lateral drain, from small excavation, 40 m westwards.

Lateral drain (eastwards/westwards)

The lateral drain was examined in hole 1 and cut 6 m from the hedge. The pipe was measured as 60 mm OD, 56 mm ID, with permeable fill (PF) at 350 mm below ground level; the trench width was 140 mm. The ground level to pipe top was 840 mm, i.e. drain depth was 900 mm.

The video camera investigation of this drain showed no distortion or blockage and only minimal roof, slot or base debris. Slot debris entry was variable with more noticeable intrusions at 40 m and 78 m from the eastern boundary. Roots were also evident throughout the drain length but no problem to the carrying capacity was evident. At the eastern end of the drain, permeable fill was absent for some 10 m from the hedge, but apart from permitting some debris entry at the time of installation, is unlikely to have caused any problems. The drain was dry throughout its length.

A further hole (hole 2) was excavated 36.2 m east of the boundary hedge. The PF was measured at 390 mm below ground level; the trench width was 140 mm. The ground level to pipe top was 870 mm, noticeably deeper than in hole (1). The permeable fill was examined and found to be variable in size, typically 40 mm diameter. The PF was clean with little broken debris or soil infill. Clayey soil was however, observed in the immediate vicinity of the drainage pipe and infilled the corrugations. The slots, located in the bottom corrugations, were therefore partially blocked although there was no evidence of a seal to water entry.

Hole (3) was excavated at 77.8 m east of the boundary hedge. The trench width was confirmed at 140 mm. The PF was measured at 400 m below ground level with the pipe top at 920 mm. Examination of the permeable fill and pipe corrugations confirmed the findings in hole (2).

Hole (4) was excavated at 112.8 m east of the boundary hedge. The trench width was 140 mm. The PF was 380 mm below ground level and the pipe top was at 980 mm.

The eastern boundary was measured at 129.8 m from the western hedge.

Topographic levels were taken at ground level along the line of the lateral and at pipe top to determine the gradients. These are given in Table 5.4.

Table 5.4. Measured gradients on lateral pipe drain and ground level

	Distance (m)	Lateral gradient (%)	Ground level (%)
Hole 1-2	30.2	0.16	4.9
Hole 2-3	41.6	4.03	4.0
Hole 3-4	35.0	2.71	2.7
Overall mean	106.8	2.90	3.9

This data confirmed that the lateral pipe did not follow the ground level gradient of 2%, (as stated in specification design for the drainage installation), the shallowest gradient was noted near to the junction with the main drain.

Main drain, northwards

The main drain was located approximately 4 m from the western hedge. The pipe was corrugated and perforated at the point of excavation but there was no trench backfill. The junction between the lateral and main was well constructed and utilised a purpose designed slip over junction collar. The main drain was 110 mm OD and 95 mm ID. No debris was observed in the main drain at the junction with the lateral.

The video camera survey showed that the main drain was generally clean throughout its length with no problems identified at each lateral junction down the slope. Laterals were identified at 20.0 m, 40.6 m, 61.0 m, 81.4 m and 93.7 m from the hole entry point. The full length of the main could not be examined although it was likely that the end extent of the survey was within 2 m of the junction at the outfall to the ditch. It was however, noted that the main consisted of a series of relatively short lengths of pipe (different makes and nominal sizes). The junctions between these sections did not appear to present any noticeable problems, occurring at 13.7 m and 55.9 m from the hole entry point. Some water was either discharging through the main at the time of the survey or had ponded intermittently along its length. (Observations in the IH mini-weir suggested that flow was occurring at the time of the inspection from at least parts of the field).

The conclusion from the field survey was that there were no major problems identified with the lateral or main drain examined other than the low gradient near to the lateral junction with the main drain. The general lack of debris observed in the drainage system (drain pipe/permeable fill) suggested that it was unlikely that a temporary blockage of the drain had occurred in the previous winter.

(ii) Laboratory investigations

The porosity of the permeable fill has yet to be determined but has been estimated at 45% based on the irregular sized stones. It is unlikely that the error in this parameter will be important or will alter the overall conclusion from the laboratory investigations.

The hydraulic capacity of the lateral pipe was tested using the FDEU developed HYDINT drainage model. This model enables the user to feed a hydrograph (related to return period and rainfall statistics) through the drainage pie to assess if and to what extent surcharge occurred.

A range of parameters were tested, the most limiting of which was likely to be the very low gradient (0.16%) of the lateral pipe at the lower end. Example runs are attached and show that the capacity of the lateral drain may be restrictive. In Run (1)/Table 1, gradient of 0.16%, the lateral pipe would be unable to carry the one year return period event, (Figs. 1 and 2, Appendix VIII). Surcharge in the drainage trench would extend to the surface. In contrast in Run (2)/Table 2 with the mean gradient of 2.9% the design capacity exceeds the one year return period event, i.e. the surcharge would be less than 200 mm, (Figs. 3 and 4, Appendix VIII). Higher return period events would however, cause surcharge in excess of this.

The data presented by the tensiometric survey suggested that problems were evident with the lateral drain on 22 January 1993, (Fig. 5, Appendix VIII)

Examination of the drainflow, using the IH mini-weir, showed that although considerable flow occurred in January (e.g. 11 January - Table 3, Fig. 6, Appendix VIII) there was virtually no drainflow in the period immediately preceding 22 January. On this day there was only a very small response to drainflow, almost too low to be recorded on the mini-weir. As it seems extremely unlikely that the effect observed was a carry over from the earlier runoff event on 11 January, no explanation can be offered at this stage to explain the tensiometric data. Of equal concern is the fact that this lateral pipe drain appears to be under-designed with potential problems of surcharge in more substantial drainflow events.

5.4.2.4 Conclusions

- There were no obvious blockages or potential blockage zones in the pipe system. Internal slot blockage and sediment deposition was minimal.

- The permeable fill was relatively clean although some sediment had collected around the external slot entry points causing some potential limitation to water entry.

- A low pipe gradient over the last 40 m of the lateral drain was likely to restrict flows and could cause excessive surcharging for even relatively low return period events.

- However, no explanation was found for the tensiometric data observed on 22 January 1991 as flow in this period was minimal.

5.5 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS - ISOPROTURON/DIMETHOATE EXPERIMENT - AUTUMN 1990

5.5.1 MAFF/BRE experiment

5.5.1.1 Introduction

See previous report for details of applications.

5.5.1.2 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 fields. One site per visit was sampled in 25 cm sections, to give four depth profile sections.

Analysis

Isoproturon

A sample of soil (40 g) was shaken with 100 ml of an acetone/water mixture (9:1 v/v) for 90 minutes and then centrifuged. A 25 ml aliquot of the liquid was removed and evaporated to the aqueous phase. Following dilution with 50 ml of water, 25 ml of hexane was added, and shaken for 1 minute; the aqueous phase was run off, the hexane re-extracted with water (50 ml) and the aqueous extracts combined. The aqueous phases were extracted twice with dichloromethane (50 ml and 20 ml), and the bulked extracts evaporated to dryness. The residue was then taken up into methanol/water (45:55 v/v) and quantitated by HPLC. Equipment and conditions used: Gilson 305 pump, Perkin Elmer Advanced LC Sampler Processor ISS 200, Gilson 115 UV detector, Apex Ethyl (C_2) column, flow rate 1 ml/minute, detection wavelength 243 nm.

Dimethoate

A sample of soil (20 g) was shaken with 2 ml of water and 50 ml of chloroform for 2 hours. After adding anhydrous sodium sulphate (25 g) to dry the samples were left to settle for 10 minutes. A 20 ml aliquot was taken, and evaporated to dryness under nitrogen. The residue was dissolved in 2 ml of toluene/trimethylpenthane mixture (1:1 v/v) for quantitation by gas-liquid chromatography. Equipment and conditions used: Hewlett Packard 5890A GC fitted with flame photometric detector in phosphorus mode, HP 7673A autosampler, 2.5% Apiezon L on Gas Chrom Q (100-120 mesh) column, injector temperature 225 °C, column temperature 140 °C to 220 °C at 40 °C/min, detector temperature 250 °C.

5.5.1.3 Results and discussion

Soil samples

Background samples were taken on 31 October 1990. Isoproturon was detected in two of the five samples at levels of 0.006 and 0.005 mg/kg; the remaining samples were all below the detection limit of 0.005 mg/kg. The two positive samples were taken from near the field edge, and the adjacent field had been sprayed with Isoproturon on 11 October 1990. Thus it appears likely that some spray drift occurred and caused this contamination. In view of the rate of Isoproturon loss seen later, residues from this drift would have been below the detection limit by the time of the study application, which occurred a month after the background sampling.

Results from the analysis of soil samples taken following the application of isoproturon on 23 November 1990 are shown in Table B1 (Appendix IX). Samples taken three days after the application showed an initial concentration in the top 1 metre of soil of 200 µg/kg wet weight. This had decreased to 56 µg/kg by 8 January 1991. Assuming first order degradation, the half life was 21 days. The profile samples show that most of the chemical was found in the top 25 cm, but with measurable levels at depth even in the first samples. The results for the profile samples were somewhat variable.

The levels of dimethoate in soil following the application on 28 November are presented in Tables B2 and B3 (Appendix IX). The initial concentration measured in Foxbridge and Longlands 2 days after spraying was 31 µg/kg; the corresponding level in Stoney and Brushes was 22 µg/kg. The levels in both fields decreased rapidly, being below the detection limit of 5 µg/kg in all samples taken from Stoney and Brushes 20 days after application, and in all

Foxbridge and Longlands samples on the next visit after 40 days. The half life for degradation assuming first order kinetics was 10 days. Only a small number of positive results was obtained from the profile samples; those from the first sampling visit to Foxbridge and Longlands showed similar levels at all depths.

5.6 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS - CARBOFURAN/ATRAZINE EXPERIMENT - AUTUMN 1991 TO SPRING 1992

5.6.1 Introduction

The rationale for this work has been fully described in previous reports. The experiments reported here are part of a series to measure concentrations of pesticides in soils and waters on Rosemaund farm. The only difference from previous experiments was that carbofuran was one of the first pesticides to be studied which was highly toxic to aquatic life, and therefore it was expected that toxic effects might be detected in the stream. The other pesticide under investigation was the triazine herbicide, atrazine, a compound known to be leach-prone. This was applied on an experimental permit to a non-recommended crop situation.

Atrazine was applied as Gesatop to 6 ha Foxbridge and Longlands at 0.85 kg/ha on 27 November 1991, and carbofuran was applied as a broadcast granule (Yaltox) to 3 ha of Stoney at 3.0 kg a.i./ha on 3 December 1991.

5.6.2 MAFF/BRE experiment

5.6.2.1 Methods

Sample collection methods were fully described in the Report for years 1-3.

Water

Samples of raw water (1 litre) were collected and stored at 4 °C at the Institute of Public and Environmental Health at the University of Birmingham. Two sets of autosampler bottles (sites 1 and 3 on 14 April 1992) were treated with an inorganic biocide, mercuric chloride, to inhibit the biodegradation of aldicarb, also being analysed in the later samples. The presence of this biocide had no impact on apparent atrazine levels, but it apparently prevented some degradation of carbofuran. The atrazine and carbofuran were co-extracted by solid phase extraction (SPE) cartridges without prior treatment of the samples.

A 250 ml portion of each sample was filtered through a 12.5 cm Whatman glass fibre (GF/C) filter by use of a water jet vacuum pump. These were then passed through preconditioned SPE cartridges at approximately 10 ml/min by use of the water jet pump. The cartridges were preconditioned by passing through 5 ml ethyl acetate followed by 5 ml methanol and lastly 10 ml distilled deionised water (DDW). The determinands were eluted from the SPE cartridges by approximately 0.5 ml ethyl acetate (determined gravimetrically). The extracts were stored in a freezer prior to analysis. Samples collected and extracted for these compounds are listed below:

Analysis of the atrazine and carbofuran was by gas chromatography linked to mass spectrometry (GC-MS). The instrument used was a Hewlett Packard 5890 GC with a Hewlett Packard 5791A Mass Selective Detector (MSD) operating in single ion mode. The column used was a 25 m x 0.2 mm Hewlett Packard HP-5 (5% phenyl methyl silicone bonded phase). The chromatography conditions are listed below.

<u>Chromatographic parameters used for atrazine, carbofuran, trietazine and terbutryn analysis</u>

Initial oven temperature	55 °C
Temperature ramp A	12 °C/min
Final temperature	220 °C
Hold time	0 min
Temperature ramp B	25 °C/min
Final temperature	280 °C
Hold time	4 mins

Quantification was achieved by external calibration standards 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 0.01 µg/l in the environmental samples.

Soil

<u>Carbofuran</u>

A sample of soil (40 g) was shaken with 100 ml of an acetone/water mixture (9:1 v/v) for 1 hour and then centrifuged. Anhydrous sodium sulphate (10 g) was added and the sample left to stand for 10 minutes. An aliquot (25 ml ≡

10 g soil) of the supernatant liquid was removed and evaporated to dryness. The residue was dissolved in toluene (2 ml) and quantitated using gas-liquid chromatography. Equipment and conditions used: Hewlett Packard 5890 Series II GC with Nitrogen-Phosphorus detector and HP 7673 auto sampler; DB 608 (bonded) column; injector temperature 200 °C, column temperature initially 120 °C, then at 15 °C/min to 190 °C, hold for 6 minutes, then 25 °C/min to 220 °C, detector temperature 250 °C.

Moisture contents were determined by heating a weighed sample overnight in an oven and re-weighing after cooling.

Atrazine

A sample of soil (10 g) was made alkaline by adding 0.5 ml of ~ 0.1 M NaOH solution and was then shaken vigorously with 10 ml ethylacetate for 5 minutes. The mixture was then allowed to stand overnight in the dark. The ethylacetate was decanted off and the soil was rinsed with a further 10 ml ethylacetate. The ethylacetate extracts were combined and the simazine internal standard was added. The extracts were then evaporated to dryness at ~ 50 °C under a stream of nitrogen. Distilled water (1 ml) and ~ 0.1 M NaOH (0.5 ml) were added to the residue and the mixture thoroughly shaken. Atrazine and simazine were extracted from the aqueous phase using 10 ml of dichloromethane; this extract was evaporated to dryness and the residue dissolved in 1 ml of ethylacetate and quantitated using GC. Equipment and conditions used: Carlo Erba Fractovap 4160 series GC with a RTx-5 capillary column, nitrogen-phosphorus thermionic detector and Trio computing integrator; column temperature initially 55 °C, then 30 °C/min to 140 °C then hold at 140 ° for 18 minutes; detector temperature 230 °C.

5.6.2.2 Results and Discussion

Water

These have not been corrected for recovery, which was 71 ± 11% for atrazine and 98 ± 8% for carbofuran. In the samples preserved with mercuric chloride (event of 14 April 1992), apparent concentrations of carbofuran were approximately 3 times higher than in the untreated samples, indicating that some degradation had occurred between sampling and analysis.

However, mercuric chloride was not used for the majority of samples during this experiment, and the results have not been corrected for this factor.

Table W1 (Appendix XII) lists the results obtained with the samples collected manually throughout the whole experiment. As with previous experiments, these indicate that concentrations of atrazine and carbofuran in the stream were generally below 0.3 µg/l (maximum 1.5 µg/l) between rainfall events, while concentrations in field drains between events were generally higher (up to 14 µg/l atrazine and 1.5 µg/l carbofuran). The ditch at Site 2 was also significantly contaminated on some between-event occasions.

Rainfall event on 8 January 1992

The first significant rainfall event was on 8 January 1992, when 71.5 mm fell during the 24 h from 14.00. The return time of this event was 50 years, and it caused some overland flow, although little if any of this reached the stream.

Bioassay organisms (the crustacean amphipod *Gammarus pulex*) had been held in cages in the stream since the beginning of the experiment and were subjected to the carbofuran and atrazine residues which appeared in the stream water on 8 January 1992 (Table W2, Appendix XII). A full report of the bioassay results has been prepared for publication in Ecotoxicology and Environmental Safety (Matthiesen *et al*, 1994) and is reproduced in full in Appendix XI. In summary, this work shows that the carbofuran reached concentrations in the stream (maximum 26.8 µg/l) which were present for sufficiently long to reduce *Gammarus* feeding rate and then kill all the test organisms. Subsequent laboratory trials showed that the 24 h LC50 of carbofuran for *Gammarus pulex* is only 21 µg/l, so it is perhaps not surprising that substantial mortalities occurred. In contrast, the peak atrazine concentration (5.7 µg/l) was below the UK Environmental Quality Standard (10 µg/l as a maximum value) so would not have contributed significantly to the observed biological effects.

This is the first demonstration at Rosemaund that field drainage can lead to toxic effects in stream organisms. Earlier *Gammarus* bioassay data reported in the Annual Report had failed to show any response to a mecoprop/dichlorprop run-off event, but this was to be expected as the phenoxy acid herbicides are much less toxic to crustacea than carbofuran. However, data to be presented in the next Annual Report for a chloropyrifos run-off event indicate that the positive bioassay results obtained with carbofuran are not unique.

The concentration/time profiles for carbofuran and atrazine in the Site 3 field drain during this event (Figure W3) were similar to those seen for other chemicals (i.e. an initial peak followed by a gradual tailing-off), although a second carbofuran peak was seen in the stream (Figure W2). The maximum levels of carbofuran and atrazine in the drain (264 and 51 µg/l, respectively) were some of the highest of any pesticide studied at Rosemaund.

Rainfall event on 25 January 1992

This was a relatively small rainfall event (9.0 mm) but resulted in even higher carbofuran concentrations in the stream (peak 49.4 µg/l) than on 8 January 1992 (Figure W4). No bioassays were being run at this time, but previous experience shows that this event would also have been acutely toxic to crustacea and insect larvae. Atrazine also peaked at a higher level than on 8 January 1993 (13.3 µg/l), a value which exceeded the UK maximum EQS and may have been harmful to some plants and algae. Carbofuran concentrations in the field drain at Site 3 (Figure W5) were even higher, peaking at 58.4 µg/l, with a subsidiary peak of 40.1 µg/l after 7 hours. Atrazine only reached a maximum of 8.9 µg/l in this field drain.

Rainfall event on 14 April 1992

This was a fairly substantial rainfall event of 19 mm. By this point in the experiment, considerable degradation of carbofuran and atrazine would have taken place in the fields, and this is reflected in the lower peak stream concentrations of 2.3 and 0.23 µg/l for carbofuran and atrazine respectively (Figure W6). This brief peak of carbofuran would have been unlikely to cause toxic effects in stream fauna. Concentrations in the Site 3 drain peaked at 9.9 and 0.65 µg/l for carbofuran and atrazine respectively (Figure W7).

Rainfall event on 28 May 1992

This was a rather discontinuous event (total 18 mm), but 10.5 mm of it fell during one half-hour period, and it was this which gave rise to a small amount of run-off. Carbofuran and atrazine were now approaching background levels, and peaked in the stream at only 0.02 and 0.13 µg/l, respectively (Figure W8). As in previous events, concentrations in the Site 3 drain were a little higher, peaking at 0.18 and 1.7 µg/l for carbofuran and

Figure W2. Rosemaund Site 1. Carbofuran/Atrazine Experiment. 8.1.92-13.1.92

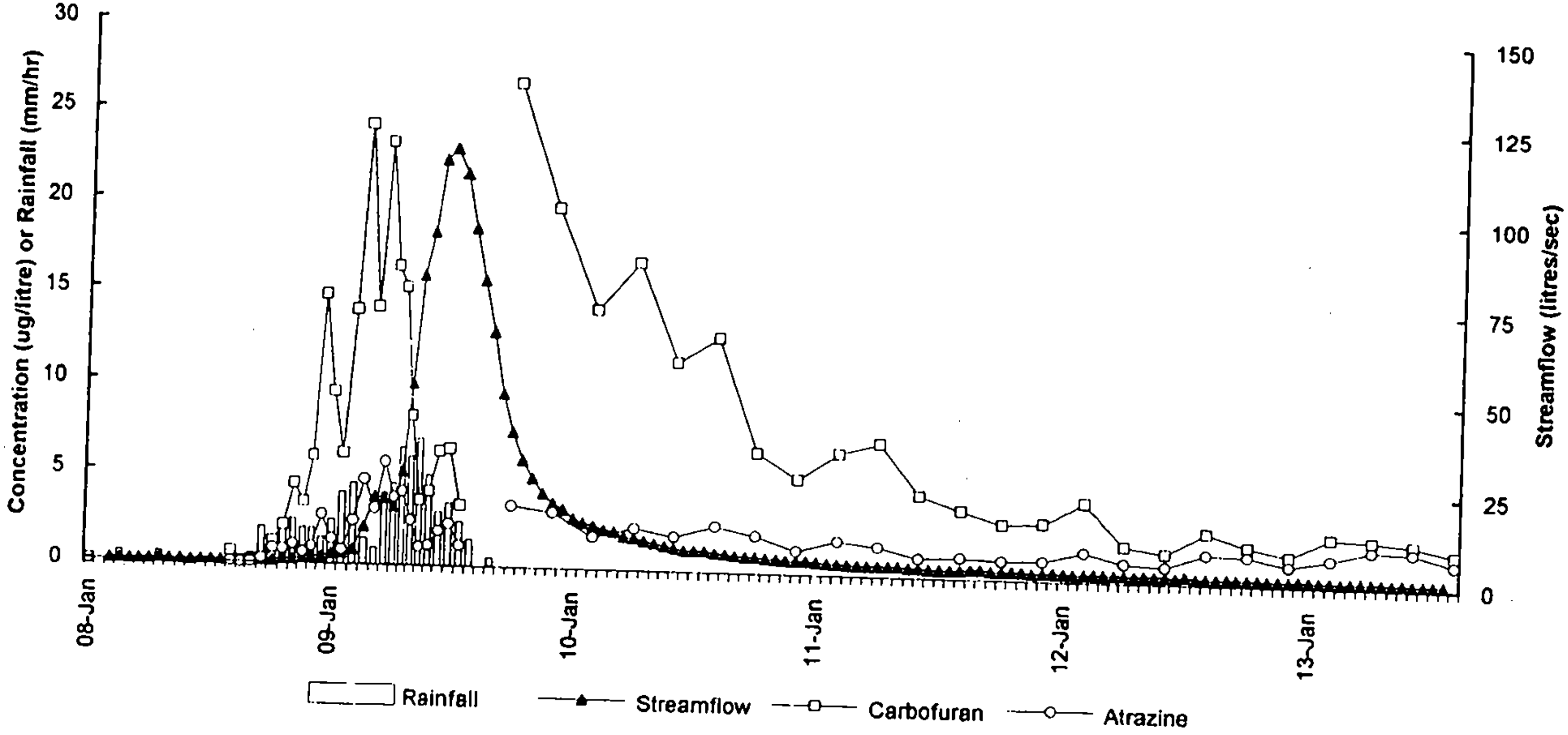


Fig W3. Rosemaund Site 3. Carbofuran/Atrazine Experiment. 8.1.92-13.1.92

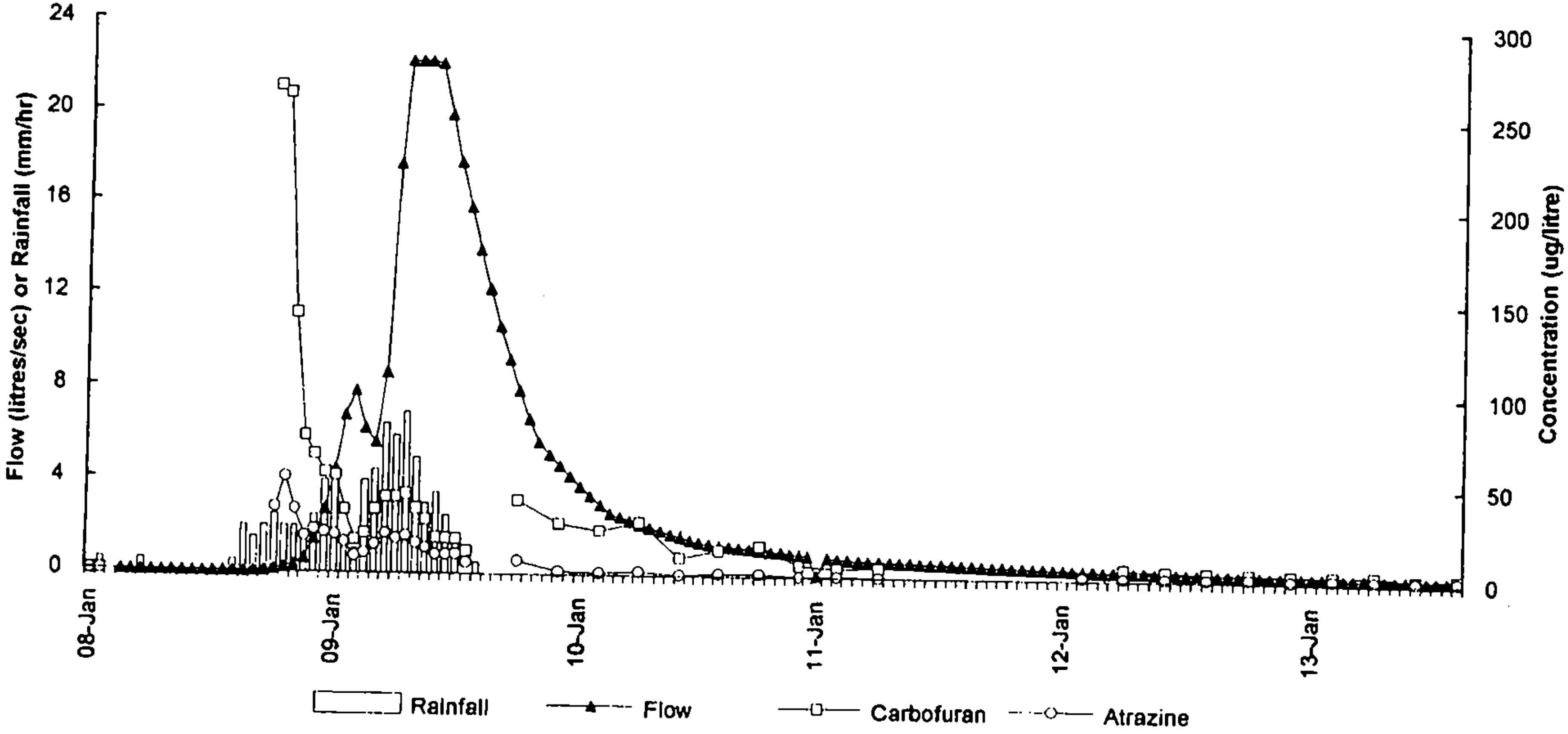


Figure W4. Rosemaund Site 1. Carbofuran/Atrazine Experiment. 25.1.92

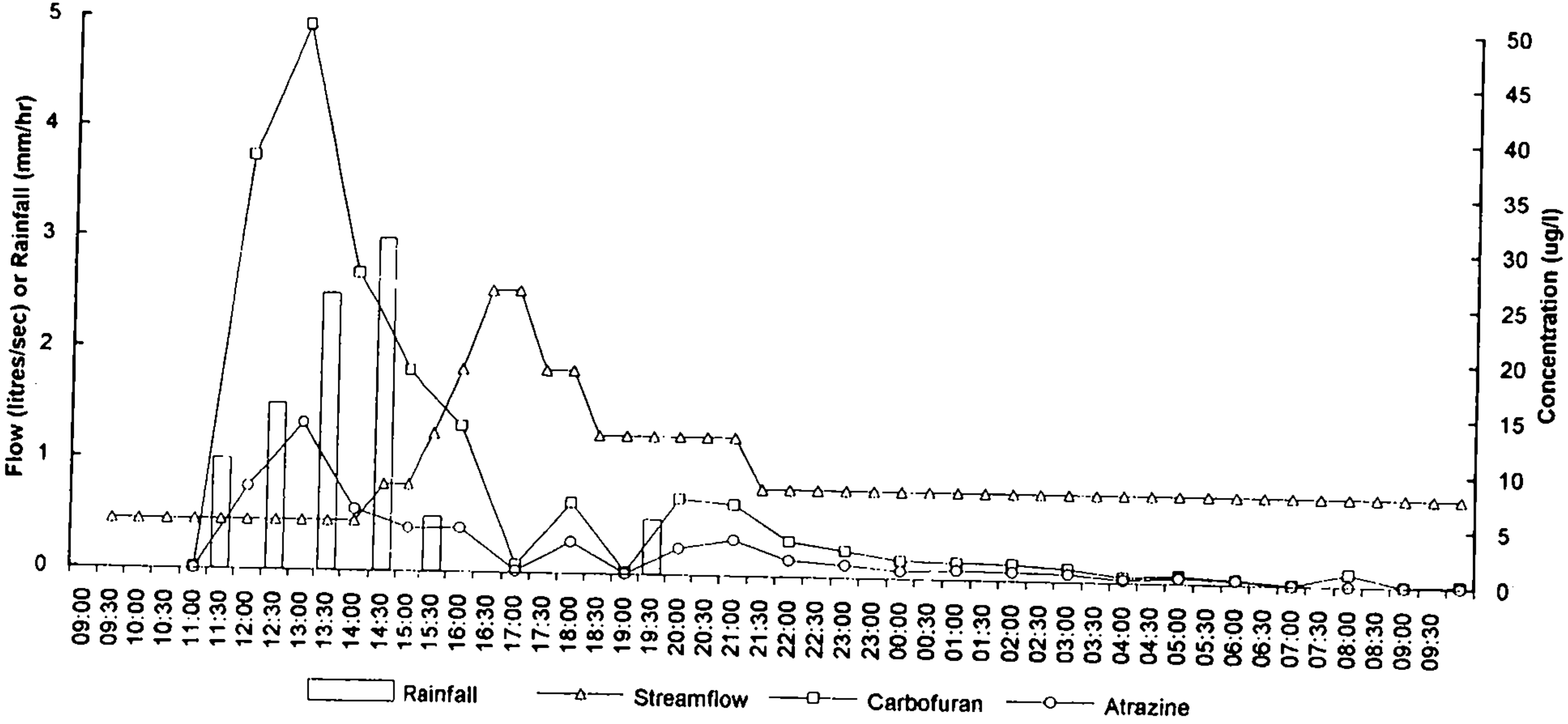


Figure W5. Rosemaund Site 3. Carbofuran/Atrazine Experiment. 25.1.92

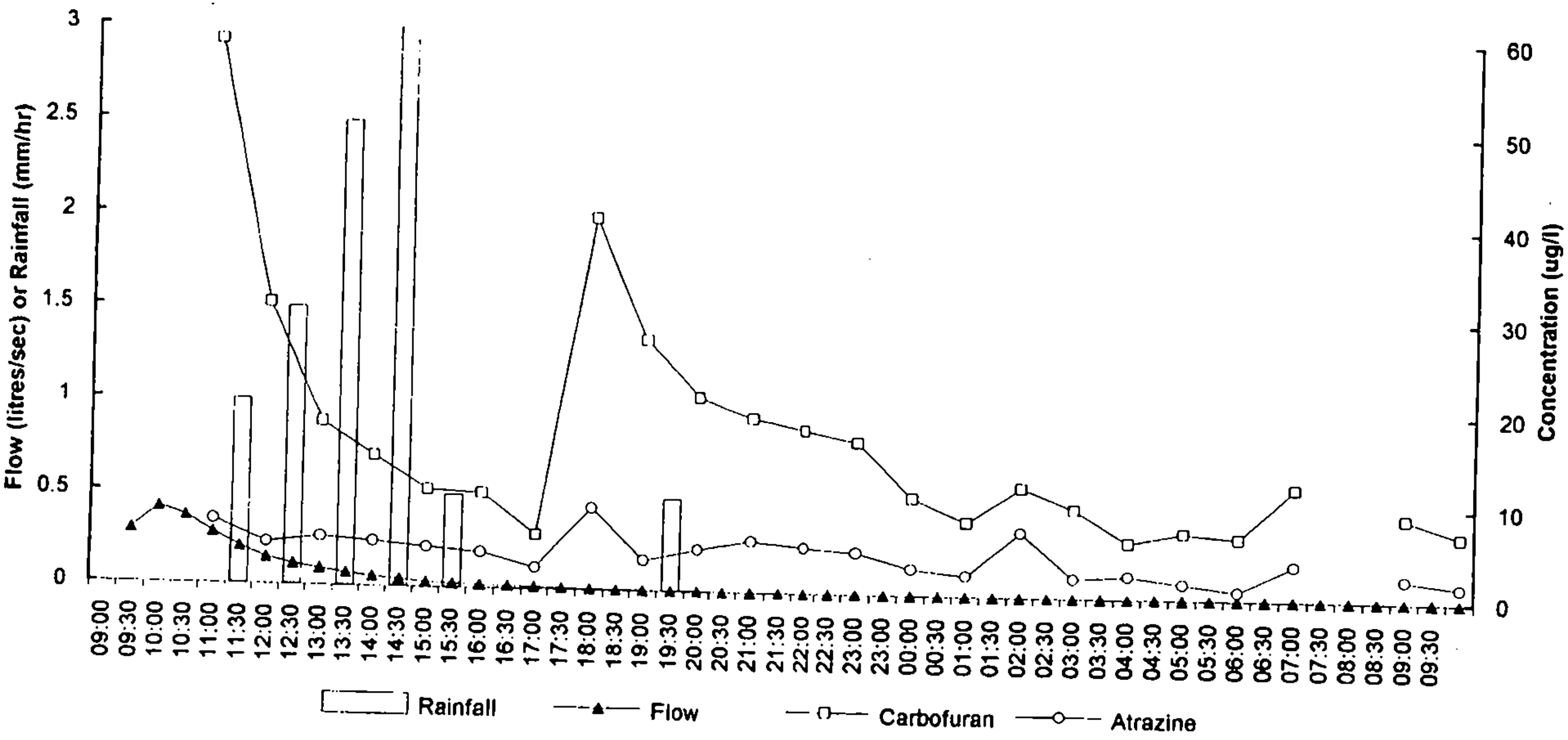


Figure W6. Rosemaund Site 1. Carbofuran/Atrazine Experiment. 14.4.92

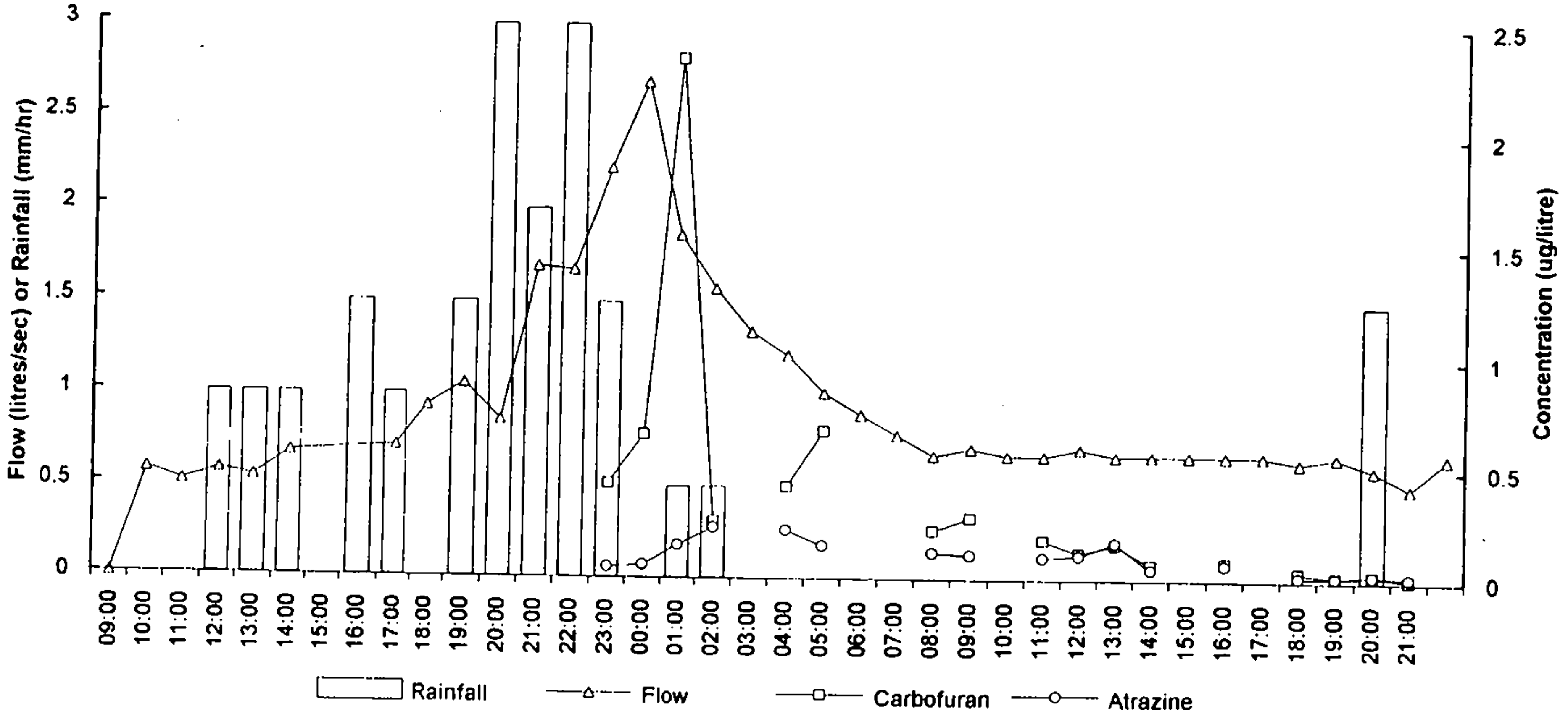


Figure W7. Rosemaund Site 3. Carbofuran/Atrazine Experiment. 14.4.92

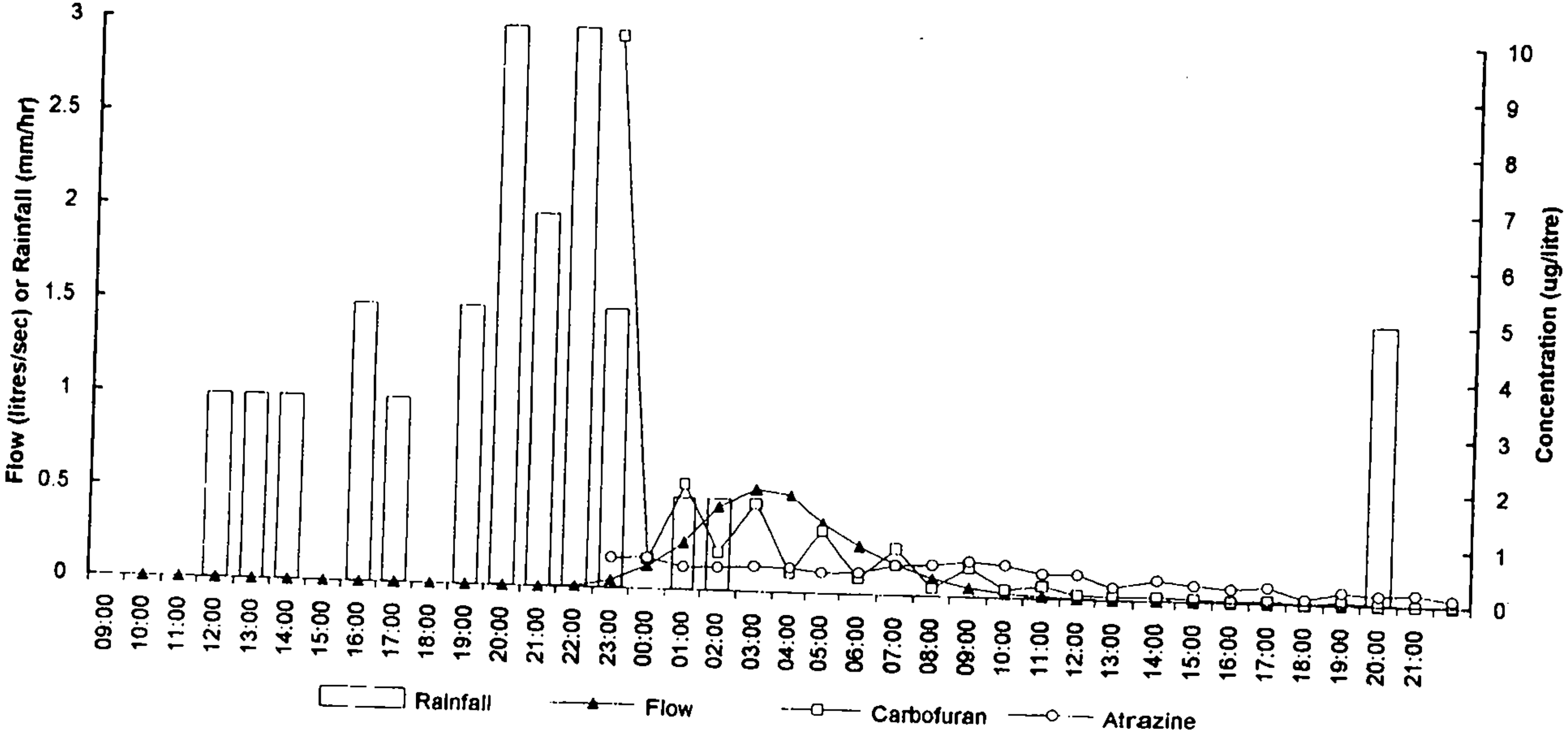
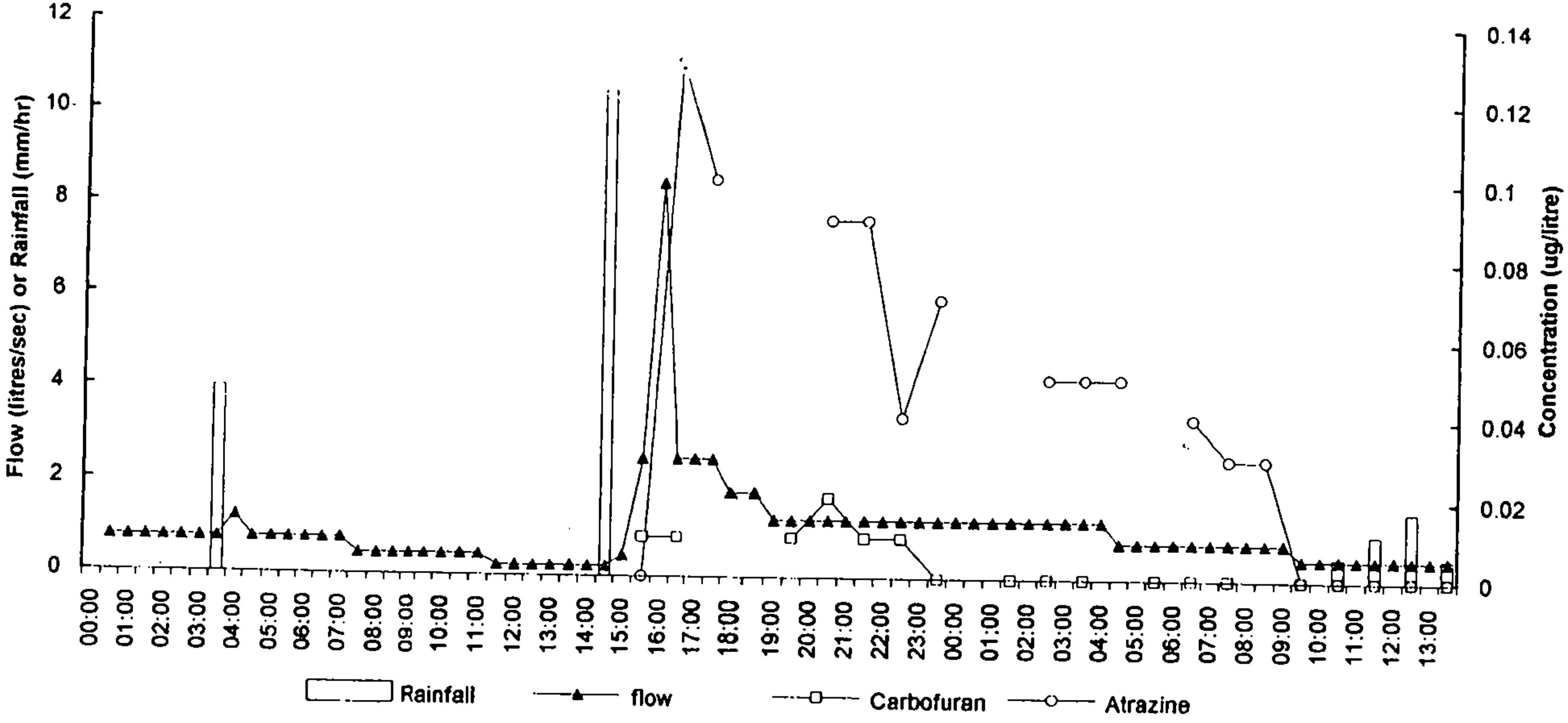


Figure W8. Rosemaund Site 1. Carbofuran/Atrazine Experiment. 28.5.92



atrazine respectively (Figure W9). It is worth noting that pesticide concentrations in the ditch at Site 2 were generally much lower than those appearing in the field drains, and this cleaner water usually provided dilution for the high field drain concentrations before water flowed down the stream to Site 1.

Soil

Data on the levels of carbofuran measured in soil samples are presented in Appendix IX, tables B5-B11 and a plot of concentration against time is shown in Figure B1. The initial samples were taken on 10 December 1991, one week after application, and had a mean concentration of 0.35 ppm. The last samples were taken on 4 March 1992, when the mean level was 0.087 ppm. All cores taken on the final sample visit contained measurable residues. The data suggest a half life of 38 days if first order degradation is assumed. In general the profile samples show the highest levels to be in the top layers, with lower but measurable concentrations at greater depths. The first profile sample appears different, with higher levels at depth. As only one such sample was taken it is not possible to determine whether this was a genuine distribution or the result of contamination.

Data on the levels of atrazine measured in soil samples are presented in Table B4 (Appendix IX). The initial level in Foxbridge and Longlands after spraying was 97 µg/kg wet weight. The last samples were taken on 1 April 1992, by which time the levels had decreased to 17 µg/kg; atrazine was still quantifiable in each sample. Assuming first order degradation, the data suggest a half life of 45 days. The profile samples show that in all cases, the majority of the chemical was found in the top 25 cm, with lower but measurable concentrations at greater depths.

5.6.2.3 Soil water

Atrazine and carbofuran residues found in soil water taken by soil suction samplers (see previous reports for details) are shown in Tables W15 and W16 respectively (Appendix XII). These show that significant amounts of both substances had reached field drain depth within about 1½ months of pesticide application. However, although peak atrazine concentrations in soil water

Fig. B1

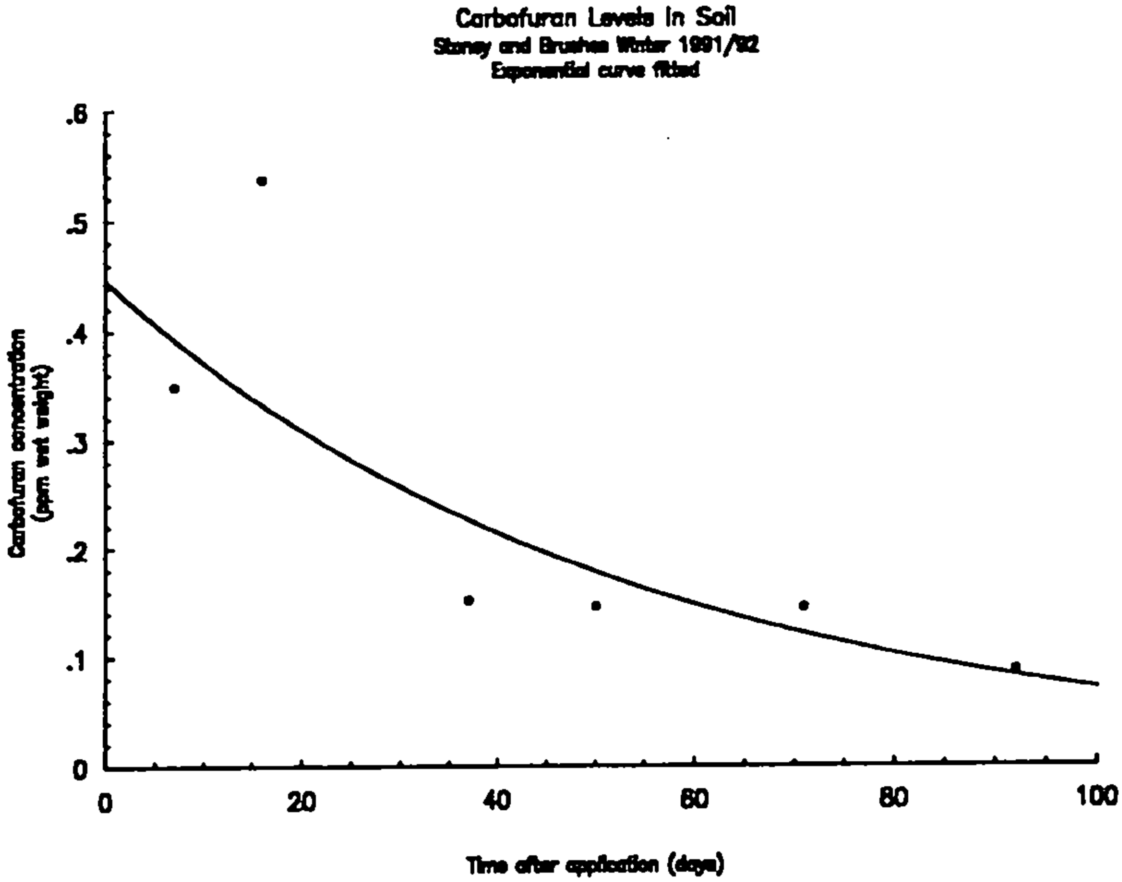
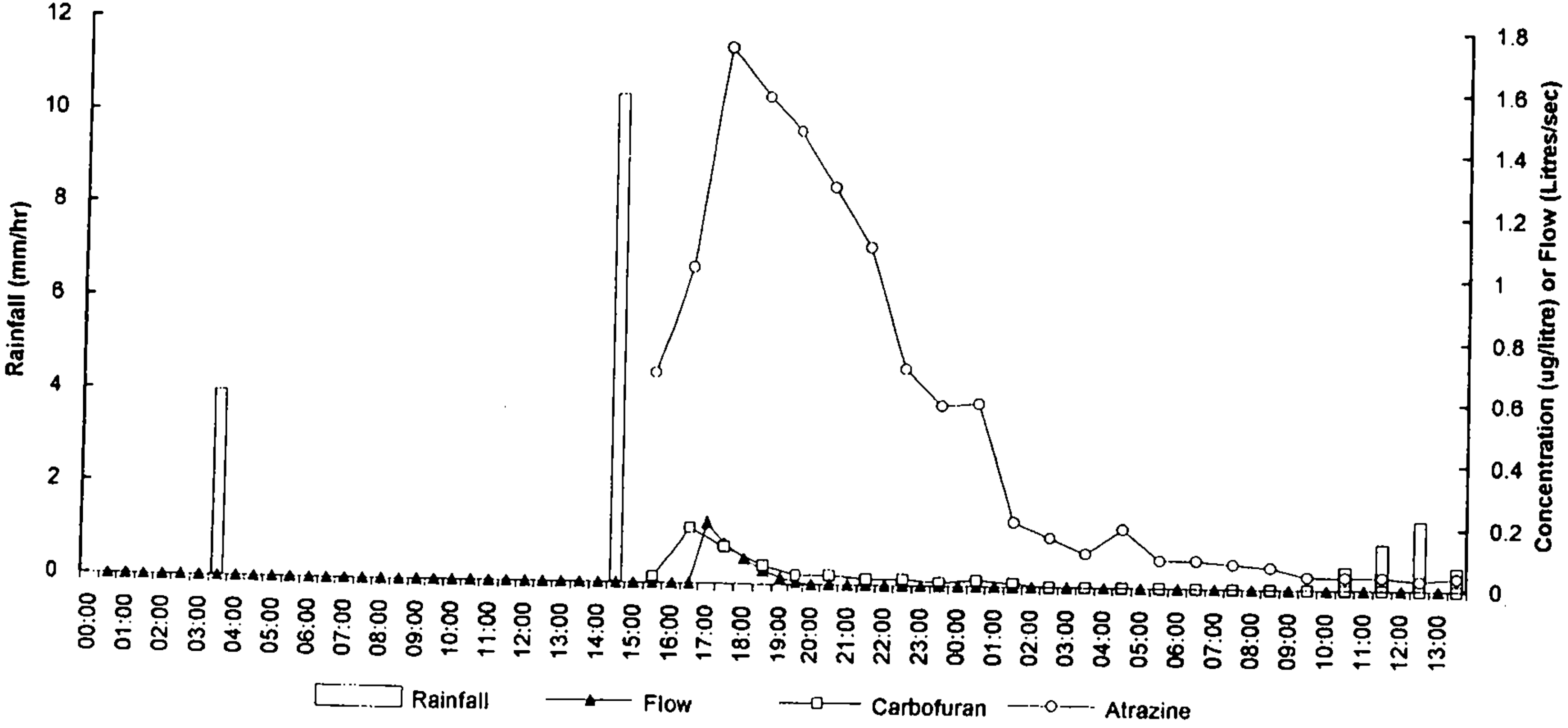

Carbofuran Levels In Soil
Stoney and Brushes Winter 1991/92
Exponential curve fitted
Carbofuran concentration
(ppm wet weight)
.6
.5
.4
.3
.2
.1
0
0
20
40
60
80
100
Time after application (days)

Figure W9. Rosemaund Site 3. Carbofuran/Atrazine Experiment. 28.5.92



(28.3 µg/l) reached and exceeded the maximum values seen in the Site 3 field drain (13.3 µg/l), carbofuran levels were always considerably lower (max. 2.6 µg/l) than in the drain (264 µg/l). The explanation for this discrepancy is that carbofuran was not applied to the field in which the suction samplers were situated (Foxbridge and Longlands). This raises the question of how any carbofuran could have reached the samplers, but it is assumed that some sub-surface lateral flow was occurring. The precise mechanism of this flow is not understood given that the samplers were on the opposite slope of the catchment to the field (Stoney) where the carbofuran was applied.

5.6.2.4 Conclusions

The overall picture of carbofuran and atrazine run-off was similar to that seen in previous experiments with other pesticides. Concentration peaks were brief, and generally slightly preceded the main flowrate peak, after which concentrations declined rather more slowly than they increased. The novel feature of this experiment was that at least two events would have caused substantial mortality of stream fauna due to the high toxicity to arthropods of carbofuran. This is one of the first recorded instances of acutely toxic field drainage water, and indicates the need for improved predictive models of pesticide run-off.

5.6.3 IH/NRA Experiment

5.6.3.1 Methods

Sample collection methods were fully described in the Report for years 1-3.

After collection, samples were delivered to the NRA laboratory at Llanelli where they were store below 4°C until analysed. Prior to analysis internal standards, Deutero D8 Napthalene and Deutero D5 Atrazine, were added to each sample bottle. Each sample was split, with one half undergoing neutral extraction with 50 ml dichloromethane (carbofuran) and the other a base extraction (pH10) again with 50 ml dichloromethane (atrazine and simazine). Both extracts were combined and concentrated to 0.5 ml using a Zymark Turbovap. The concentrated extract was split in to two 250 µl portions.

Atrazine and simazine were analysed from one extract using Capillary Gas Chromatography with Mass Spectrometric Detection in Selective Ion Monitoring mode (GC-MS-SIM). A 50 m by 0.32 mm BPX 5 column was used with helium as the carrier gas flowing at 1.5 ml/min (ambient). A 5 µl splitless injection at 250 °C was used, the transfer line was at 280 °C and the column programmed to 250 °C. A detection limit of 0.02 µg/l from a 1 l sample was estimated from the internal standards.

For the carbofuran analysis dichloromethane was removed from the remaining extract under Nitrogen steam and the residue resolvated in acetonitrile. Analysis was then carried out using High Performance Liquid Chromatography (HPLC) with Diode Array Detection. A 150 by 4.6 mm hypersil C18 column was used at a temperature of 40 °C. The carrying solvent was an acetonitrile/water mixture flowing at 1 ml/min. Carbofuran was detected at a wavelength of 220 nm. External standard calibration estimated a detection limit of 1.0 µg/l from a 1 l sample.

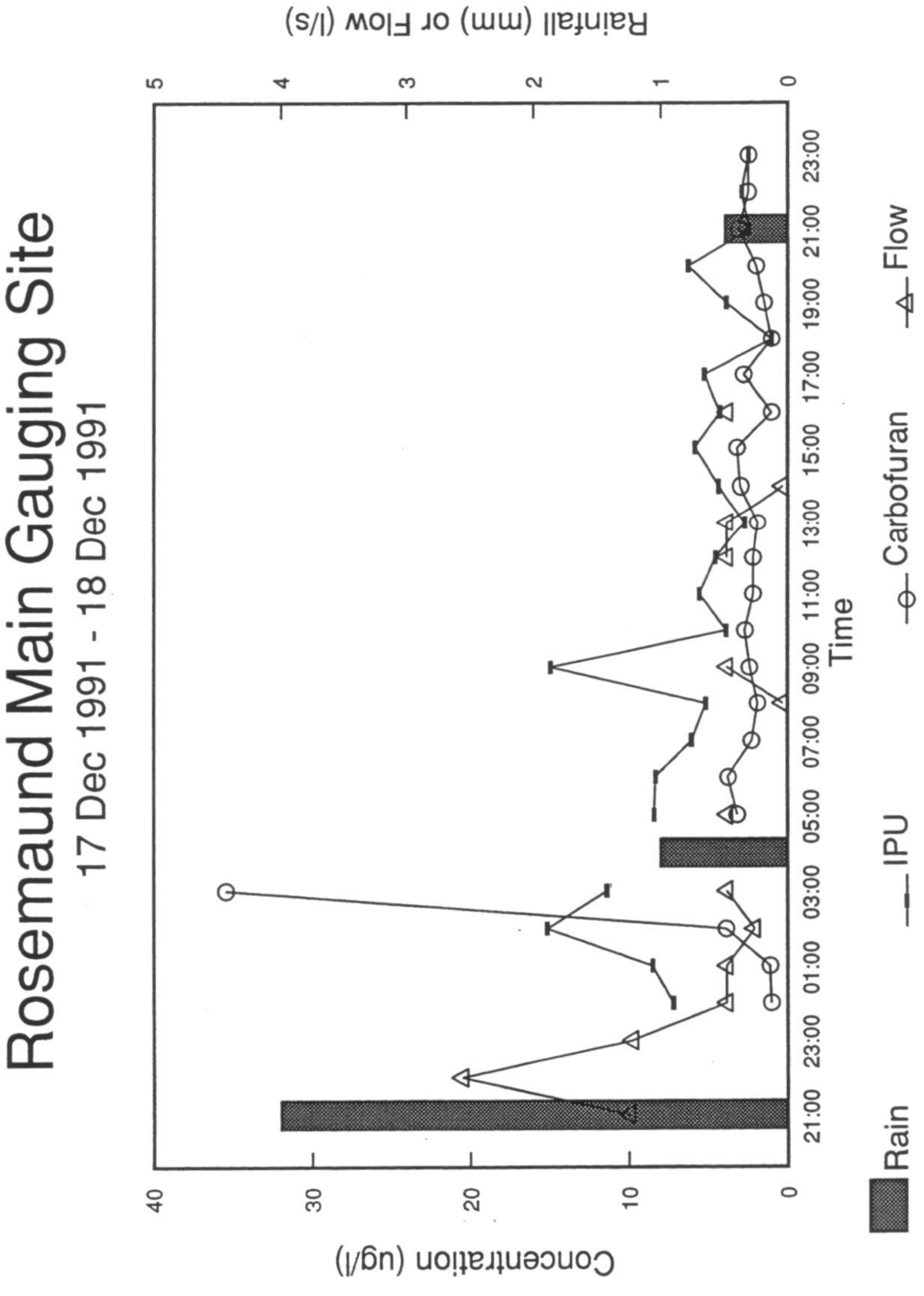
5.6.3.2 Results and Discussion

Rainfall event on 17 December 1991

A short rainfall event of 5 mm between 2100 on 17 December 1991 and 0500 the following day caused a rise in stage at the main gauging site (SO 5582 4789). This rise should not have been sufficient to trigger the sampler, however, the sample was triggered at midnight. A total of 24 samples were taken at one hourly intervals and analysed for atrazine, simazine, isoproturon and carbofuran. The results of the analysis are given in Table A1, Appendix X. The autosampler on Longlands Drain (SO 5688 4847) was not triggered by this event.

Isoproturon concentrations showed an initial rise to a peak value of 15.1 µg/l, subsequent values followed a general falling trend to concentrations around 2-3 µg/l (Figure IH1). Carbofuran also peaked early in the sample run at a value of 35.5 µg/l (Figure IH1). Although the carbofuran concentrations appeared to follow the pattern of a peak followed by a rapid decline to base levels, it is hard to justify this with only one point defining the peak. It is unfortunate that one of only two autosampler failures should have occurred during the possible carbofuran peak. Simazine and atrazine concentrations showed no obvious pattern through the event

Fig. IH1


Rosemaund Main Gauging Site
17 Dec 1991 - 18 Dec 1991
Concentration (ug/l)
0
10
20
30
40
Rainfall (mm) or Flow (l/s)
0
1
2
3
4
5
21:00
23:00
01:00
03:00
05:00
07:00
09:00
11:00
13:00
15:00
17:00
19:00
21:00
23:00
Time
Rain
IPU
Carbofuran
Flow

(Figure IH2). Both pesticides peaked in the latter half of the event at 1.17 µg/l and 1.79 µg/l for simazine and atrazine respectively. The similarity of the concentrations reflect a similar level of usage in the catchment.

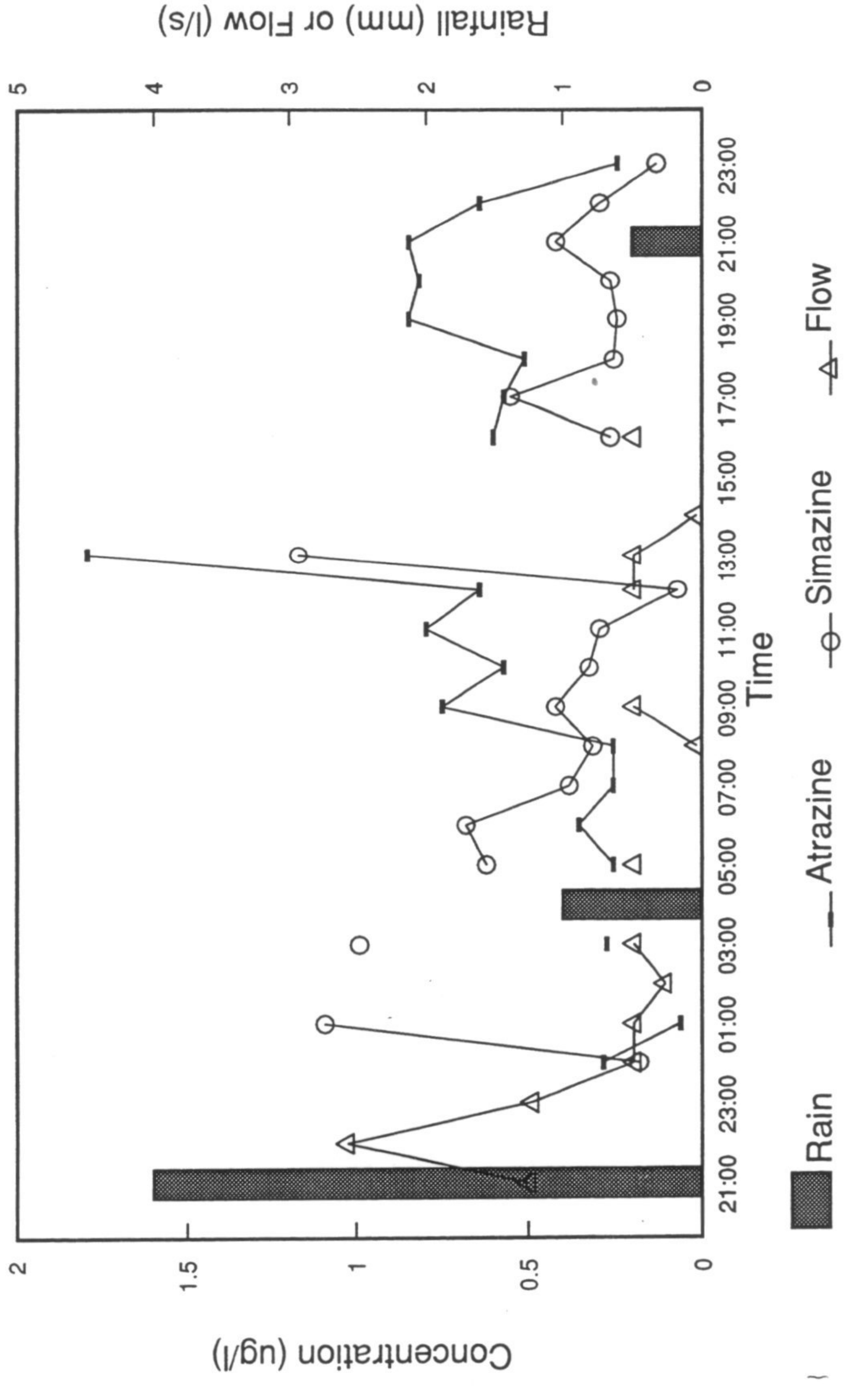
Rainfall event on 4 January 1992

Rainfall of 4 mm between 2200 on 4 January 1992 and 0300 the following day caused a small increase in drainflow at Longlands Drain (SO 5688 4849) which was not sufficient to close the trigger on the float switch. However the sampler at the linked sampler at the MAFF drain site (SO 5672 4842) was triggered which in turn started the sampler on Longlands drain. A total of 24 samples were collected and analysed for atrazine, simazine and carbofuran. The results of the analysis are given in Table A3, Appendix X. The sampler at the main gauging site (SO 5582 4789) was not triggered by this event.

Atrazine concentrations were consistently high throughout the event with a peak value of 51.1 µg/l and all values above 20 µg/l (Figure IH3). Simazine is often found in samples from various water courses around ADAS Rosemaund and, thus, it would be no surprise to find background levels in samples from this event despite its not having been applied to Longlands field. In general the concentrations found are at background levels, however, two samples showed unexpectedly high concentrations, most notably a value of 10.3 µg/l (Figure IH3). An analysis of the atrazine applied was carried out at the Institute of Hydrology laboratories and was found to contain some simazine, but only about 1%, clearly not enough to account for such high concentrations. Simazine was also found in a latter event (14 April 1992) from this drain and the reason for its appearance is under investigation.

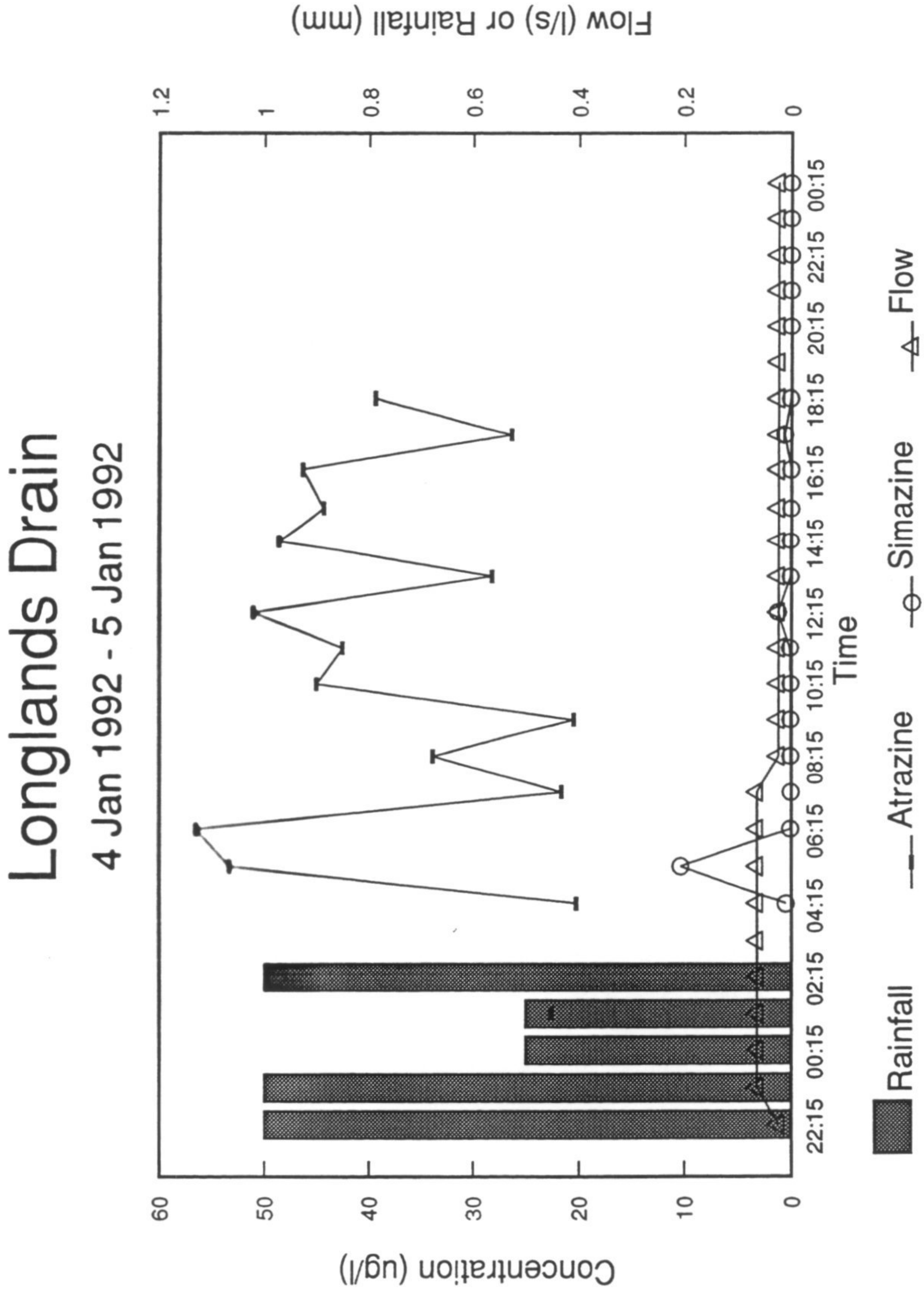
Carbofuran concentrations were generally below the detection limit as would be expected since it had not been applied to the field. Three concentrations were measured above the detection limit of 1 µg/l (max. 3.1 µg/l). Carbofuran had been applied to Stoney and Brushes (Appendix I), the adjacent field although on the other side of a valley. It is just possible that carbofuran may have migrated to the lowest most drainage lateral in Longlands field. This possibility is being investigated.

Fig. IH2


Rosemaund Main Gauging Site

17 Dec 1991 - 18 Dec 1991

Fig. IH3



Longlands Drain
4 Jan 1992 - 5 Jan 1992
Concentration (ug/l)
0
10
20
30
40
50
60
Flow (l/s) or Rainfall (mm)
0
0.2
0.4
0.6
0.8
1
1.2
Time
22:15
00:15
02:15
04:15
06:15
08:15
10:15
12:15
14:15
16:15
18:15
20:15
22:15
00:15
Rainfall
Atrazine
Simazine
Flow

Rainfall event on 8 January 1992

72 mm of rain fell between 1400 on 8 January 1992 and 1500 on the following day, this resulted in a significant rise in the flow rate from Longlands drain (Figure IH4). The sampler started before this rise in stage, being triggered by the linked sampler on the MAFF drain (SO 5672 4842). Samples were collected from 1100 on 8 January 1992 at hourly intervals for 24 hours. The sampler was reset at 1620 on 10 January 1992 and triggered manually to take a further 7 hourly samples from the tail of the event. Both sets of samples were analysed for atrazine, simazine and carbofuran, the results of these analyses are in Tables A4 and A5, Appendix X. The sampler at the main sampling site failed to trigger on the rising stage and was triggered manually at 1700 on 11 January 1992, 24 samples were collected at hourly intervals and analysed for atrazine, simazine, carbofuran and isoproturon. The results of the analyses are given in Table A2, Appendix X.

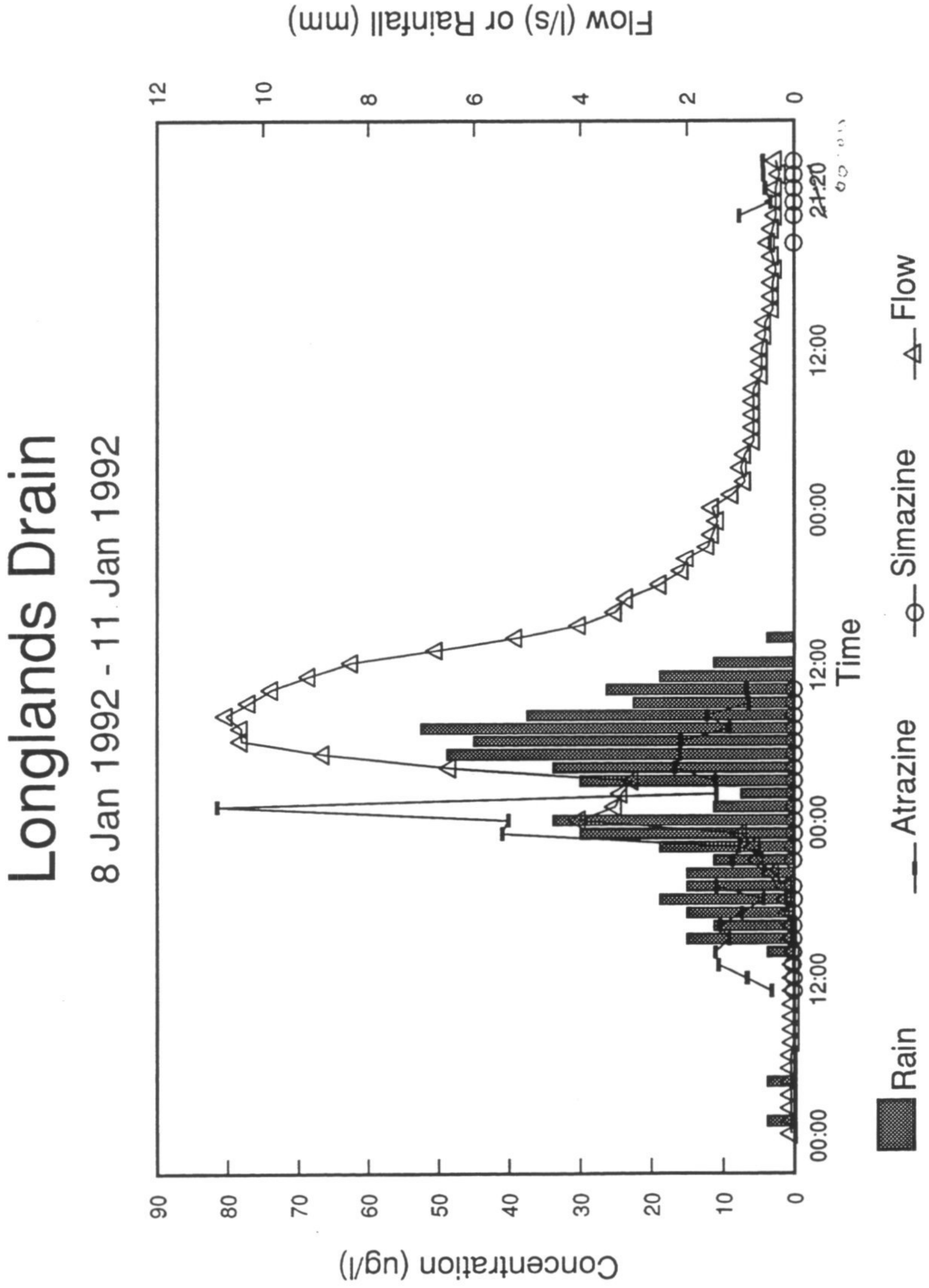
Longlands Drain

Atrazine concentrations were high throughout the event with a very noticeable peak of 81.4 µg/l occurring just before the peak flowrate (Figure IH4). The concentrations declined quickly after the peak and by the tail of the event had reached levels of around 4 µg/l. Simazine concentrations are generally below detection limits, those samples which show higher concentrations are consistent with the impurities of the atrazine applied as described above. Carbofuran concentrations are generally below the detection limit. Concentrations detected above this limit may have been caused in the same way as for the previous event described above.

Main gauging site

Atrazine and simazine were measured at similar concentrations with peak concentrations of 0.59 µg/l and 0.37 µg/l respectively (Figure IH5). Carbofuran concentrations are always below the detection limit. Isoproturon concentrations remain below the detection limit for the first half of the samples but then increase dramatically to a peak of 44.3 µg/l.

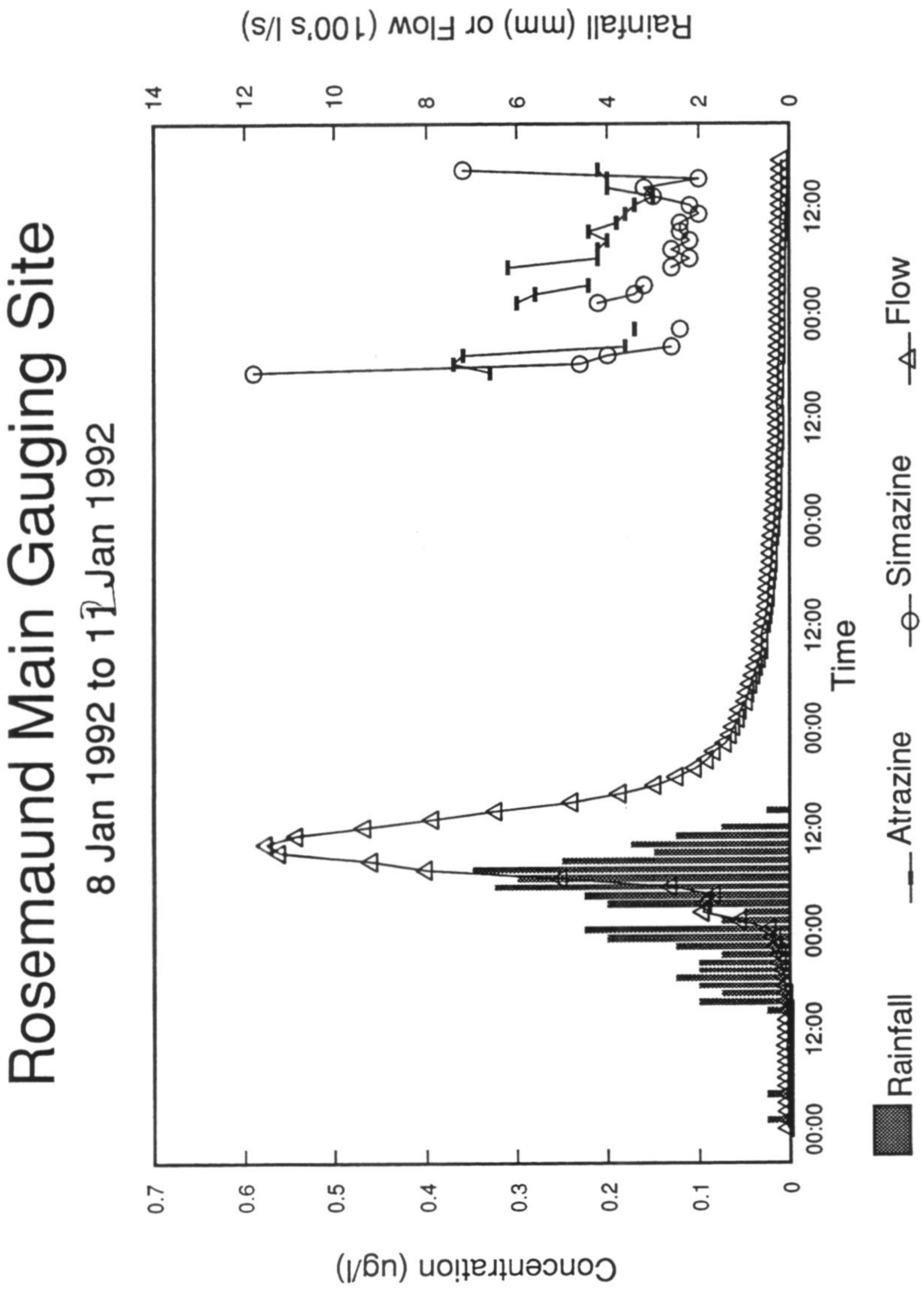
Fig.IH4



Longlands Drain

8 Jan 1992 - 11 Jan 1992

Fig. IH5


Rosemaund Main Gauging Site

8 Jan 1992 to 11 Jan 1992

5.7 VALIDATION OF PREDICTIVE PESTICIDE LEACHING/RUN-OFF MODELS -TRIETAZINE/TERBUTRYN/ALDICARB EXPERIMENT SPRING 1992

5.7.1 Introduction

The sampling set-up was identical with that described previously. The carbamate nematicide aldicarb (as Temik 10G granules) was applied to 4.2 ha of Foxbridge and Longlands on 27 February 1992 at a rate of 5.5 kg/ha active ingredient. The triazine herbicides terbutryn and trietazine were applied as the mixed formulation Senate to Foxbridge and Longlands (6 ha) at 1 kg/ha each on 5 March 1992.

5.7.2 MAFF/BRE Experiment

5.7.2.1 Methods

Sample collection methods were fully described in the Report for years 1-3.

Water

Sample treatment and analysis of the triazines was similar to the procedures described above for atrazine. The detection limit for terbutryn and trietazine was 0.01 µg/l and results have not been corrected for recovery efficiency, which was 91 ± 3% for trietazine. Recovery of terbutryn was poor, so results for the latter compound should be treated with caution. Some samples were treated with mercuric chloride to prevent biodegradation or residues during storage, but this had no effect on apparent concentrations of the triazines.

It was not expected to detect aldicarb, due to its rapid environmental degradation behaviour, and from the outset the analytical methodology was set up to detect the two major degradation products, aldicarb sulphoxide and aldicarb sulphone. The principle of the analysis requires raw water with no prior treatment, therefore samples were brought straight to Birmingham University and stored at 4 °C. It was hoped that these samples could be analysed soon after sampling; however, hardware improvisations meant that the analytical equipment took some months to develop. Due to this delay, as mentioned earlier with respect to carbofuran, it was decided to add a biocide, mercuric chloride, to every other sample from the rainfall event of 14 April 1992. The results indicate some preservation of the samples was achieved by this procedure, generally 10 to 20%, considerably less influence than shown earlier for carbofuran. No alteration of the results on the basis of storage or biocide has been undertaken and it is clear that these results must be treated cautiously. Analysis was performed by reversed phase HPLC coupled with post-column hydrolysis and reaction with mecaptoethanol and orthophthalaldehyde (OPA). This produced a fluorescent moiety for detection by specific fluorescence wavelengths. Instruments used were a Philips PU4100 HPLC and a Jasco programmable fluorescence detector. The excitation wavelength was set at 340 nm and the emission wavelength to 455 nm. The column was a 25 cm x 4.6 mm Spherosorb ODS2 C18 supplied by Phase Separations Ltd. The sample was injected through 0.2 µm 'Anotop 10' on-line syringe filters into a 500 µl sample loop. The column flow was set at around 1000 ml/min, although this was often reduced to prevent the back pressure exceeding the limit of 6000 psi. The peristaltic pump was set to deliver approximately 150 µl/min through each channel. These flow rates were reset for each period of analysis to optimise the sensitivity. Baseline stability was crucial for detection approaching 0.1 µg/l. Fresh solutions were also made up within 5 days. All solvents/solutions were degassed continually by a stream of helium. Quantification was achieved by direct injections of external calibration standard reference materials. All three of these were kindly supplied by the manufacturers of aldicarb, Rhone-Poulenc.

The initial post-column reaction is the hydrolysis of the parent compounds, all N-methyl carbamates, to release the primary amine. This required a temperature of 98 °C in the presence of sodium hydroxide. This was achieved by taking the eluent from the analytical column and mixing this with a flow of sodium hydroxide (0.2M) from the first channel of the peristaltic pump. This then passed down a 0.01" i.d. x 3m stainless steel capillary column held within the HPLC column oven to provide the required stable heat source of 98 °C. The second channel of the peristaltic pump fed a solution of orthophthalaldehyde and mercaptoethanol to the eluent of the stainless hydrolysis column. The solution was prepared weekly by dissolving sodium tetraborate decahydrate (5 g) in 900 ml DDW and using sonication to aid solution. Separately, OPA (1 g) was dissolved in methanol (50 ml), this was then added to the borate solution. Finally, to this was added mercaptoethanol

(1 ml), in a fume hood and the final volume then brought to 1000 ml by the addition of DDW. The presence of this OPA solution led to the formation of the fluorescent isoindole molecule. A short length (1 m) of narrow bore PTFE tubing prior to entering the flow cells in the detector was sufficient to complete the reaction at room temperature.

The instrumentation took some time to complete, due largely to the lack of suitable low volume, low pressure post-column delivery pumps. Three discrete systems were attempted; firstly using a steady back pressure of air above the two post column solutions. This proved unstable, allowing oscillations in the flow at the 'T piece' mixing points which resulted in excessive detector baseline oscillations. Secondly, a syringe pump was used but this did not have sufficient back pressure handling capacity and tended to spontaneously leak, thus changing mixing ratios with the secondary columns. Finally, a two channel peristaltic pump with thick walled silicone tubing provided a delivery system capable of sustaining a smooth enough baseline to reach the detection limit desired. This system was not totally reliable but allowed completion of the analysis to a limit of detection not less than 0.3 µg/l by direct injection of the sample into a 500 µl loop.

Soil

The soil sampling strategy and techniques were the same as for the Autumn 1990 experiments.

A sub sample of soil (30g) was shaken for two hours with an acetone-water mixture (9:1 v/v, 150 ml) and peracetic acid (2 ml) to ensure complete oxidation to aldicarb sulphone. After standing for 15 minutes, the supernatant liquid was filtered through Whatman GF/A paper and the first aliquot (100 ml) collected. The solution was evaporated to the aqueous layer; this was then transferred quantitatively, with the aid of a 10% sodium hydrogen carbonate solution (50 ml) to a separating funnel. The aqueous solution was partitioned with chloroform (60 ml) and the lower organic layer dried with anhydrous sodium sulphate. The partition was repeated with a further aliquot of chloroform (40 ml). The sodium sulphate was washed with chloroform (20 ml). All the organic fractions were combined and evaporated to a small volume (approximately 5 ml).

A column was prepared in chloroform using Florisil (6g) capped with anhydrous sodium sulphate (5g). The chloroform was eluted down to the sodium sulphate, and the sample extract added to the column. An aliquot of an acetone-diethyl ether mixture (5:95 v/v) was added and eluted. All fractions up to this point were discarded. An aliquot of a second acetone-diethyl ether mixture (25:75 v/v) was added and eluted. This fraction was collected and evaporated to dryness. The residue was dissolved in acetone and quantitated using gas-liquid chromatography. Equipment and conditions used: Hewlett-Packard 5890 Series IIGC with Nitrogen-Phosphorous detector and HP 7673 autosampler; 2% Carbowax 20M and 5% DC200 on Diatomite CLQ (80-100 mesh) column; injector temperature 200°C, column temperature 180°C, detector temperature 250°C.

Moisture contents were determined by heating a weighed sample overnight in an oven and reweighing after cooling.

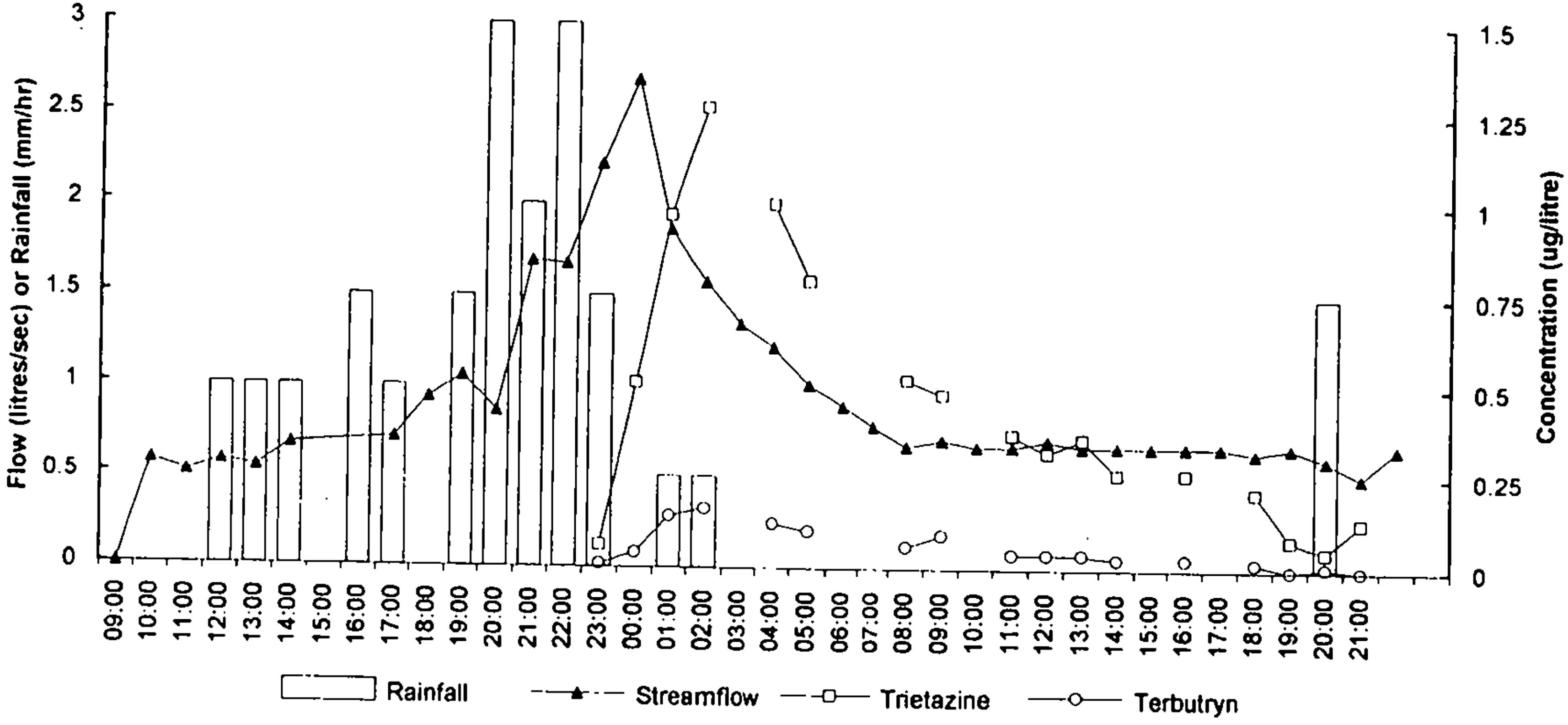
5.7.2.3 Results and discussion

Manual water samples analysed for the triazines and aldicarb are shown in Table W10 (Appendix XII). Background concentrations of triazines in the stream were low (max. 0.23 µg/l trietazine), and aldicarb was never detected, although the sulphoxide and sulphone were present at 0.3 µg/l respectively. Maximum background concentrations seen in the field drains and ditch were 2.9 µg/l trietazine, 0.31 µg/l terbutryn, 0.7 µg/l sulphoxide, 0.8 µg/l sulphone, and no unchanged aldicarb. However, it should be noted that these results only cover two sampling occasions, so are probably not representative.

Rainfall event on 14 April 1992

This was a 19 mm event in which trietazine peaked in the stream at 1.3 µg/l and terbutryn peaked at only 0.16 µg/l (but note the low extraction efficiency for this compound). Both materials behaved in a similar way to other water soluble herbicides (Figure W11). The aldicarb data have not been plotted, but only low levels of the sulphoxide and sulphone (max. 0.5 µg/l of each) were seen in the stream, and aldicarb was not detected. As expected, higher maximum levels of all determinands were seen in the Site 3 field drain (trietazine 3.6 µg/l, terbutryn 0.24 µg/l, sulphoxide 1.1 µg/l, sulphone

Figure W11. Rosemaund Site 1. Trietazine/Terbutryn Experiment. 14.4.92



1.1 µg/l). Again, highest levels were generally seen just before the peak water flow (Figure W12).

Rainfall event on 28 May 1992

Following the 10.5 mm rainfall pulse in the middle of this 18 mm event, peak concentrations of 0.52 and 0.06 µg/l of trietazine and terbutryn, respectively, were measured in the stream at Site 1 (Figure W13). No residues of aldicarb or its metabolites were found. Peak levels in the Site 3 drain were 0.52 µg/l trietazine, 0.06 µg/l terbutryn 0.7 µg/l sulphoxide and 1.5 µg/l sulphone (Figure W14). No unchanged aldicarb was detected.

Soil water

Trietazine, terbutryn and aldicarb residues in soil water are shown in Tables W17, W18 and W19 respectively (Appendix XII). Concentrations of both the triazines were generally somewhat lower than in the field drains (max. levels: trietazine 0.21 µg/l, terbutryn 0.17 µg/l) although both were found intermittently at field drain depth. In general, triazine residues did not appear in the soil water until 1-2 months after spraying, and many samples contained no detectable residues, reflecting the sparse rainfall during this period. Unchanged aldicarb was not detected in soil water, but the sulphoxide and sulphone made an appearance 1½ months after application, reaching peak concentrations of 9.1 and 12.8 µg/l respectively. Average levels were comparable with those seen in field drains, and aldicarb residues in soil water were still present at significant concentrations some 2½ months after application.

Soil

Results from the analysis of soil samples taken following the application of aldicarb to Foxbridge and Longlands on 27 February 1992 are shown in Appendix IX, Tables B12-B17. The first samples were taken on 5 March, one week later, and show a mean level of 0.03 ppm. Two weeks later the mean level had risen to 0.06 ppm, and then decreased to 0.02 ppm in the last samples taken on 6 May. There is no obvious reason for the increase in concentration between the first two samples, although the fact that the chemical was applied in a granular form means that the early distribution of the chemical may not have been as even as for others applied as a spray.

Figure W12. Rosemaund Site 3. Trietazine/Terbutryn Experiment. 14.4.92

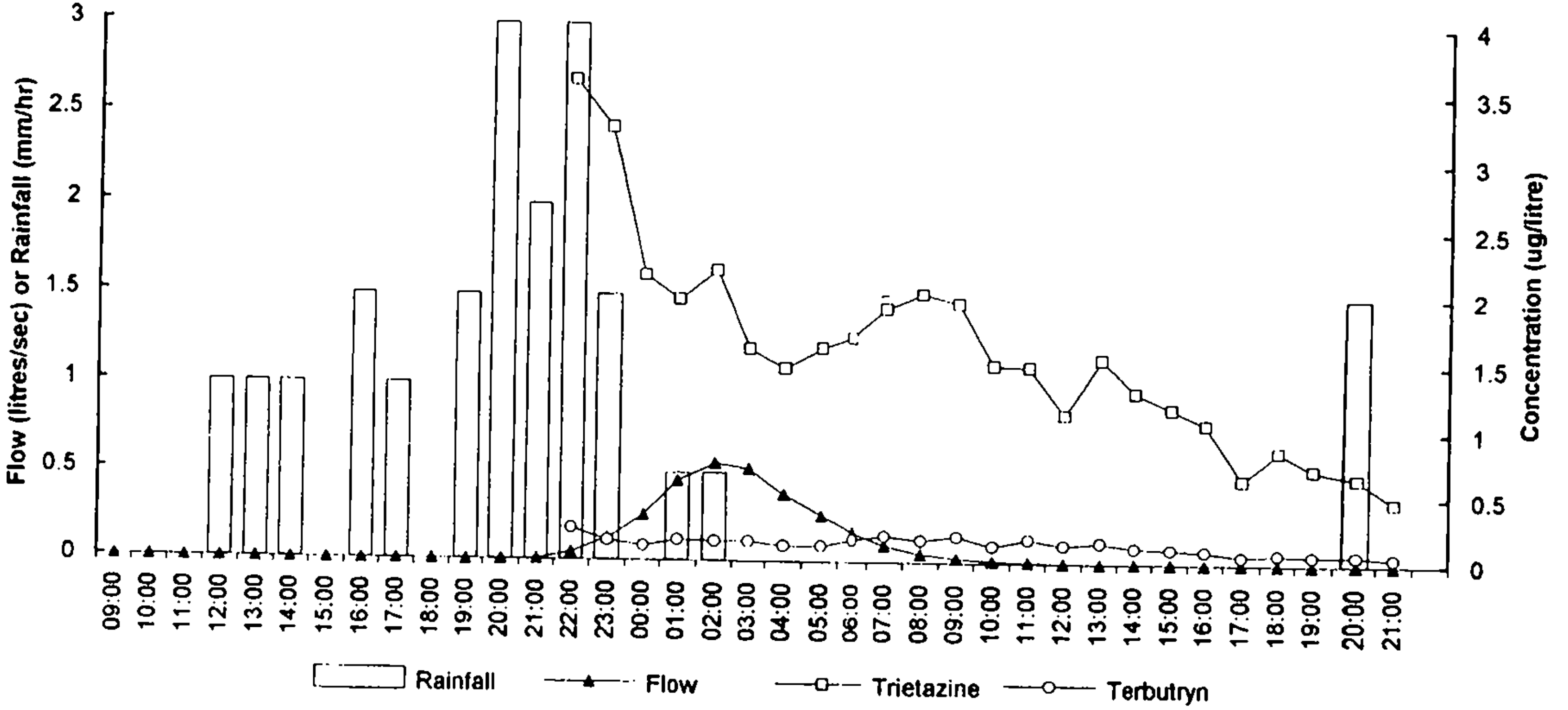


Figure W13. Rosemaund Site 1. Trietazine/Terbutryn Experiment. 28.5.92

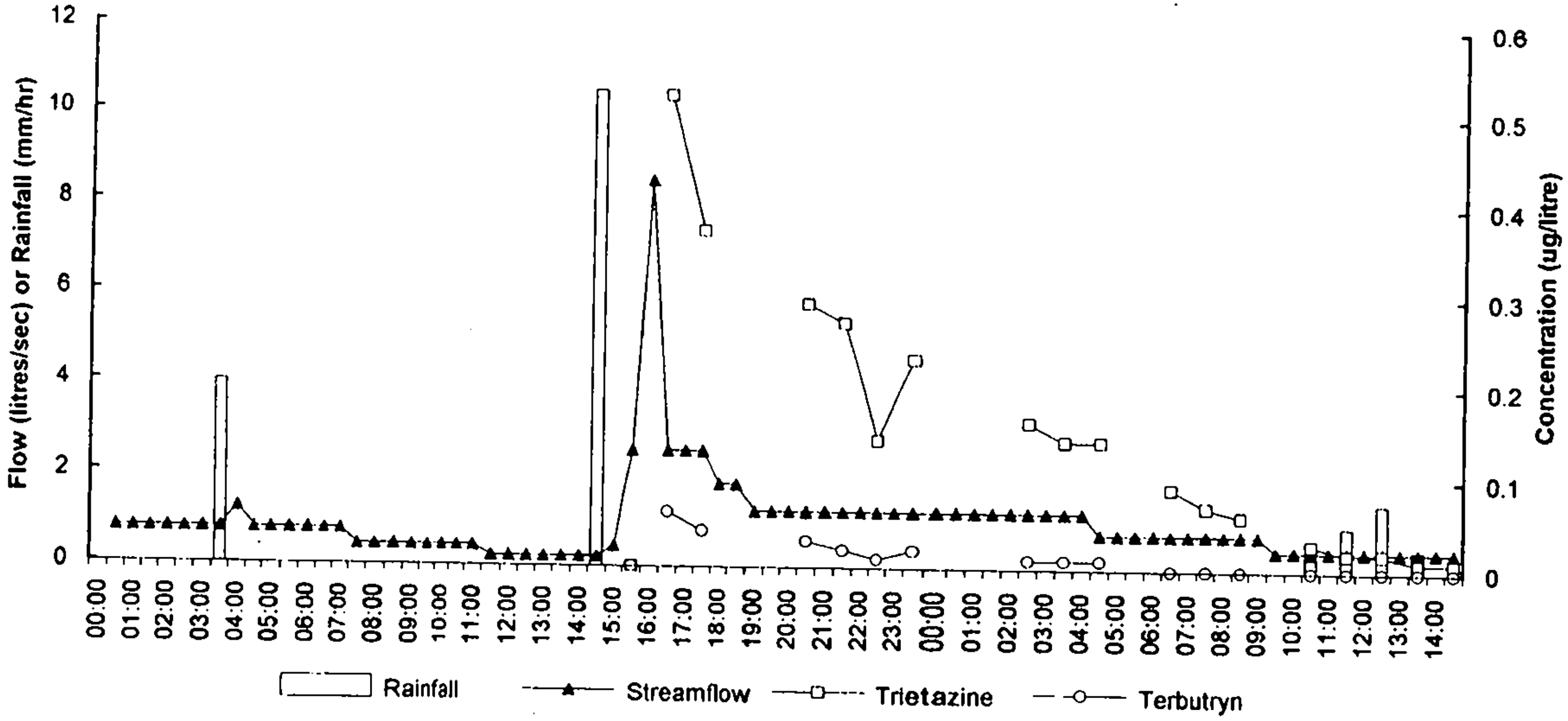
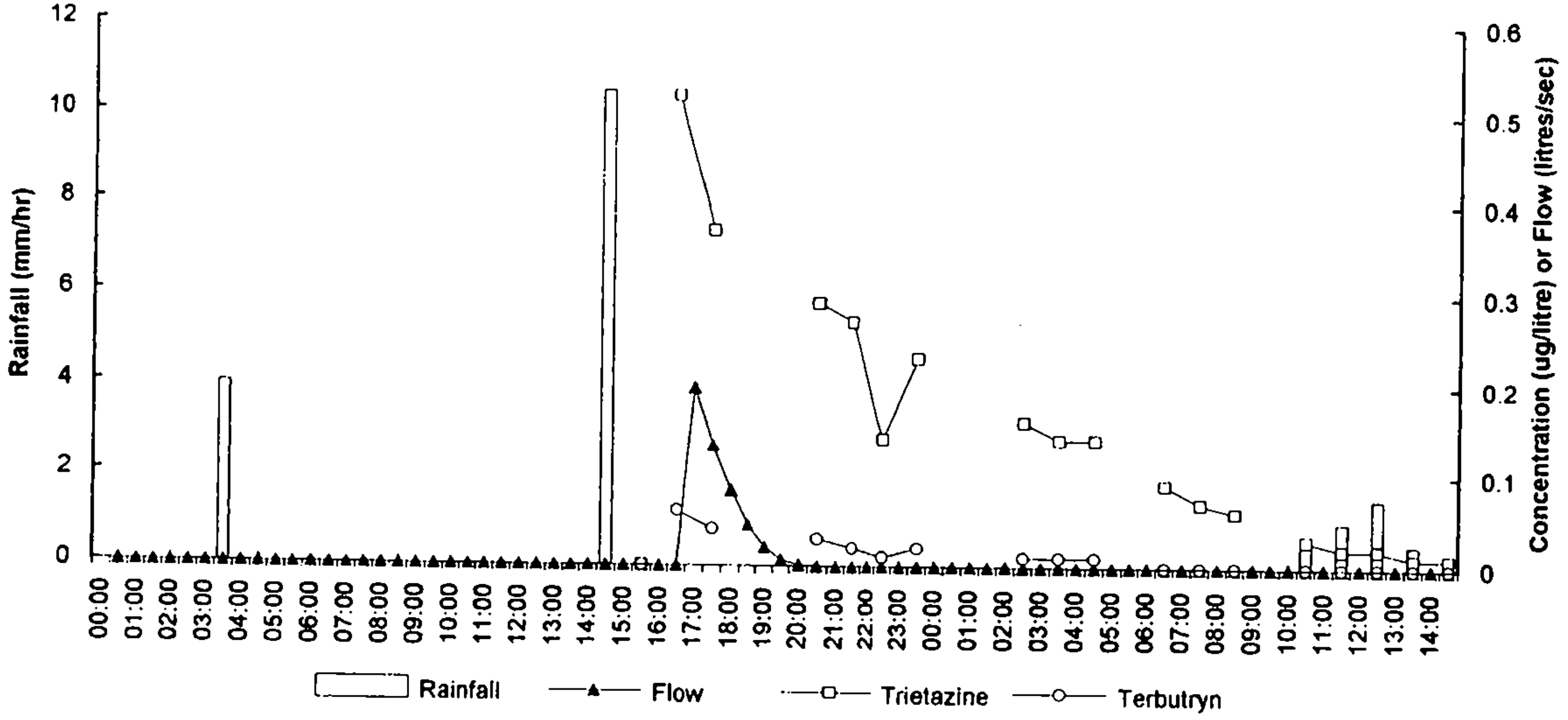


Figure W14. Rosemaund Site 3. Trietazine/Terbutryn Experiment. 28.5.92



The plot of concentration against time (Figure B2) shows considerable scatter. Fitting a first order exponential decay to the data gives an estimated half life of around 50 days. If the first sampling point is left out, the half life decreases to 25 days. The curve shown includes all the data.

5.7.2.5 Conclusions

The trietazine data, not unexpectedly, show that this herbicide translocates from soil to water is a similar manner to other triazines such as simazine and atrazine (max. concentration in stream water = 1.3 µg/l). The same also applies to terbutryn, although the reported concentrations are likely to be underestimates due to the poor recovery efficiency for this compound.

Unchanged aldicarb was not detected in any sample, but the sulphoxide and sulphone metabolites were seen in the stream at up to 0.5 µg/l each. However, these values should also be treated with caution due to the partial degradation which may have occurred during storage.

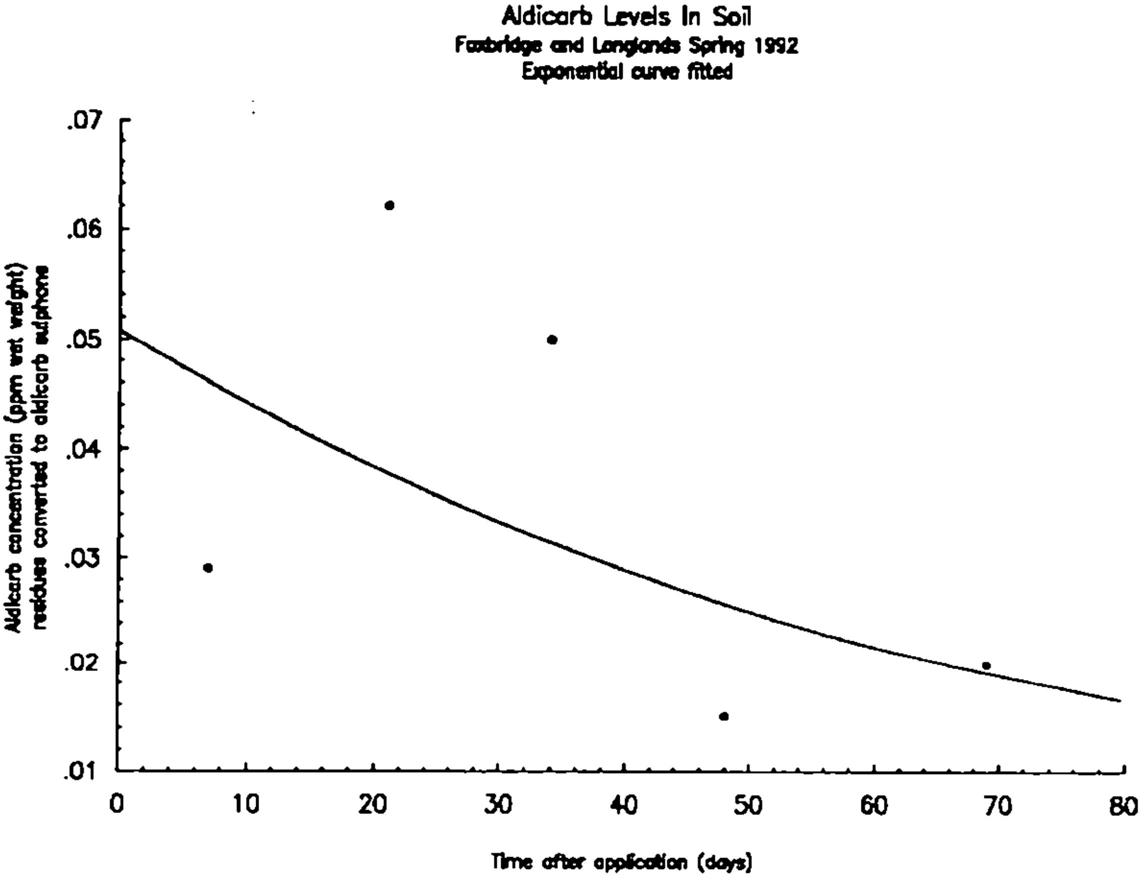
5.7.3 IH/NRA Experiment

5.7.3.1 Methods

The analysis of the samples collected during the spring event was carried out at the Institute of Hydrology. In addition to aldicarb and its degradation products, simazine, atrazine and isoproturon were measured.

Samples were stored at the Institute at a temperature below 4°C prior to analysis. For simazine, atrazine and isoproturon, 100 g of sodium chloride was dissolved in each sample which was then extracted sequentially with 100, 50 and 30 ml of dichloromethane. The combined extract was dried with anhydrous sodium sulphate and evaporated to dryness in a rotary evaporator. The residue was redissolved in 2 ml of pesticide grade ethyl acetate. Aldicarb and aldicarb sulphoxide and sulphone underwent further extraction. 300 µl of the ethyl acetate extract was evaporated in the dark and under nitrogen was dissolved in 300 µl of methanol, which was then diluted with 300 µl water.

Figure B2.


Aldicarb Levels In Soil
Foxbridge and Longlands Spring 1992
Exponential curve fitted
Aldicarb concentration (ppm wet weight)
residues converted to aldicarb sulphone
.07
.06
.05
.04
.03
.02
.01
0
10
20
30
40
50
60
70
80
Time after application (days)

Atrazine and simazine were analysed by Capillary Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC), isoproturon was analysed by HPLC alone and aldicarb and the sulphoxide and sulphone were analysed by HPLC with post column derivitization. For GC analysis a PTE-5, 30 m by 0.25 mm column was used with helium acting as the carrier gas. Injection mode was split/splitless at a temperature of 200 °C, using a 1 µl volume. The column temperature started at 60 °C for 1 minute then increased at 4 °C/min to 148 °C, and then at 10°C/min to 210 °C and then reduced back to 60 °C at -70 °C per/min. External standardisation gave a detection limit of 0.05 µg/l.

Isoproturon analysis by HPLC used a C8, 25 cm by 4.6 mm column, eluted by a 5%/95% acetonitrile and water mixture followed by a 95%/5% acetonitrile and water mixture both, at a rate of 1 ml/min. Detection was by ultra-violet at 220 nm wavelength for atrazine and simazine and 240 nm for isoproturon. Calibration using external standards gave a detection limit of 0.02 µg/l for simazine and atrazine and 0.04 µg/l for isoproturon.

Aldicarb analysis by HPLC used a C18, 15 cm by 4.6 mm column, eluted at a rate of 0.8 ml/min. The first eluent was an acetonitrile and water mixture (5%/95%) and the second an acetonitrile, methanol and water mixture (78%/23%/5%). Post column derivitization was in two stages. In stage 1, 50 mM sodium hydroxide was added and heated to 95 °C. The second stage involved the addition of a solution made up by adding 2-mercaptoethanol in acetonitrile (1:1, 100 µl) to a solution of o-phthalaldehyde (100 g in 10 ml) which in turn was added to a sodium borate solution (0.05 M in 1000 ml). Finally detection was by fluorescence, with an excitation wavelength of 230 nm and emission wavelength of 418 nm. Calibration was by external standards and was determined to be 0.2 µg/l.

Aldicarb sulphoxide and sulphone analysis by HPLC differed only in the composition and flow rate of the eluents used. The first eluent was an acetonitrile and water mixture (95%/5%) and the second an acetonitrile, methanol and water mixture (78%,23%,5%). The flowrate was 1 ml/min. External standards were used and a detection limits of 0.15 µg/l and 0.05 µg/l were obtained for aldicarb sulphoxide and sulphone respectively.

5.7.3.2 Results and Discussion

Rainfall event on 14 April 1992

46.5 mm of rain fell between 1200 on 14 April 1992 and 0200 the following day. This had a very slight effect on the flow from Longlands drain (SO 5688 4847) but the sampler was triggered by the linked sampler at the MAFF drain site (SO 5672 4842). A total of 24, one hourly samples were taken and analysed for simazine, atrazine, aldicarb and its degradation products sulphoxide and sulphone. The results of the analyses are given in Tables A6, Appendix X. The sampler at the main gauging site was not triggered by this event.

Atrazine concentrations rose to peak early in the event 16.2 µg/l and fell away slowly to around 9 µg/l (Figure IH6). Remarkably, because it had not been applied to Longlands, simazine follows the same pattern. The peak value measured was 13.2 µg/l which fell away more rapidly than atrazine to around 1 µg/l. The source of the simazine is not yet understood but the concentrations have been confirmed and are being investigated.

Concentrations of aldicarb are always below the detection limit however the two degradation products were both found (Figure IH7). The concentrations were very similar and followed the pattern of the atrazine concentrations but fell away more quickly. The peak values measured were 1.38 µg/l for the sulphoxide and 1.77 µg/l for the sulphone.

Rainfall event on 28 May 1992

10.5 mm of rain fell in the hour starting at 1400 on 28 May 1993. This caused a rise in stage sufficient to trigger the sample at the main gauging station (SO 5598 4789) at 1645 the same day. Samples were taken each hour for 24 hours and the samples taken to the Institute of Hydrology and analysed for isoproturon, simazine, atrazine and aldicarb and its degradation products. The results are presented in Table A9, Appendix X. The automatic sampler on Longlands drain was not triggered by this event.

The concentration of aldicarb was only above the detection limit in the second of the 24 samples, while concentrations of the sulphoxide degradation product were all below the detection limit. The secondary degradation product, the sulphone, was found most often with a maximum concentration

Fig. IH6

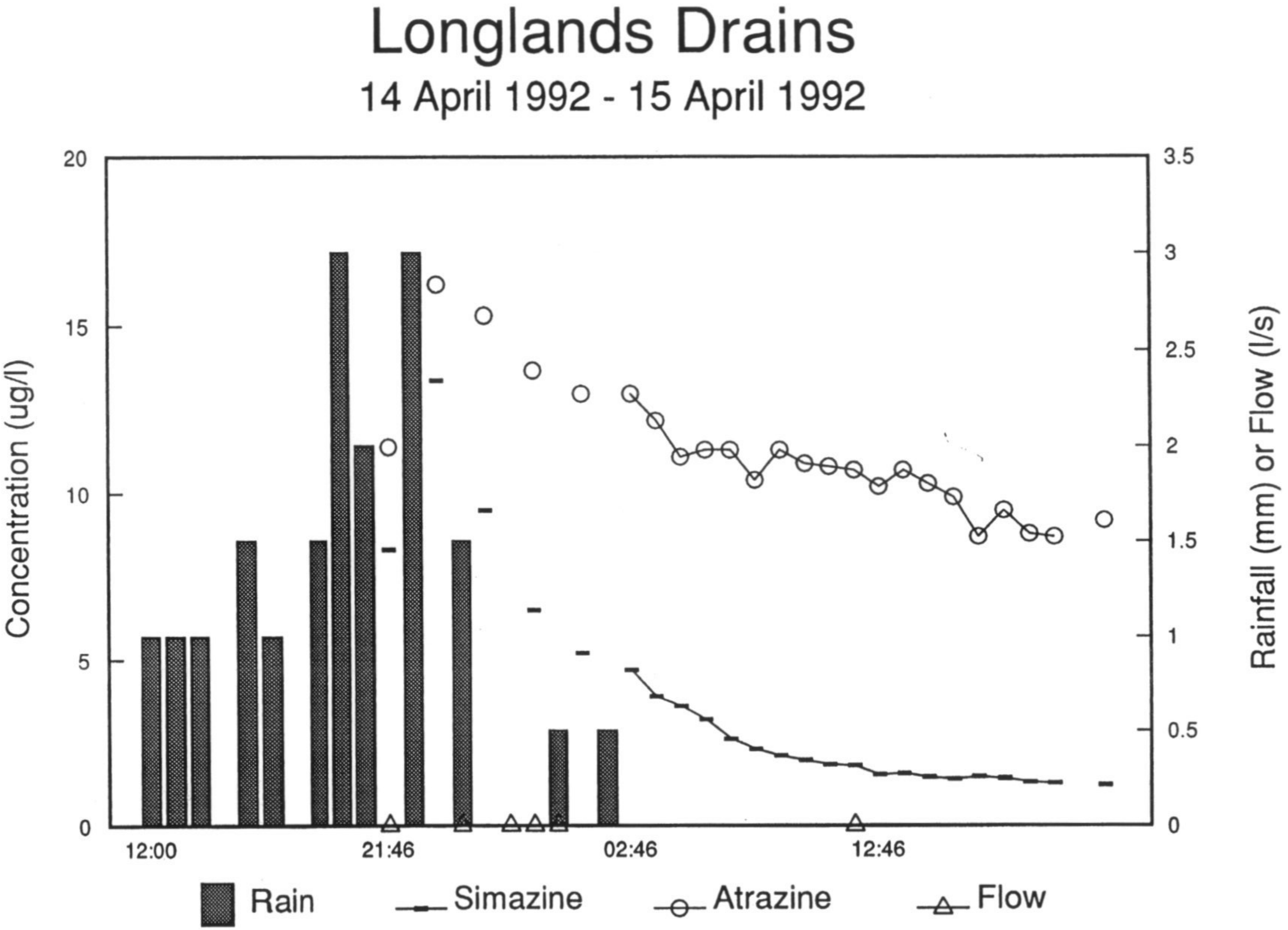
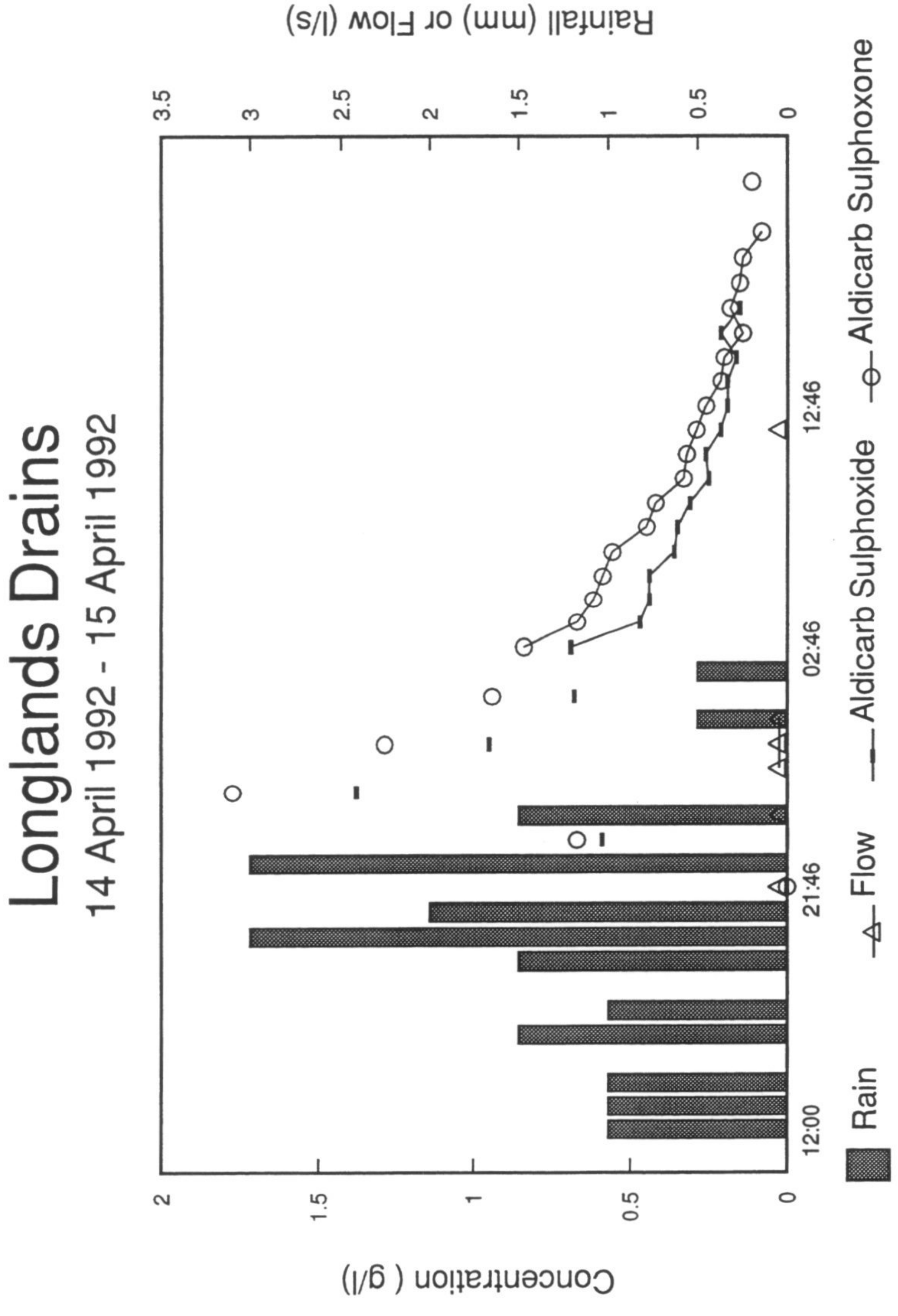

Longlands Drains
14 April 1992 - 15 April 1992
Concentration (ug/l)
0
5
10
15
20
Rainfall (mm) or Flow (l/s)
0
0.5
1
1.5
2
2.5
3
3.5
12:00
21:46
02:46
12:46
Rain
Simazine
Atrazine
Flow

Fig. IH7


Longlands Drains
14 April 1992 - 15 April 1992
Concentration (g/l)
0
0.5
1
1.5
2
Rainfall (mm) or Flow (l/s)
0
0.5
1
1.5
2
2.5
3
3.5
12:00
21:46
02:46
12:46
Rain
Flow
Aldicarb Sulphoxide
Aldicarb Sulphone
Aldicarb Sulphoxone

of 0.21 µg/l. Figure IH8 shows the variation of flow, rainfall and aldicarb sulphone through the rainfall event. There is no obvious link between sulphone concentrations and either the rainfall or the flow.

Isoproturon showed a very interesting pattern through the rainfall event (Fig IH9), quite different to the patterns shown in previous events at Rosemaund. The initial concentration was high around 8 µg/l, this quickly dropped down to 1 µg/l within 2 hours. Levels then recovered through the event returning to close to the initial value. This type of response is typical of a contaminant that is being supplied with the baseflow at a roughly constant level, when the rain comes it is clean compared to the baseflow and thus dilutes it reducing the stream concentration. Routine samples taken under low flow conditions support this theory, showing isoproturon concentrations between 6 and 7 µg/l. This result is important since it suggests that isoproturon applied in November and December has percolated to the deep soil water which supplies the baseflow to the stream. It is possible that at this depth the isoproturon will be degraded much more slowly. The analysis of routine samples taken through the summer months (Table A8, Appendix X) show some very high isoproturon levels which also support this hypothesis.

Atrazine and simazine showed a very similar pattern to isoproturon although simazine had some extra features (Fig IH10). Simazine started from a peak value (3.5 µg/l) above its base value of around 1 µg/l, and fell quickly to below 0.5 µg/l. A second simazine peak was then observed (2.9 µg/l) before concentrations fell back to baseflow levels. It is hard to explain this pattern, although its more recent application (March) may explain the peaks, and its general ubiquity in the environment the base levels. The atrazine follows exactly the pattern described for isoproturon. The results from the following event which are not yet available will be particularly interesting, as to whether they confirm or otherwise the interpretations made above.

Rainfall event on 7 June 1992

Routine samples taken from the main gauging site and Longlands drain throughout the autumn and spring are given in Tables A8 and A7 in Appendix X.

Fig. IH8

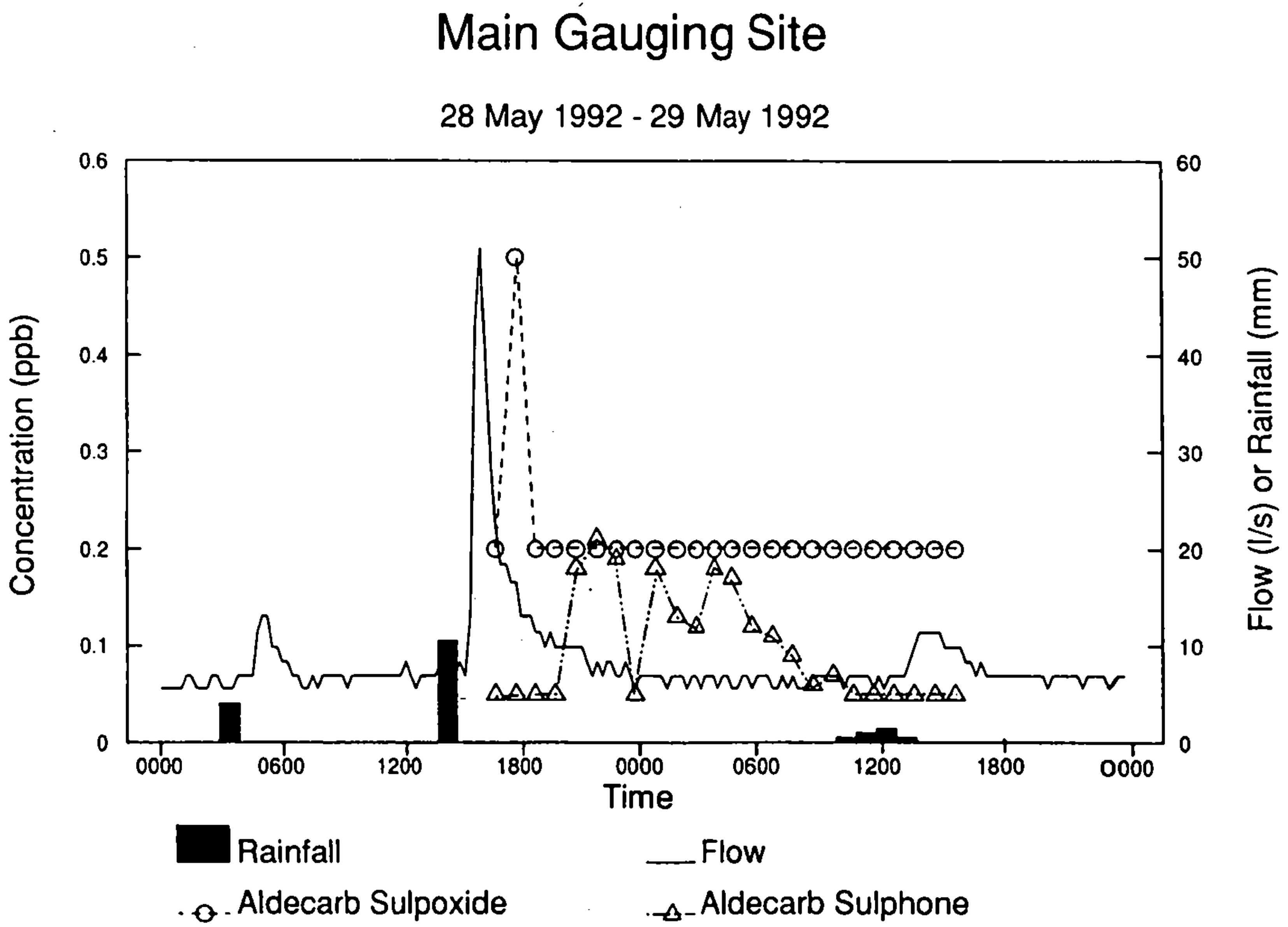

Main Gauging Site
28 May 1992 - 29 May 1992
Concentration (ppb)
0.6
0.5
0.4
0.3
0.2
0.1
0
Flow (l/s) or Rainfall (mm)
60
50
40
30
20
10
0
0000
0600
1200
1800
0000
0600
1200
1800
0000
Time
Rainfall
Flow
Aldecarb Sulpoxide
Aldecarb Sulphone

Fig. IH9

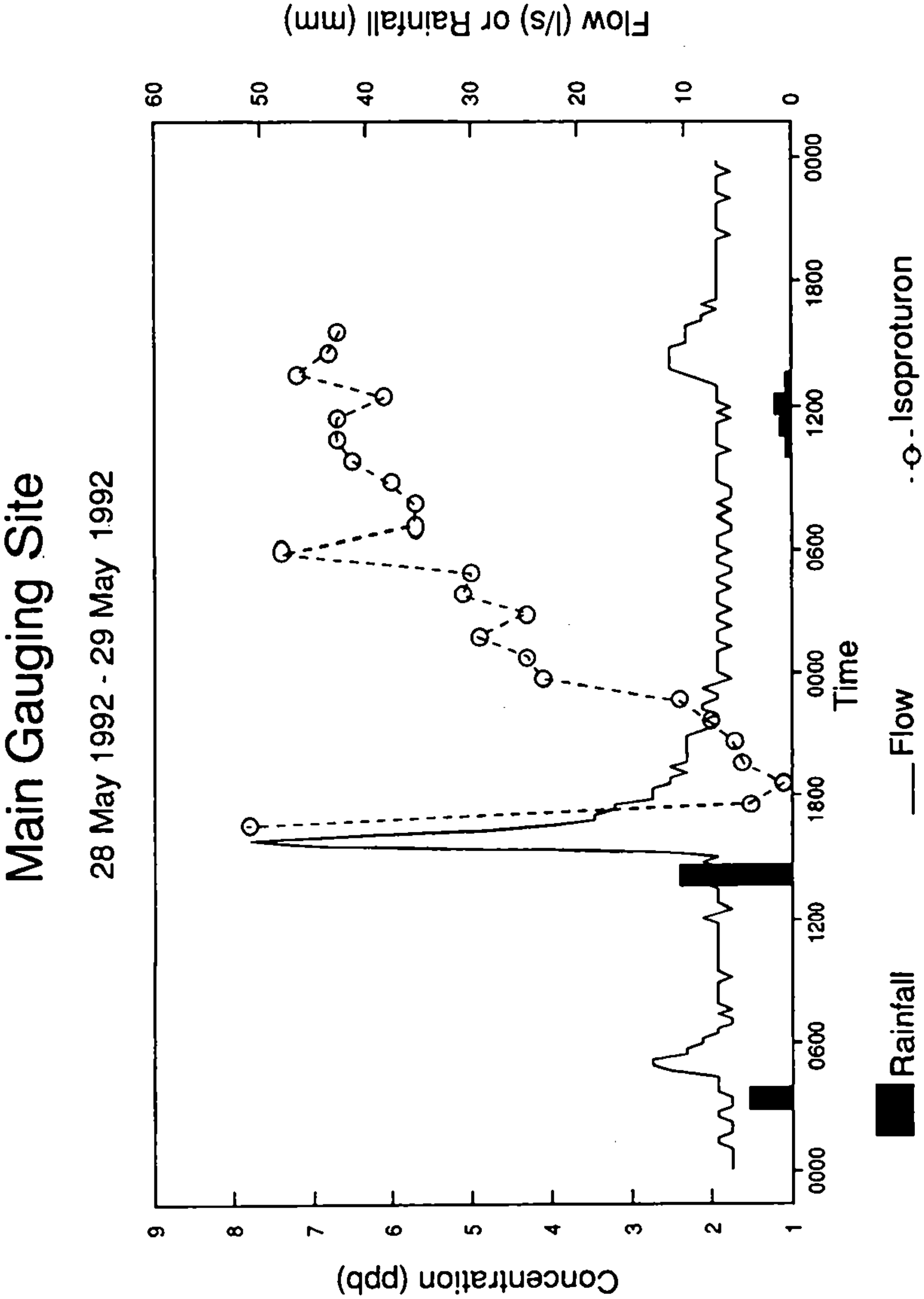

Main Gauging Site
28 May 1992 - 29 May 1992
Concentration (ppb)
1
2
3
4
5
6
7
8
9
Flow (l/s) or Rainfall (mm)
0
10
20
30
40
50
60
Time
0000
0600
1200
1800
0000
0600
1200
1800
0000
Rainfall
Flow
Isoproturon

Fig. IH10

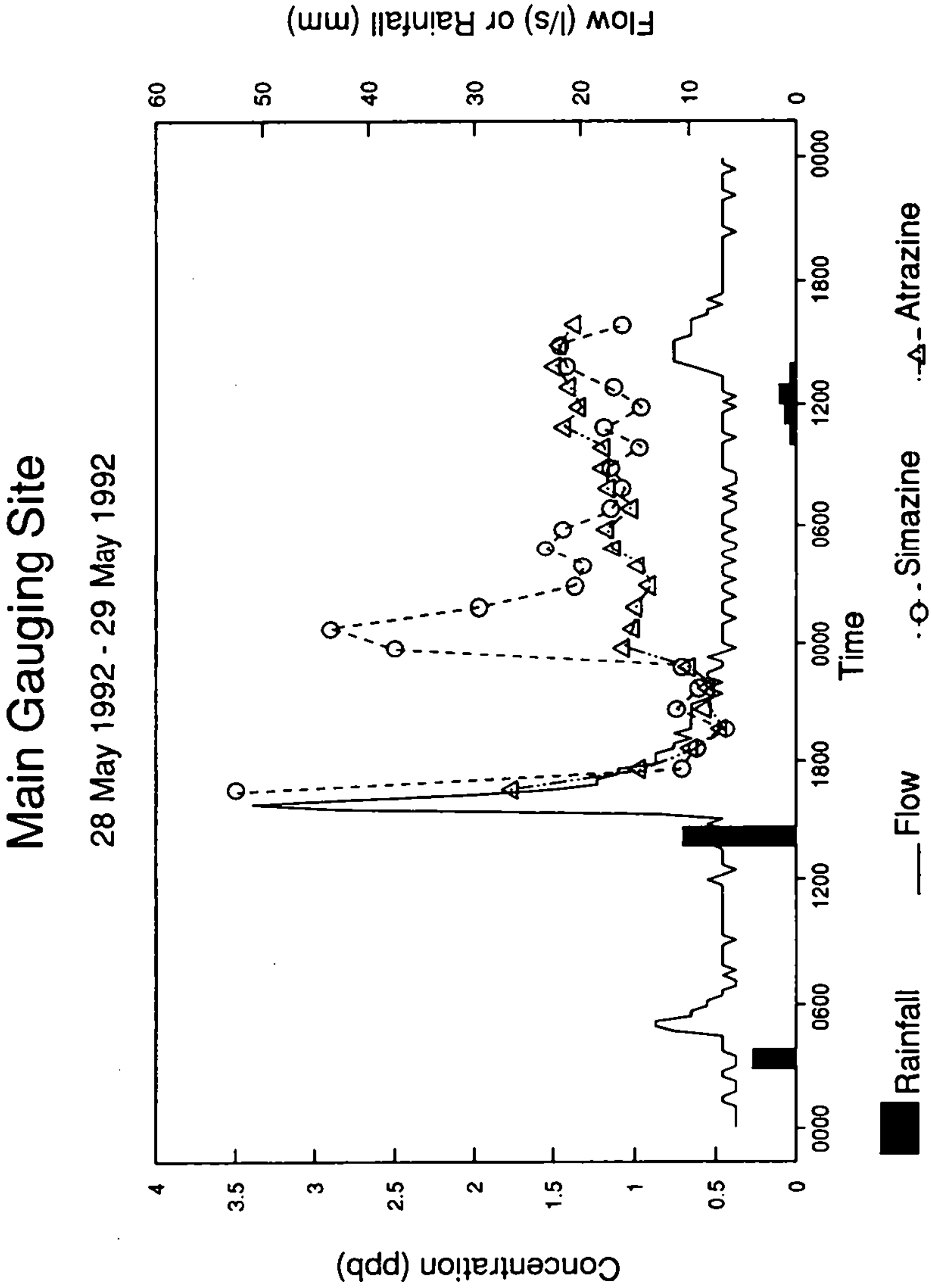
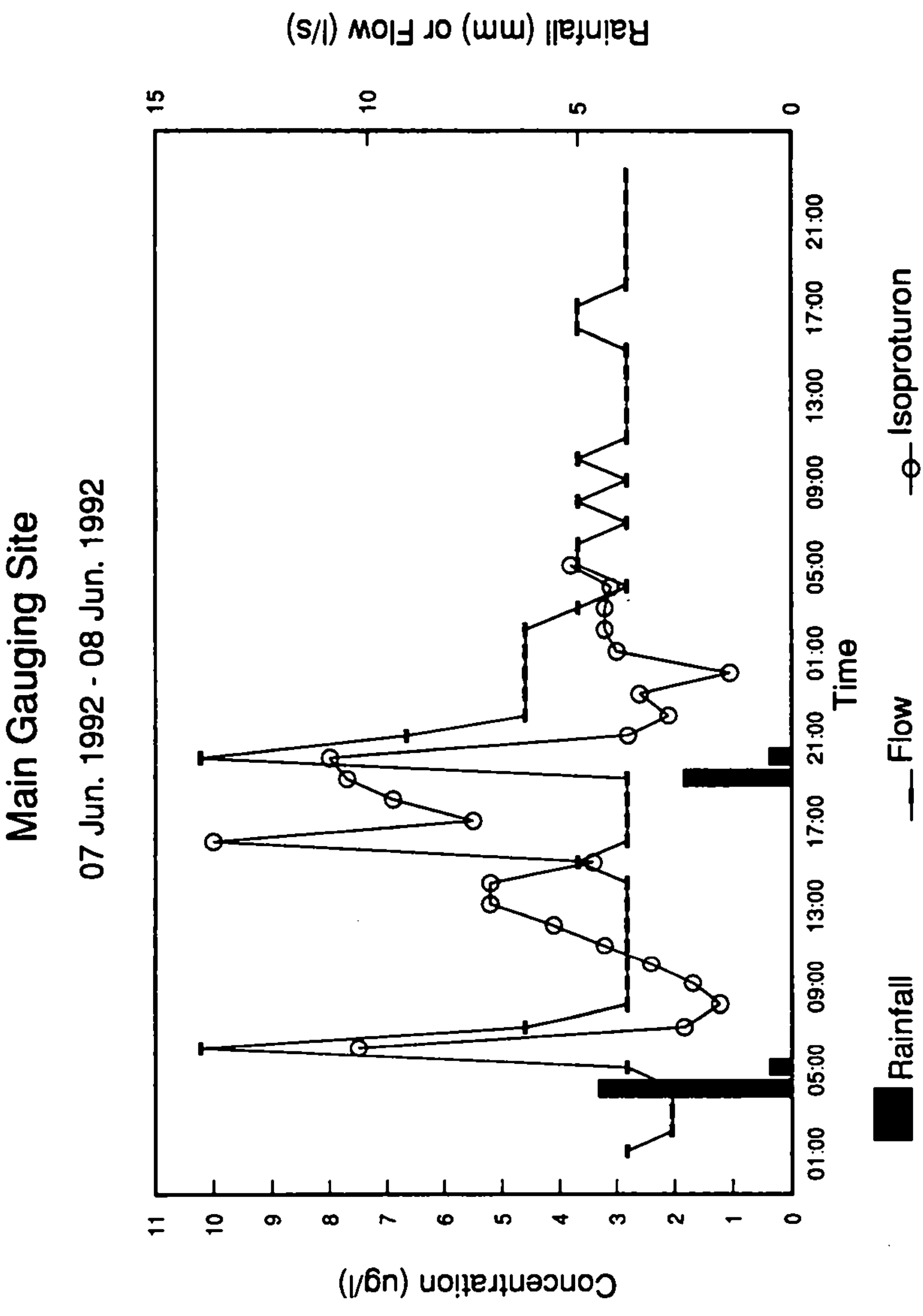

Main Gauging Site
28 May 1992 - 29 May 1992
Concentration (ppb)
0
0.5
1
1.5
2
2.5
3
3.5
4
Flow (l/s) or Rainfall (mm)
0
10
20
30
40
50
60
Time
0000
0600
1200
1800
0000
0600
1200
1800
0000
Rainfall
Flow
Simazine
Atrazine

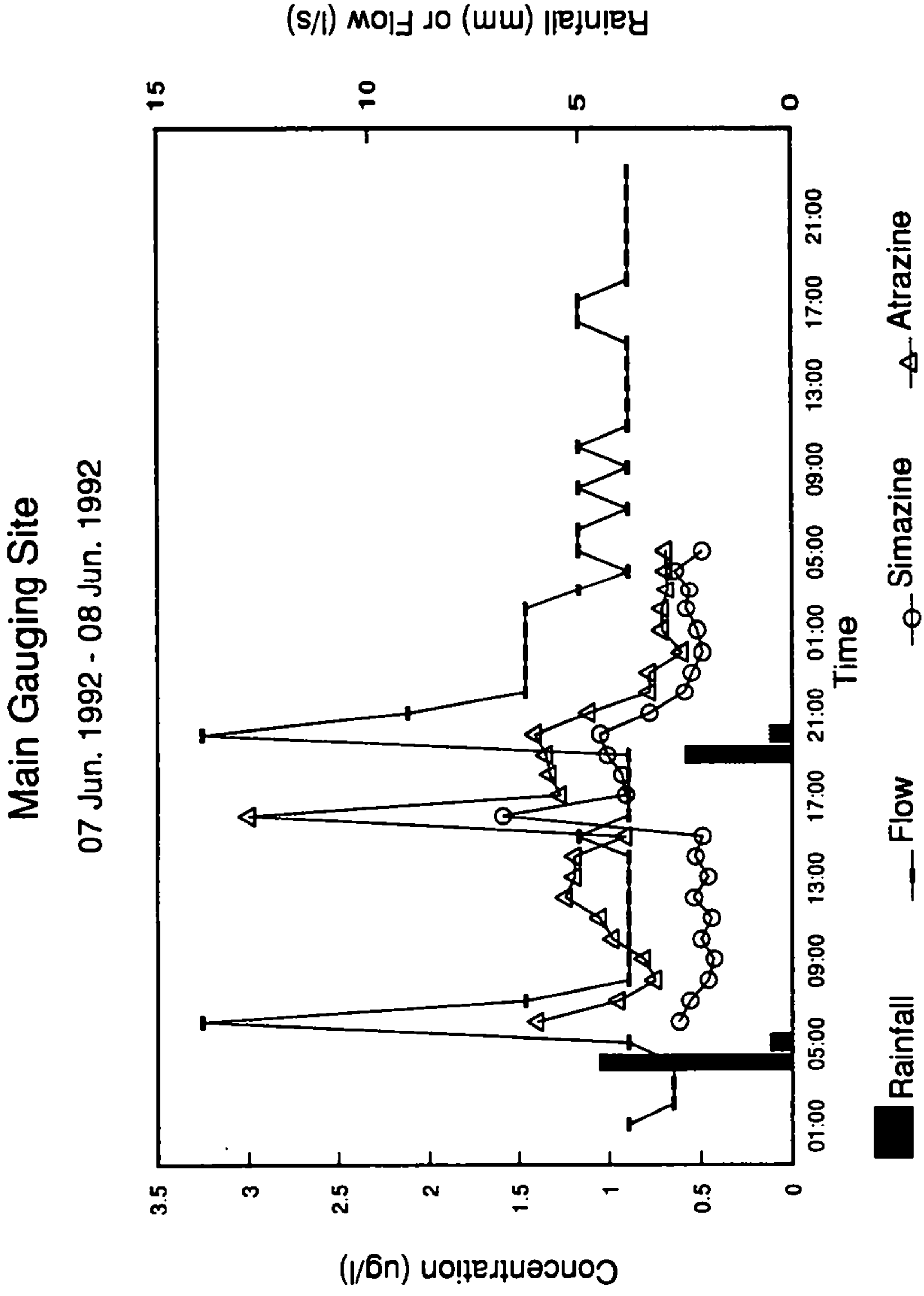
Fig IH 11



Main Gauging Site

07 Jun. 1992 - 08 Jun. 1992

Fig IH 12


Main Gauging Site
07 Jun. 1992 - 08 Jun. 1992
Concentration (ug/l)
0
0.5
1
1.5
2
2.5
3
3.5
Rainfall (mm) or Flow (l/s)
0
5
10
15
Time
01:00
05:00
09:00
13:00
17:00
21:00
01:00
05:00
09:00
13:00
17:00
21:00
Rainfall
Flow
Simazine
Atrazine

A small rainfall event of 5 mm over the two hours starting 0400 on 7 June 1992 caused a rise in stage sufficient to trigger the automatic sampler at the main gauging station (SO 5598 4789) at 0600 the same day. Samples were taken each hour for 24 hours. A further small rainfall event of 3 mm in two hours occurred during the sampling run. The results are presented in Table A10, Appendix X. The automatic sampler on Longlands drain was not started by this event.

Only three of the samples, early in the sample run, showed aldicarb concentrations above the detection limit. The degradation product, sulphoxide, had a concentration slightly above the detection limit in the second sample, otherwise it, and the sulphone, were below detection limit until the 15th sample. From this point the sulphone gave small positive detections while the sulphoxide reached quite high values (maximum 2.5 µg/l). These levels are an order of magnitude higher than those recorded in the preceding event of 28 May 1992. This is as a result of additional applications of aldicarb to the hop yards within the farm. In particular the application of Temik at a rate of 1.3 kg a.i./ha to parts of the Coronation hop yard on 4 and 5 June 1992. The occurrence of the sulphoxide rather than the parent compound shows the speed at which aldicarb is oxidised in the environment. The lower concentrations of sulphone, the second degradation product indicate that the second degradation step is slower than the first.

Isoproturon concentrations followed a pattern similar to that followed in the event of 28 May 1992. Each rainfall event produced a reduction in isoproturon concentration which then returned to an original base line value through the recession limb of the hydrograph (Fig IH11). The baseline levels, around 8 µg/l, observed in this event were also similar to those in the previous event. The hypothesis put forward in the discussion of the event of 28 May 1992 with regard to isoproturon would seem to be confirmed by the results from this rainfall event.

Atrazine again showed a very similar behaviour to isoproturon and to its own behaviour in the previous event (Fig IH12). Concentrations of simazine were lower in this event than the previous event, a peak of 1.6 g/l compared to 3.5 g/l previously. Its behaviour was similar to that of atrazine, although the first fall in concentration with flow rate was not as marked.

6. SUMMARY DISCUSSION OF RESULTS

Studies by SSLRC into the soil and soil hydrology linking with work previously reported investigated the processes and pathways controlling the movement of soil water by the use of suction samplers to obtain mobile water. As noted in the Second Annual Report (Hack, 1992), baseline samples were collected before pesticides were applied, although because of the high soil moisture deficit at this time only limited samples could be collected. Atrazine and the two degradation products of aldicarb (the sulphoxide and the sulphone) were found in the soil water. Measurements of hydraulic conductivity linked with subsequent methylene blue dye studies indicated that where low conductivities occurred they were mainly due to water flow in the soil matrix and in minor pores, but where high conductivities were measured, both matrix and macropore flow were involved.

Again the problems of clay smearing during installation of equipment were highlighted and some sealing of macropores may have occurred, which could lead to lower macropore flow than would normally be the case.

The examination of the drains by ADAS SWRC was undertaken in Autumn 1991 in response to queries about the effectiveness of the drains in Foxbridge and Longlands. This extensive survey showed no obvious blockage in the drains and indicated that they were operational with relatively clean permeable backfill. One problem identified was the low pipe gradient found in the last 40m of the lateral drain which was likely to restrict the drain flow. This could also lead to excessive surcharging for relatively small events.

Three pesticides were specifically targeted to be monitored this season; carbofuran, atrazine and aldicarb. Isoproturon was applied as a commercial application and monitored to give continuity by linking with previous seasons. The two triazines, trietazine and terbutryne were also applied as a commercial necessity in Spring 1992 and were monitored as 'add-ons' to the atrazine as they required no extra analysis.

During this season, following a dry autumn a rainfall event on January 8 consisted of 72 mm falling during a 24 hour period. The return time of this event was 50 years and it caused a limited amount of overland flow.

The insecticide carbofuran was one of the first pesticides to be tested at Rosemaund which was highly toxic to aquatic life, leading to the possibility of toxic effects detected in the stream. The run-off patterns of both carbofuran and atrazine were similar to those observed in previous experiments at Rosemaund with other pesticides. Concentration peaks were brief and occurred just before the main flowrate peak. An important result of this investigation was that the concentrations of carbofuran during two of the events were high enough to cause mortality of stream fauna due to the high toxicity of carbofuran to arthropods. This is one of the first recorded instances of acutely toxic field drainage water and underlines the significance of the Rosemaund Project and its improvement of predictive models of pesticide run off. The importance of the results from this experiment has warranted its publication as a stand-alone paper (Appendix XI).

As was expected no aldicarb was detected due to its rapid environmental degradation behaviour, but levels of the two main degradation products, aldicarb sulphoxide and aldicarb sulphone were detected at an approximate 1:1 ratio. Problems with degradation during storage occurred with some samples, but levels in the order of 0.5 µg/l of each metabolite were detected.

Triazine residues did not generally appear in the soil water until 1-2 months after spraying although this was likely to be a reflection on the low rainfall during this period. Trietazine was found to translocate from soils to water in a similar way to the other triazines already investigated in this study with maximum concentrations of 1.3µg/l in the stream water. Results for terbutyne were similar, but the poor recovery efficiency for this compound lead to probable underestimates of concentrations.

7. REFERENCES

BIRD, S C and WHITEHEAD P G (1985). A Review of the Agrochemical Problem and Related Hydrochemical Models. Report on DoE Contract PECD 7/7/170, November 1985.

BIRD, S C, WILLIAMS, R J, BROOKE, D and MATTHIESSEN P (1988). Pesticide transport into streams. Poster paper presented at 'Since Silent Spring' symposium, Institute of Biology, Cambridge, March 1988.

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 (1990-91). SSLRC Research Contract 82/3823, undertaken for the Ministry of Agriculture, Fisheries and Food, Silsoe.

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, Soil Survey and Land Research Centre.

COUNCIL OF THE EUROPEAN COMMUNITIES. Directive of 15th July 1980 relating to the quality of water intended for human consumption. 80/778/EEC; 05 1 229, 30th August 1980.

DIGUARDO, A, WILLIAMS R J, MATTHIESSEN, P, BROOKE, D N, and CALAMARI, D.(1994). Simulation of pesticide runoff at Rosemaund Farm (UK) using the SoilFug model. Environmental Science and Pollution Research. In press.

DRINKING WATER INSPECTORATE (1992). Nitrate, Pesticides and Lead 1989 and 1990. DoE report.

FRANK, R, BRAUN, H E, HOLDRINET VAN HOVE, M, SIRONS, G J and RIPLEY, B D (1982). Agriculture and water quality in the Canadian Great Lakes Basin; V Pesticide use in 11 agricultural water sheds and presence in stream water, 1975-1977. J. Environ. Qual., 11, pp 497-505.

GOMME, J, SHURRELL, S, HENNINGS, S M and CLARKE, L (1992). Hydrology of Pesticides in a Chalk Catchment: Ground Water. Journal of the Institute of Water and Environmental Management 6, pp 172-178.

HACK, C M (1992). Pesticide Runoff Study at ADAS Rosemaund. Report of years 2 to 4, Autumn 1989 to Spring 1991. ADAS Rosemaund, Preston Wynne, Hereford.

HENNINGS, S and MORGAN D (1987). The Granta catchment pesticide study: progress report, Water Research Centre, Medmenham WRC Report No. PRU 1716-M/1, 37 pp.

JOHNSTON, W R, ITTHADIEH, F T, CRAIG K R and PILLSBURY A F (1967). Insecticides in tile drainage effluent. Wat. Resources Res., 3 pp 525-537.

KEYWORTH, N. (1992). The development of quantitative techniques to assess the influence of soil structure and by-pass systems on water movement. MSc Thesis, Department of Physiology and Environmental Science, University of Nottingham.

LEES, A and McVEIGH, K (1988). An investigation of pesticide pollution in drinking water in England and Wales. Special Report, Friends of the Earth, London

MATTHIESSEN, P, SHEAHN, D, HARRISON, R, KIRBY, M, RYCROFT, R, TURNBULL, A, VOLKNER, C and WILLIAMS, R. (1994). Use of a *Gammarus pulex* bioassay to measure the effects of transient carbofuran runoff from farmland. Ecotox . Environ. Saf. In press

MUIR, D C G and GRIFT, N P (1987). Herbicide levels in rivers draining two prairie agricultural watersheds. J Environ. Sci, Health, B22 pp 259-284.

SPENCER, W F, CLIATH, M M, BLAIR, J W and LEMERT, R A (1985). Transport of pesticides from irrigated fields in surface run-off and tile drain waters. UK Dept of Agriculture, Agricultural Research Service, Conservation Branch Report No. 31, National Technical Information Service, Springfield, 76 pp.

THOMAS, K and NICHOLSON, B C (1989). Pesticide losses in run-off from a horticultural catchment in S Australia and their relevance to stream and reservoir water quality. Environ, Technol. Lett., 10 pp 117-129.

WAUCHOPE, R D (1978). The pesticide content of surface waters draining from agricultural fields - a review. J. Environ. Qual., 7, pp 459-472.

8. ACKNOWLEDGEMENTS

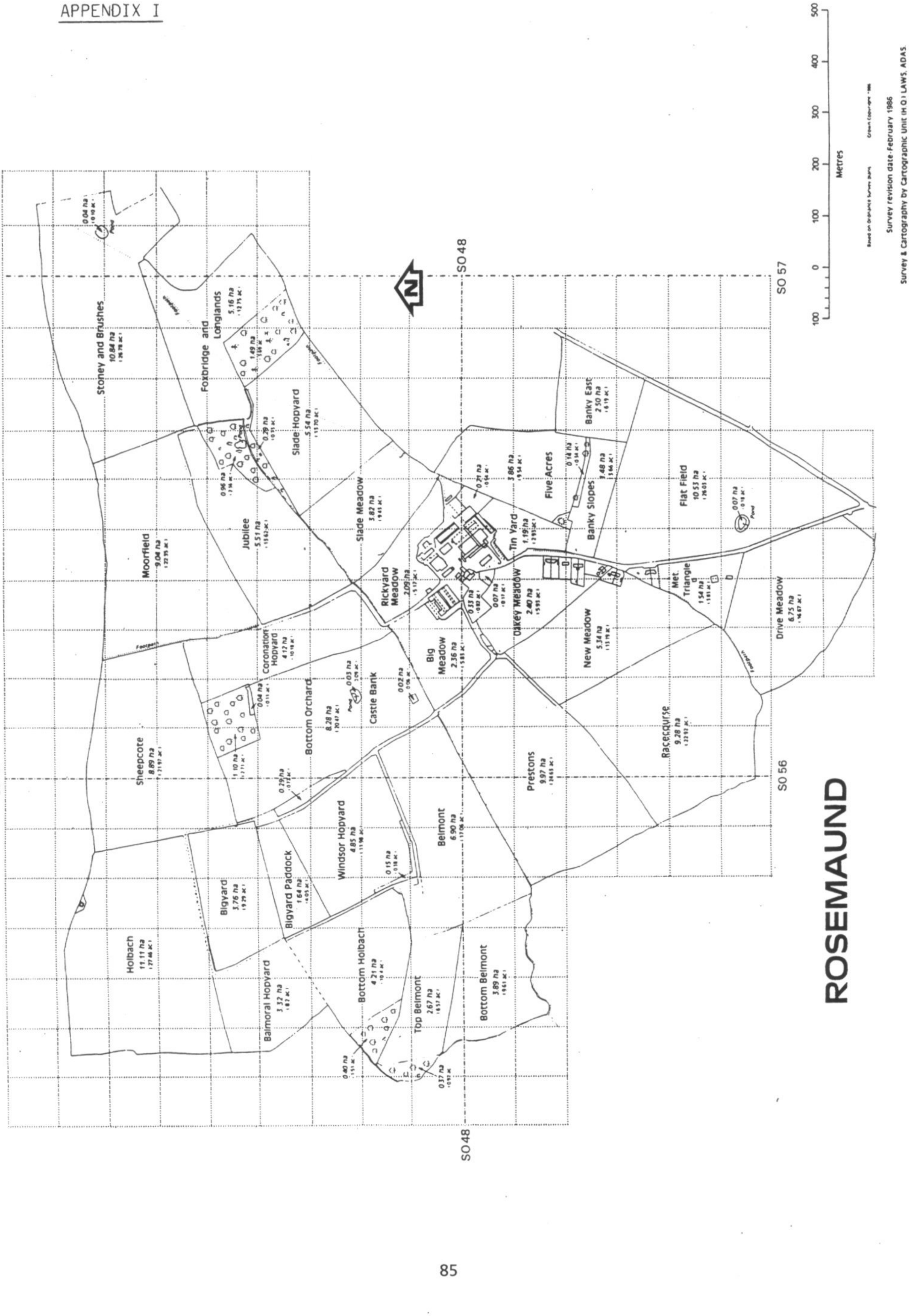
The assistance of Mr D Price, the Farm Manager at ADAS Rosemaund, and his staff is gratefully acknowledged by all participating bodies. Thanks are due to ADAS staff based at Rosemaund; Mr R Laverick, Mr J Spink and particularly Mr R Edwards for their technical assistance. The work of ADAS SWRC staff, particularly Mr A Talman, is also acknowledged.

The technical assistance of Mr M Kirby and Ms P Neall of MAFF Fisheries (Burnham on Crouch) has been invaluable, as was that of Mr M Conyers, Miss I Nielsen, Dr V Paul, Mr J Rea and Mr B Willis of BRE.

The expertise and experience of Dr D Cope and Mr J Hodgson of SSLRC is gratefully acknowledged.

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

APPENDIX I



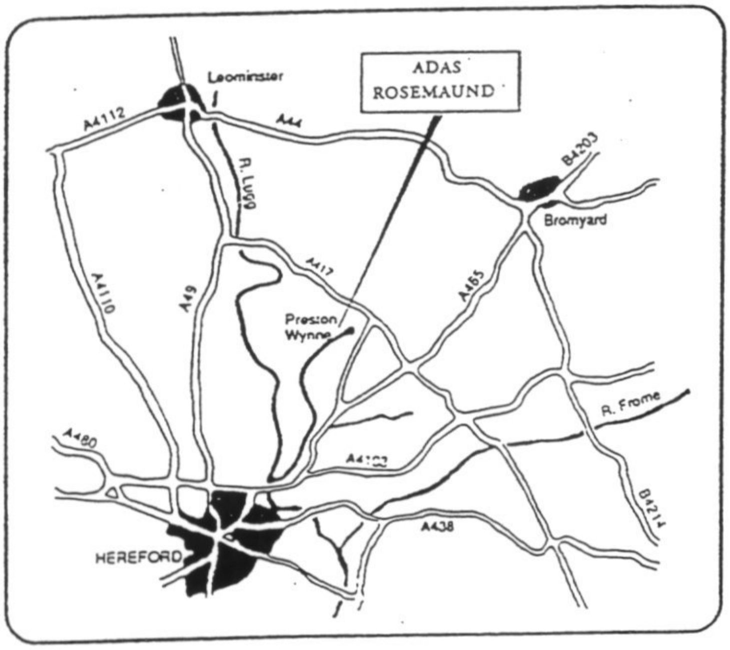
ROSEMAUND

Based on Ordnance Survey plans Crown Copyright 1986

Survey revision date February 1986

Survey & Cartography by Cartographic Unit (H.Q.) LAWS, ADAS

Location of Rosemaund Farm



Field boundaries and extent of catchment

APPENDIX II

WEATHER DATA SUMMARY FOR ADAS ROSEMAUND (1990-1992)

1990

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

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

LTM = Long-term mean since 1951.

1991

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

LTM = Long-term mean since 1951

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

1992

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

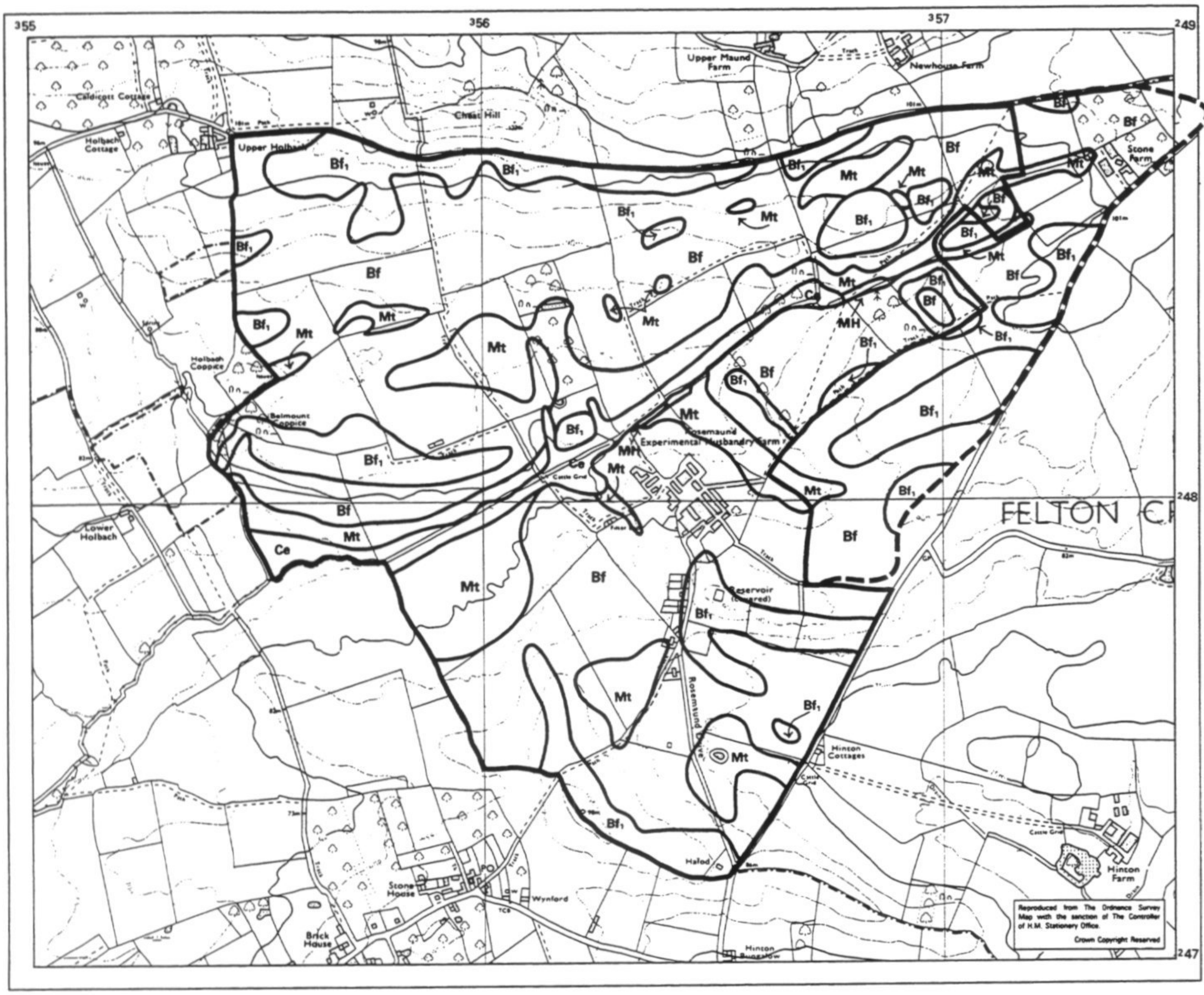
Summary: January wet, February and March dry and mild; dull in April; Warm May and June, July and August wet and dull; September to November wet and dull. December average.

LTM = Long-term mean since 1951.

APPENDIX III

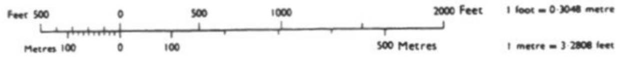
The Soils of Rosemaund Catchment, Worcester and Hereford

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



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

CONVERSION SCALE



1 foot = 0·3048 metre
1 metre = 3·2808 feet

SSLRC

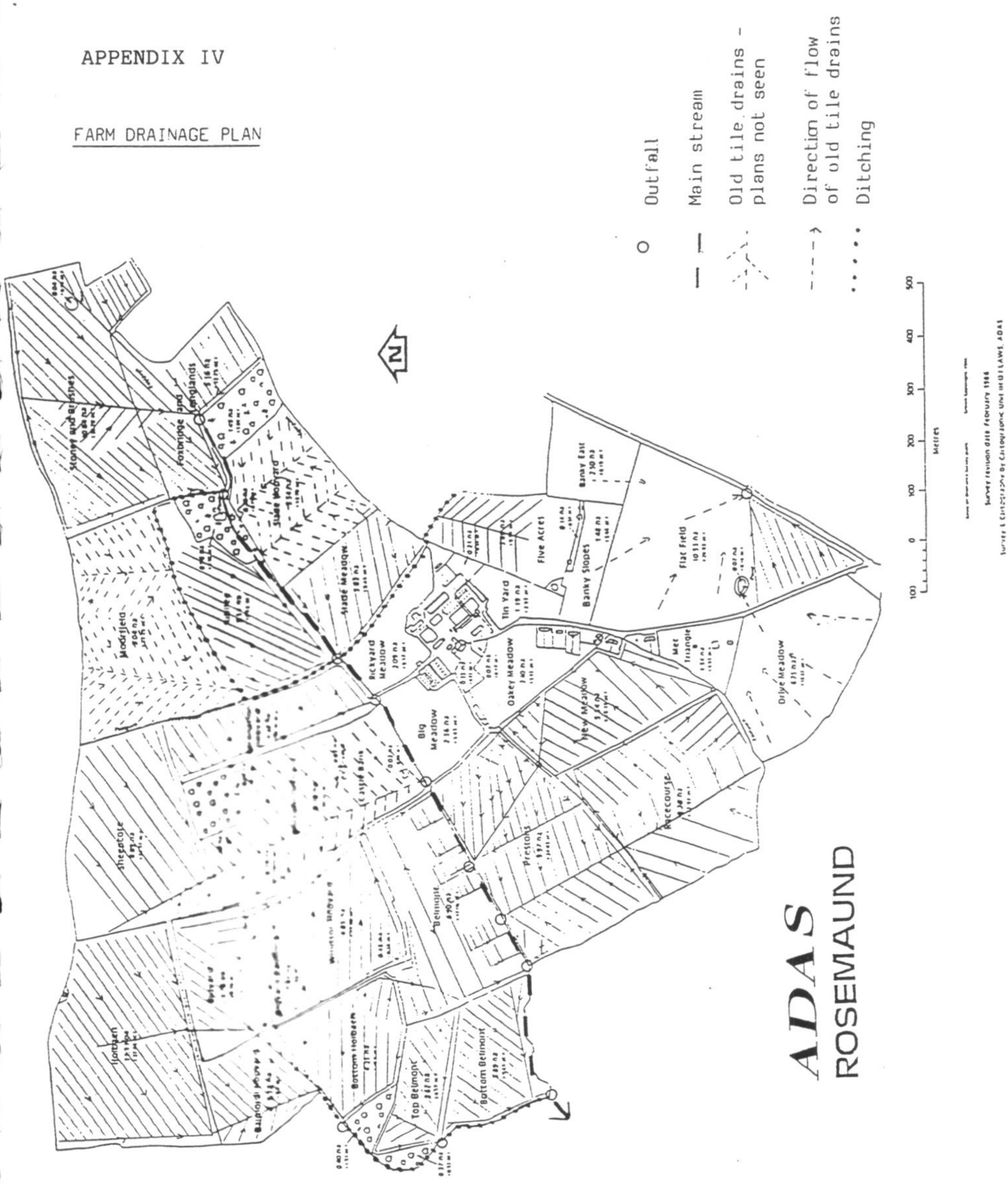
Symbol	Soil series	Topsoil characteristics	Subsoil characteristics	Soil water regime
Bf	Bromyard	Stoneless silty clay loam	Permeable stoneless reddish silty clay loam passing to soft blocky reddish and greenish grey siltstone and mudstone at about 55 cm depth	Slight seasonal waterlogging. Upper subsoil is wet for short periods during winter and early spring. Possibility of by-pass flow and surface runoff
Bf_1	Bromyard (shallow phase)	Stoneless silty clay loam	Permeable stoneless reddish silty clay loam over soft blocky reddish and greenish grey siltstone and mudstone at about 35 cm depth. Locally over harder siltstone or sandstone	
Ce	Compton	Stoneless silty clay loam	Deep moderately permeable prominently mottled stoneless reddish alluvial clay	Waterlogged for most of the winter and spring by fluctuating groundwater
MH	Mathon	Stoneless silty clay loam	Deep moderately permeable slightly mottled stoneless reddish alluvial silty clay loam	Waterlogged for part of the winter and spring by fluctuating groundwater
Mt	Middleton	Stoneless silty clay loam	Moderately permeable slightly mottled stoneless reddish silty clay loam becoming slowly permeable below 70 cm depth	Slight seasonal waterlogging. Subsoil is wet for short periods during winter and early spring. Possibility of by-pass flow but less risk of surface runoff

━━ Rosemaund Experimental Husbandry Farm boundary

╍╍ Watershed above the farm

APPENDIX IV

FARM DRAINAGE PLAN



APPENDIX V

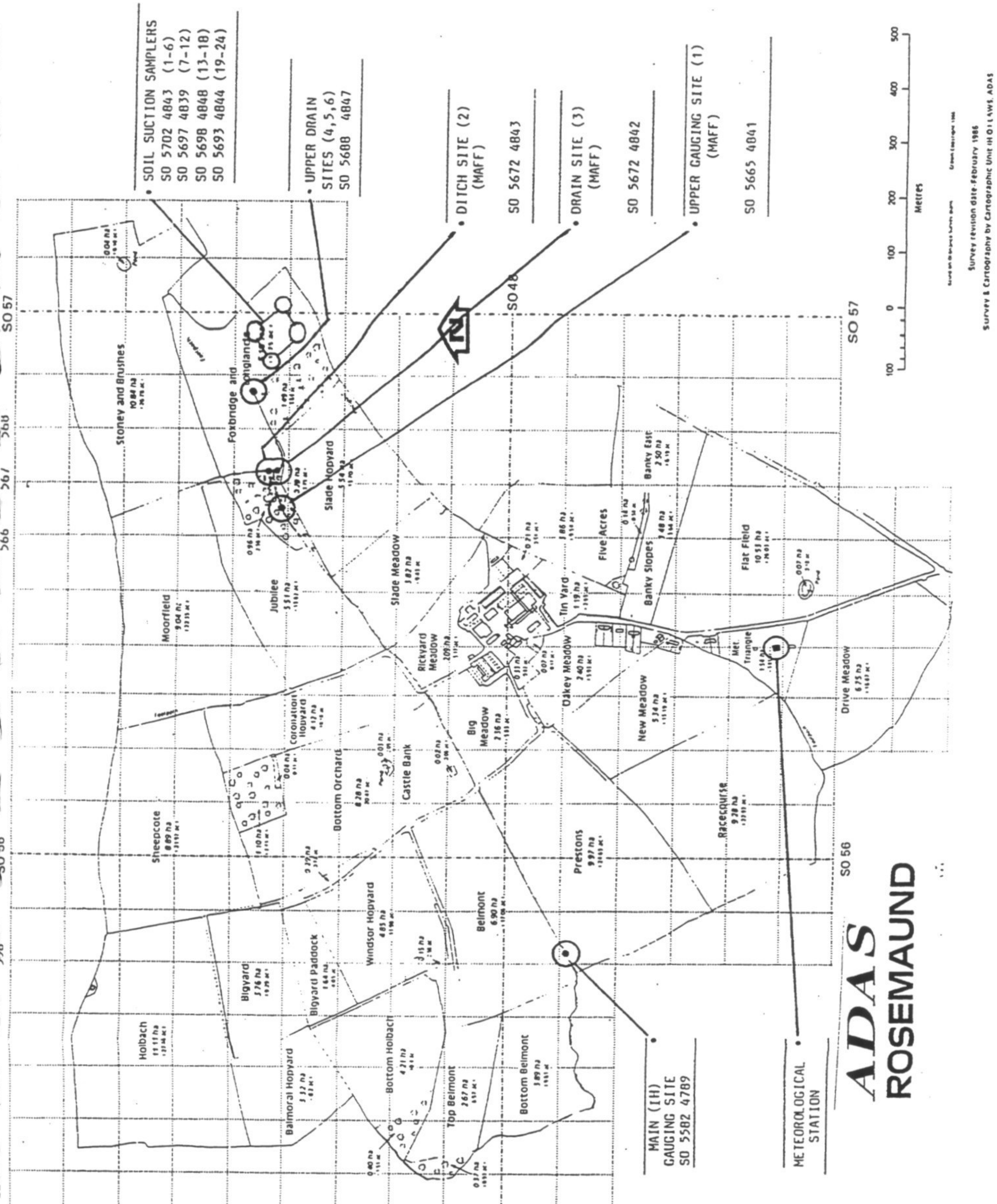
CROPPING HISTORY OF EACH FIELD 1985-1992

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

Appendix VI



SOIL SUCTION SAMPLERS
SO 5702 4843 (1-6)
SO 5697 4839 (7-12)
SO 5698 4848 (13-18)
SO 5693 4844 (19-24)
UPPER DRAIN SITES (4,5,6)
SO 5688 4847
DITCH SITE (2) (MAFF)
SO 5672 4843
DRAIN SITE (3) (MAFF)
SO 5672 4842
UPPER GAUGING SITE (1) (MAFF)
SO 5665 4841
MAIN (IH) GAUGING SITE
SO 5582 4789
METEOROLOGICAL STATION
ADAS
ROSEMAUND
Metres
100
0
100
200
300
400
500
Survey revision date-February 1986
Survey & Cartography by Cartographic Unit IH O1 LWS, ADAS
N
SO 57
SO 56
SO 48
485
484
479
478
Stoney and Brushes
Foxbridge and Ringlands
Slade Hopyard
Moorfield
Jubilee
Slade Meadow
Five Acres
Banky East
Banky Slopes
Flat Field
Tin Yard
Rickyard Meadow
Oakey Meadow
Met. Triangle
Drive Meadow
New Meadow
Big Meadow
Coronation Hopyard
Sheepcote
Bottom Orchard
Castle Bank
Racecourse
Prestons
Belmont
Windsor Hopyard
Bigyard
Bigyard Paddock
Holbach
Balmoral Hopyard
Bottom Holbach
Top Belmont
Bottom Belmont
Pond

APPENDIX VII

Table G1.Sample volume and date, Autumn 1991 - Spring 1992

Batch No.	1	2	3	4	5	6	7	8	9	10	11	12
							Date					
Sample No.	24/10/91	6/11/91	4/12/91	8/1/92	14/1/92	6/2/92	6/3/92	24/3/92	8/4/92	17/4/92	8/5/92	13/5/92
1	-	100	180	100	370	-	150	200	175	200	140	-
2	-	-	600	530	900	880	900	550	400	475	410	180
3	-	-	80	300	1100	1000	1000	1000	700	200	180	-
4	-	-	100	250	520	-	-	-	-	-	-	-
5	-	-	480	290	950	790	950	400	300	320	350	150
6	-	-	780	770	1100	1100	700	350	700	550	500	360
7	-	400	550	410	510	500	500	380	300	310	140	50
8	-	-	1000	790	950	950	975	850	700	650	700	400
9	-	-	550	710	900	680	650	550	500	500	500	450
10	-	-	600	410	440	360	-	-	-	-	-	-
11	-	-	950	950	1000	950	950	900	800	800	650	600
12	-	-	50	100	100	100	200	-	-	-	-	-
16	-	75	-	170	500	-	500	300	-	-	300	180
17	-	340	400	370	950	1000	1000	1000	1000	1000	980	300
18	-	50	200	180	1100	1050	1100	1100	1000	1000	1000	1000
19	-	130	100	90	140	110	250	50	120	210	100	100
20	-	-	360	300	1000	410	350	350	300	300	300	120
21	100	660	800	1050	1050	1100	1100	1100	1100	410	550	1000
22	-	390	380	360	400	320	375	-	-	290	180	-
23	350	900	900	910	1000	1000	1000	1000	1000	900	800	1000
24	-	-	700	650	950	890	850	800	700	625	600	500
25	50	400	450	480	460	450	400	400	250	100	-	300
26	-	-	670	480	980	200	600	200	600	-	-	-
27	-	-	1000	1000	1100	1100	1000	1000	1000	1000	1000	1000

Table G4. Soil water-table heights in dipwells, Foxbridge and Longlands, Autumn 1991-Spring 1992

Sample No.		Sample date					
Batch	Date	Sites 16-21			Sites 22-27		
1	24 10 91	60	100	140	60	100	140
2	6 11 91	-	-	-	-	-	-
3	4 12 91	0	0	0	0	0	116
4	7 11 92	-	-	-	-	-	116
5	14 1 92	-	99	92	-	75	75
6	6 2 92	-	99	125	-	91	91
7	6 3 92	-	-	120	-	91	91
8	24 3 92	-	99	124	-	99	101
9	8 4 92	-	-	125	-	99	111
10	17 4 92	-	-	119	-	-	109
11	8 5 92	-	-	98	-	-	98
12	13 5 92	-	-	127	-	-	129

APPENDIX VIII

Table 1. Run (1) One year return period, lowest gradient (0.16%):

Pipe type	Plastics
S/D line (corrugations)	0.09
Lateral length	125 m
Spacing	20 m
Drainage area	0.25 ha
Derived 6 hour rainfall	21.9 mm
Pipe size (ID)	53.0 mm
Trench width	140.0 mm
Backfill porosity	0.45%
Pipe gradient	0.16%
Depth of pipe	840.0 mm
Max. flow (original)	1.83 litre/s
Max. flow (capacity)	1.41 litre/s
Max. surcharge	840. mm

Table 2. Run (2) One year return period, average gradient (2.9%):

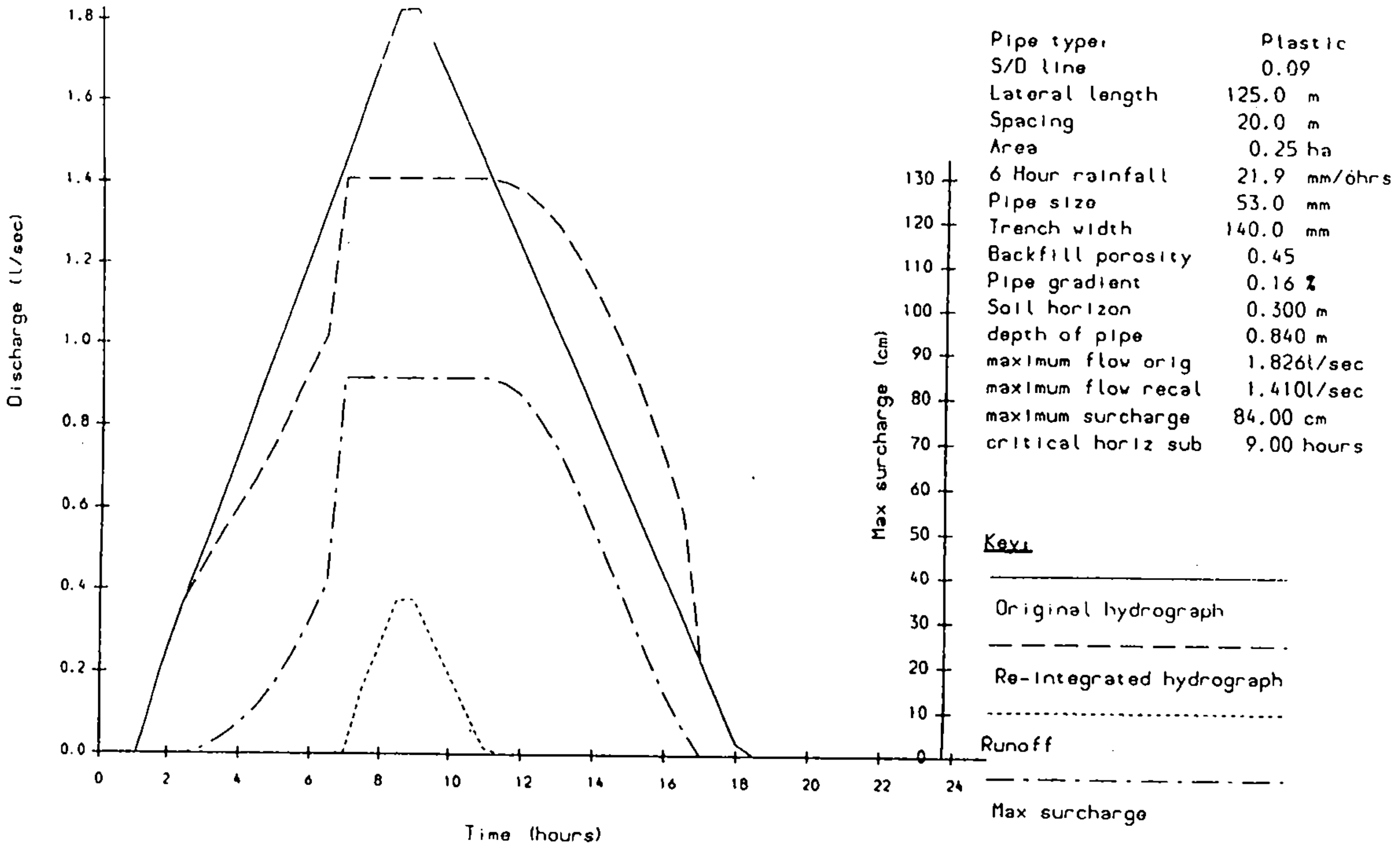
Pipe type	Plastics
S/D line (corrugations)	0.09
Lateral length	125 m
Spacing	20 m
Drainage area	0.25 ha
Derived 6 hour rainfall	21.9 mm
Pipe size (ID)	53.0 mm
Trench width	140.0 mm
Backfill porosity	0.45%
Pipe gradient	2.90%
Depth of pipe	840.0 mm
Max. flow (original)	1.83 litre/s
Max. flow (capacity)	1.82 litre/s
Max. surcharge	90.0 mm

Table 3. Drainflow (mm) from Foxbridge and Longlands site, recorded IH mini-weir, January 1-21, 1991.

Date	Drainflow	Date	Drainflow	Date	Drainflow
1	0.08	9	0.41	17	0.16
2	0.15	10	0.97	18	0.12
3	0.11	11	2.08	19	0.10
4	0.07	12	0.91	20	0.06
5	0.07	13	0.86	21	0.35
6	0.20	14	0.51		
7	0.13	15	0.33		
8	0.09	16	0.21		

Fig 1 FDEU program HRMODEL

Synthetic hydrograph for agroclimatic area : 25N User : TP00TP

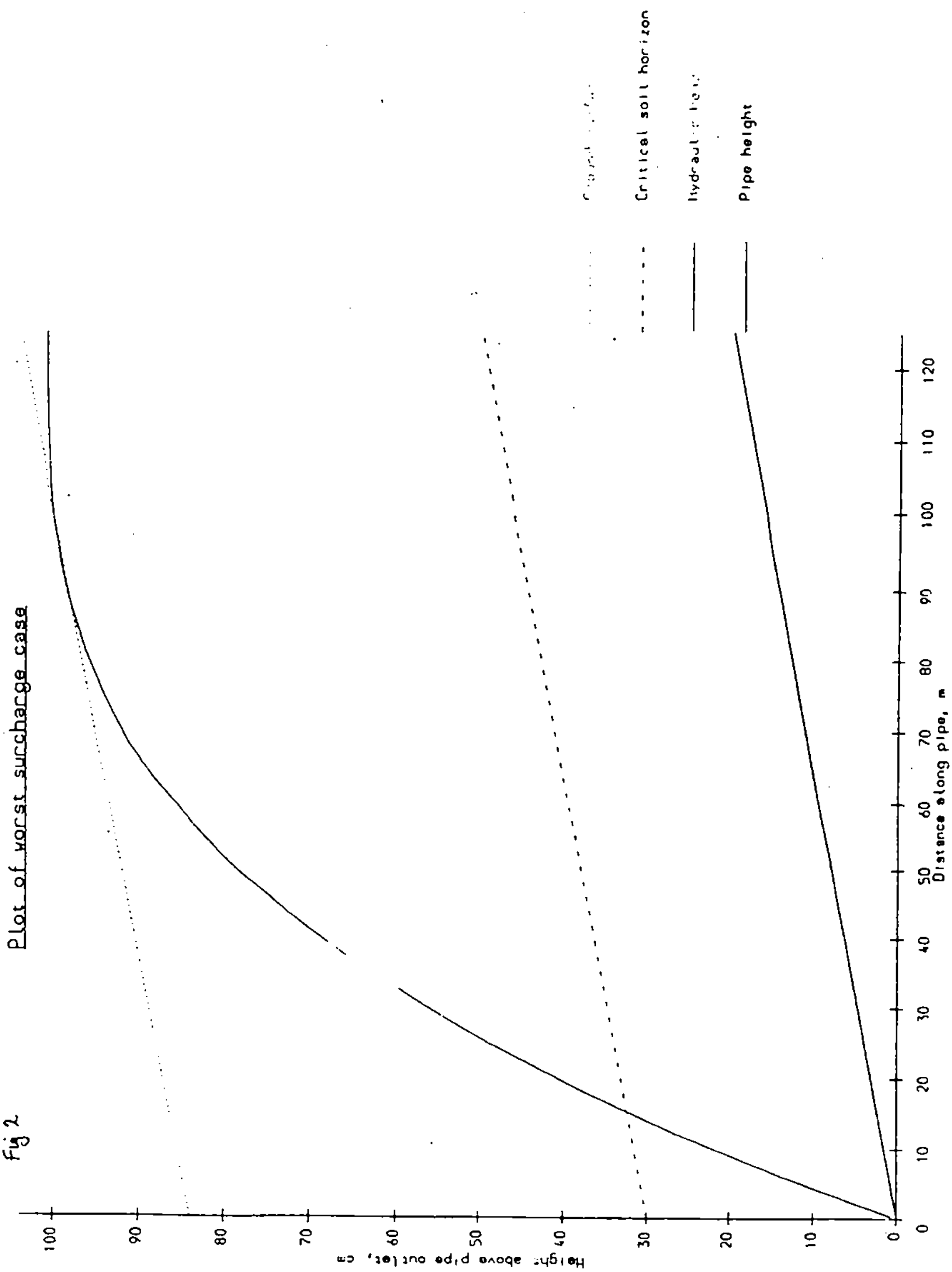


Field Drainage Experimental Unit
Anstey Hall, Maris Lane, Trumpington
Cambridge, UK CB2 2LF

A D A S

Fig 2

Plot of worst surcharge case



Field Drainage Experimental Unit
Anstey Hall, Maris Lane, Trumpington
Cambridge, UK CB2 2LF

A D A S

Fig 3 FDEU program HRMODEL
Synthetic hydrograph for agroclimatic area : 25N User : TPOOTP

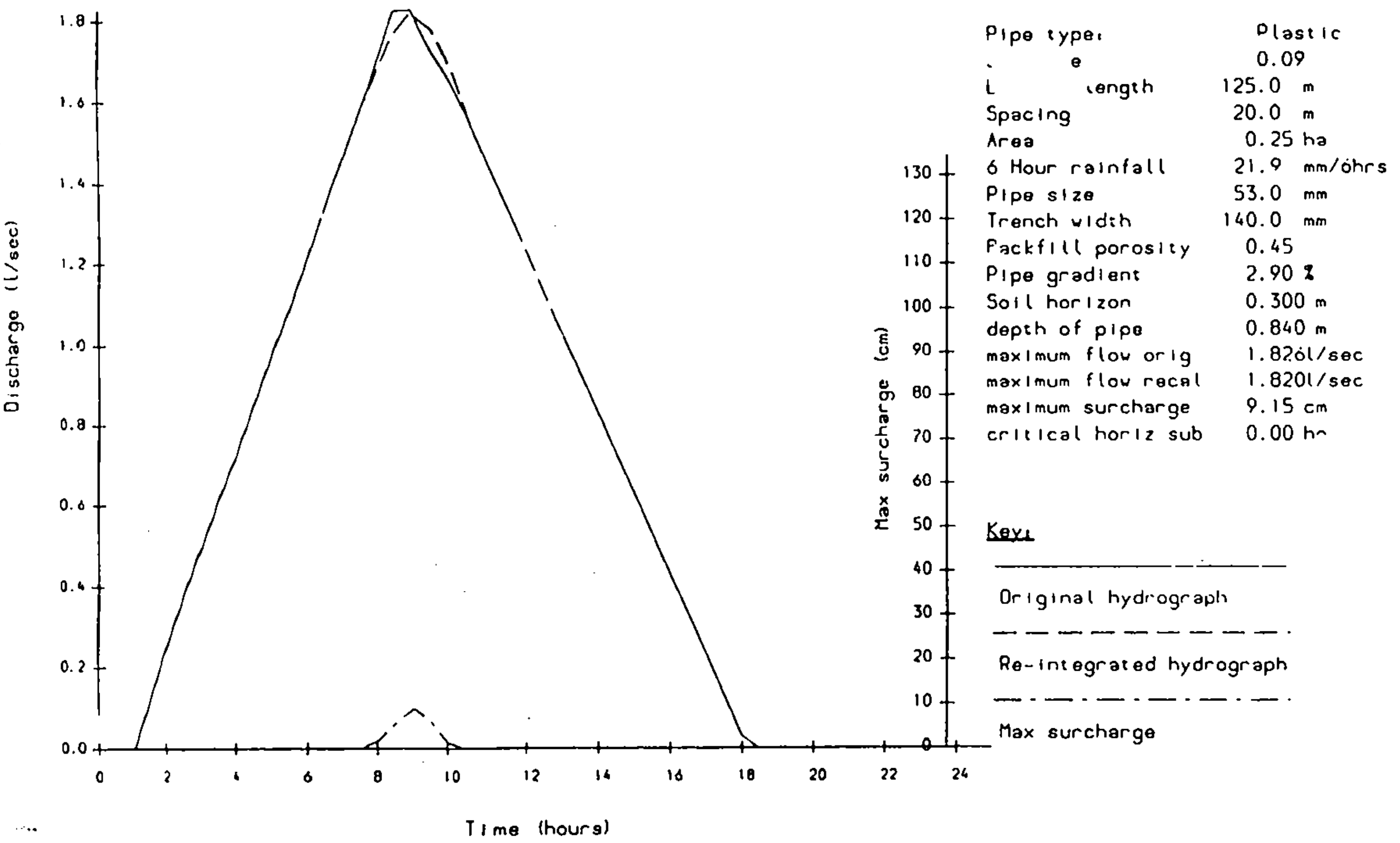
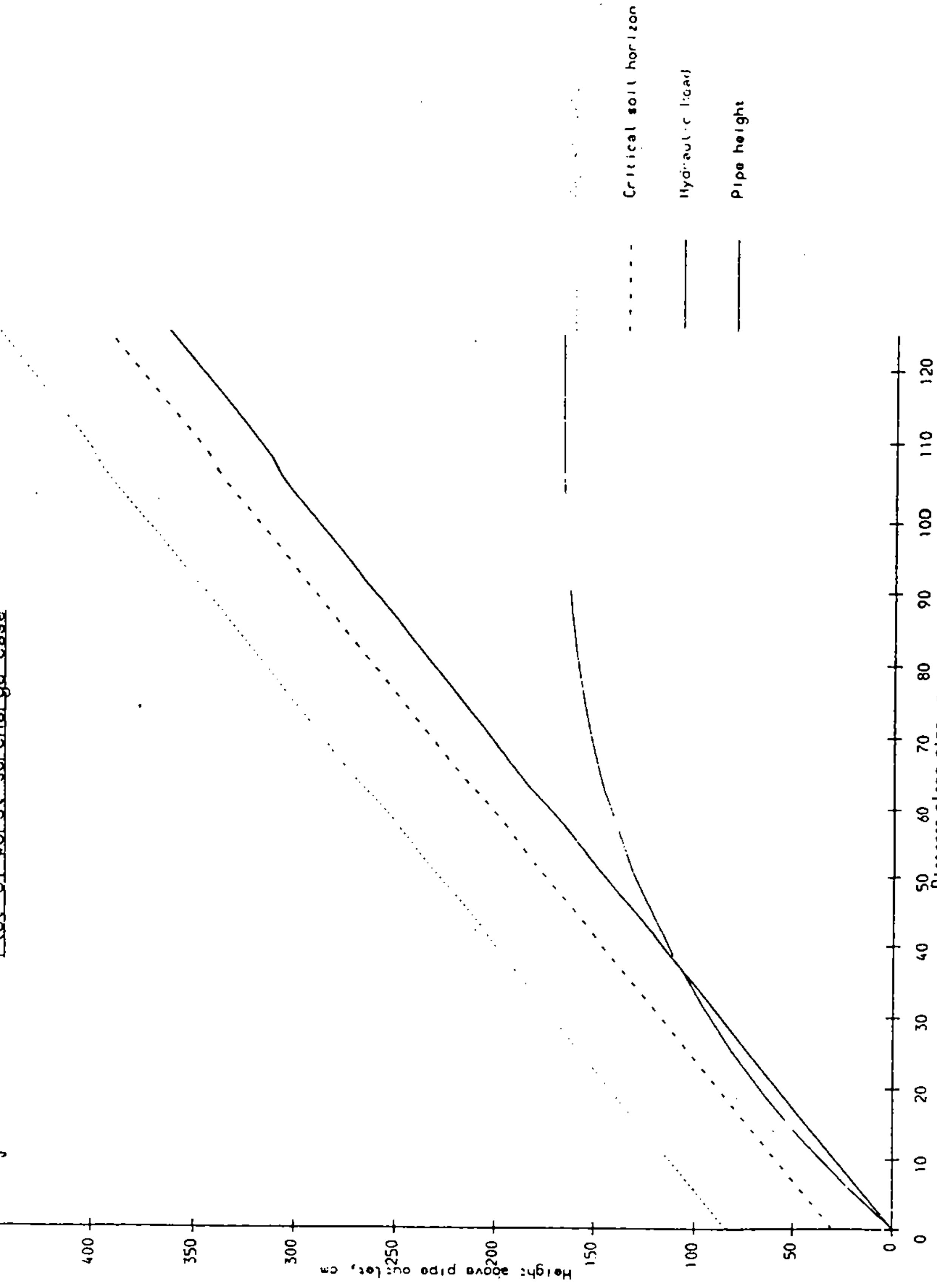


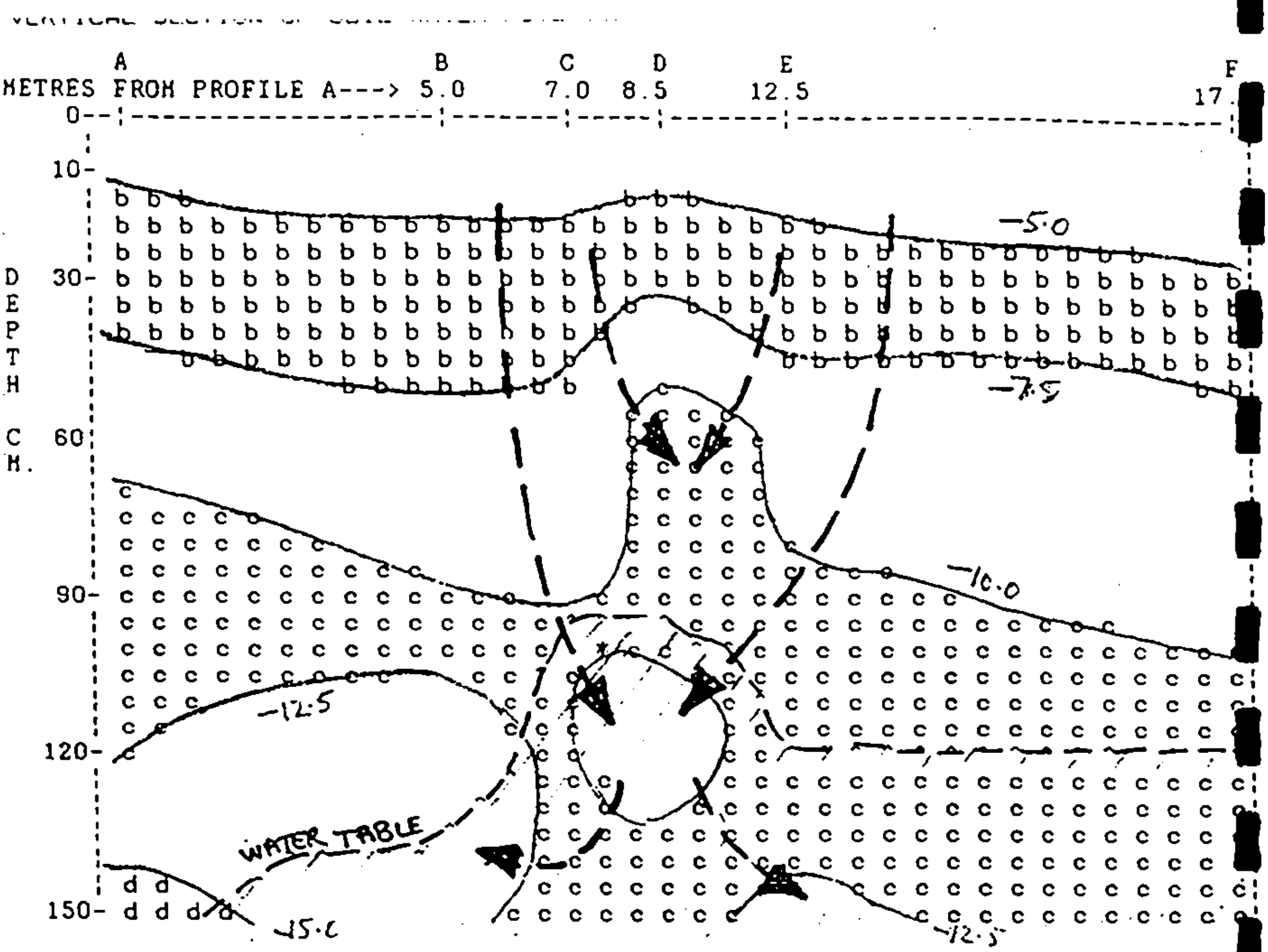
Fig 4



Plot of worst surcharge case

Field Drainage Experimental Unit
Anstey Hall, Maris Lane, Trumpington
Cambridge, UK CB2 2LF

ADAS



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

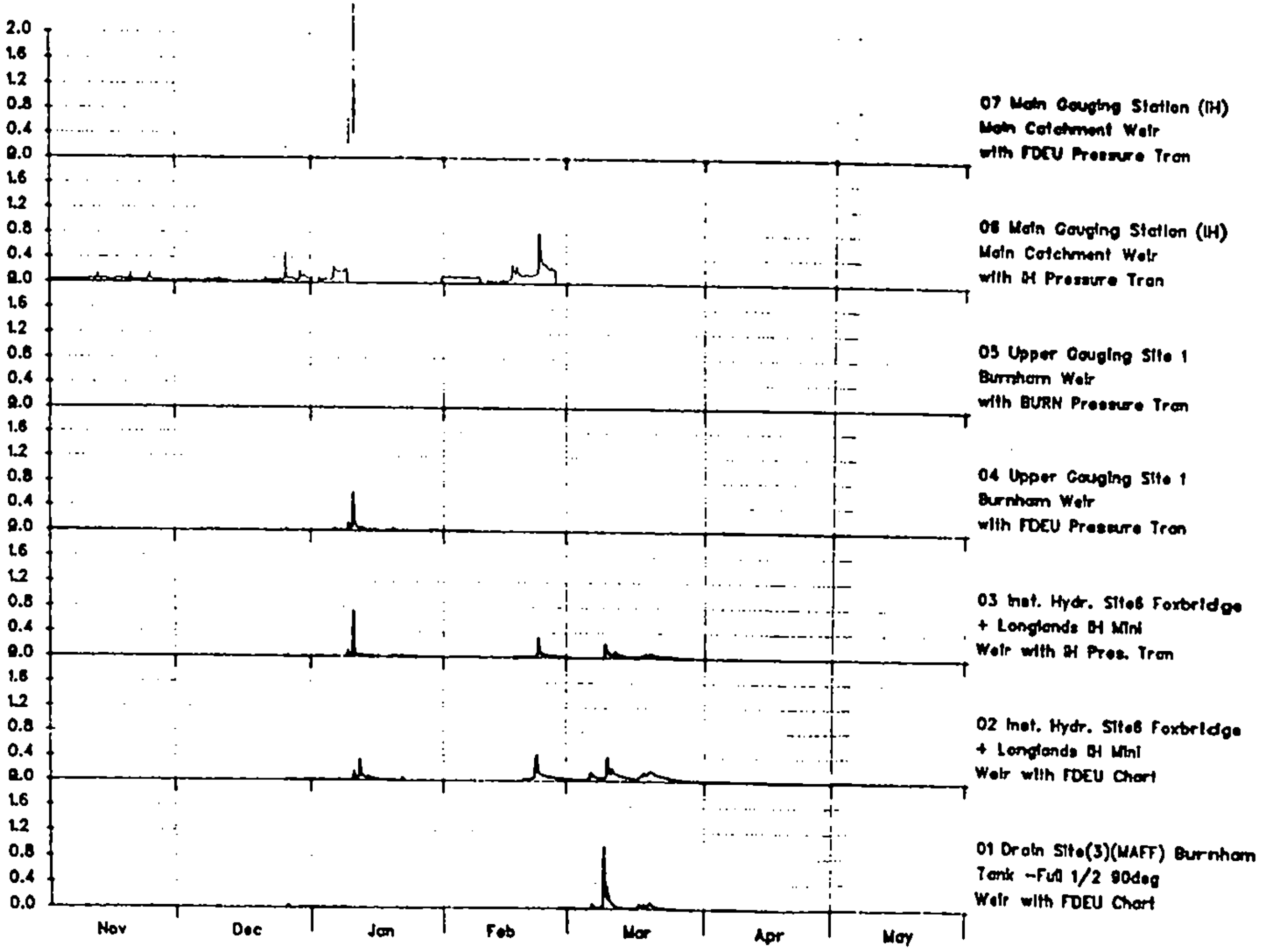
h = -50.0 to -55.0
i = -60.o to -65.0
j = -77.0 to -75.0
~ = <-75.0

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

* = POSITION OF FIELD DRAIN   ——➤ = Flux   = SATURATED

FIGURE 5. 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.

Fig 6 Corrected ROSEMAUND data from : 90-91 All flows in mm/hr



Field Drainage Experimental Unit
Anstey Hall, Maris Lane, Trumpington
Cambridge, UK CB2 2LF

ADAS

APPENDIX IX

Results of Isoproturon analysis

Table B1. Soil levels of isoproturon in Foxbridge and Longlands following Autumn 1990 application.

Values are averages over top 1 m unless indicated; data are ppm (mg/kg) on wet weight basis.

Date	26.11.90	30.11.90	5.12.90	11.12.90	18.12.90	8.1.91
	0.190	0.091	0.084	0.044	0.259	0.005
	0.155	0.086	0.073	0.050	0.081	0.017
	0.090	0.135	0.040	0.093	0.275	0.018
	0.034	0.096	0.212	0.062	0.059	0.172
	0.372	0.265	0.441	0.151		
	0.240		0.301	0.072		
	0.227		0.101	0.115		
	0.129		0.215	0.073		
	0.252		0.061	0.235		
	0.087					
	0.516					
	0.416					
	0.107					
	0.401					
Profile:						
0-25 cm	0.369		0.205	0.032	1.165	0.089
25-50 cm	0.041		0.026	nd	0.067	nd
50-75 cm	0.071		0.029	0.046	0.014	0.015
75-100 cm	0.166		0.037	nd	0.035	0.007

nd: not detected (detection limit 0.004 mg/kg wet weight)

Results of Dimethoate analysis

Table B2. Soil levels of dimethoate in Foxbridge and Longlands following Autumn 1990 application.

Values are averages over top 1 m unless indicated; data are ppm (mg/kg) on wet weight basis.

Date	30.11.90	5.12.90	11.12.90	18.12.90	8.1.91
	0.018	nd	0.009	0.040	nd
	0.023	0.028	0.007	0.005	nd
	0.032	nd	0.022	0.020	nd
	0.026	0.037	0.007	nd	nd
	0.056	0.049	0.025		
		0.045	0.009		
		0.015	nd		
		0.032	nd		
		0.019	0.007		
Profile:					
0-25 cm		0.034	0.010	0.021	nd
25-50 cm		nd	nd	nd	nd
50-75 cm		0.021	nd	nd	nd
75-100 cm		0.034	nd	nd	nd

nd: not detected (detection limit 0.005 mg/kg wet weight)

Background samples taken on 30 October 1990 had less than detection limit.

Table B3. Soil levels of dimethoate in Stoney and Brushes following Autumn 1990 application

Values are averages over top 1 m unless indicated; data are ppm (mg/kg) on wet weight basis.

Date	30.11.90	6.12.90	12.12.90	18.12.90	8.1.91
	0.008	0.034	nd	nd	nd
	0.033	0.022	nd	nd	nd
	0.043	nd	nd	nd	nd
	0.014	0.063	nd	nd	nd
	0.014	0.012	0.017	nd	nd

nd: not detected (detection limit 0.005 mg/kg wet weight)

Background samples taken on 31 October 1990 had less than detection limits.

Results of Atrazine analysis

Table B4. Soil levels of atrazine in Foxbridge and Longlands following Autumn 1991 application.

Values are averages over top 1 m unless indicated; data are ppb (μg/kg) on wet weight basis.

Date	28.11.91	11.12.91	10.1.92	23.1.92	13.2.92	1.4.92
	125.3	38.1	44.2	66.8	51.9	29.8
	95.7	73.9	15.5	26.3	20.1	16.3
	134.1	77.6	145.9	42.7	42.8	10.7
	30.7	61.3	38.1	88.3	18.6	11.1
	139.1	123.4	39.3	79.9	21.6	9.9
	83.7	129.1	22.9	46.4	21.0	16.1
	124.3	96.5	18.6	26.9	55.9	15.0
	91.2	55.0	37.9	88.6	9.8	10.3
	63.0	131.4	47.9	61.8	16.7	26.0
Profile:						
0-25 cm	213.6	334.0	78.0	104.2	107.1	
25-50 cm	64.9	19.2	12.9	2.3	24.8	
50-75 cm	35.3	12.7	8.4	8.1	20.1	
75-100 cm	8.8	10.5	3.6	2.5	20.0	

Background samples taken on 30 October 1991 had less than detection limit (2-3 μg/kg).

Results of Carbofuran analysis

Soil levels of carbofuran in Stoney and Brushes following application in Winter 1991.

Values are averages over top 1 m except for those marked 3.1, 3.2 etc, which are succesive 25 cm increments down to 1 m. Concentrations are reported as ppm (mg/kg) on a wet weight basis; moisture contents are percentage by weight.

Table B5 Carbofuran. Sampling date 30.10.91 Background samples

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	<0.004	14.7
2	0.016	12.7
3	<0.004	14.0
4	0.031	12.5
5	<0.004	14.8

Table B6 Carbofuran. Sampling date 10.12.91

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.093	19.2
2	0.196	15.0
3	0.440	14.1
4	0.430	20.8
5	0.278	16.3
6	0.529	11.7
7	0.556	14.7
8.1	0.172	20.1
8.2	0.181	18.0
8.3	0.505	16.2
8.4	0.367	15.9
9	0.313	14.3
10	0.347	20.1

Mean conc: 0.349 ± 0.153 ppm   Mean moisture content: 16.4 ± 3.0%

Table B7 Carbofuran. Sampling date 19.12.91

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.362	14.0
2	1.155	13.8
3	0.256	13.9
4	0.490	16.8
5	1.334	19.0
6	0.339	18.5
7	0.024	13.4
8	0.018	15.3
9.1	3.597	22.2
9.2	0.157	19.5
9.3	0.203	15.2
9.4	0.378	12.6
10	0.265	16.5

Mean conc: 0.537 ± 0.478 ppm Mean moisture content: 15.9 ± 2.1%

Table B8 Carbofuran. Sampling date 9.1.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.145	18.5
2	0.217	15.0
3	0.187	20.6
4.1	0.391	24.9
4.2	0.106	21.8
4.3	0.091	19.6
4.4	0.133	19.1
5	0.110	17.0
6	0.057	16.3
7	0.185	18.7
8	0.140	17.8
9	0.197	18.2
10	0.097	19.3

Mean conc: 0.152 ± 0.051 ppm Mean moisture content: 18.3 ± 1.9%

Table B9 Carbofuran. Sampling date 22.1.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.150	16.2
2.1	0.032	20.7
2.2	0.024	16.0
2.3	0.016	13.1
2.4	0.015	12.5
3	0.082	18.9
4	0.140	16.7
5	0.145	11.9
6	0.184	16.6
7	0.250	14.1
8	0.339	15.9
9	0.034	15.3
10	0.112	17.9

Mean conc: 0.146 ± 0.096 ppm Mean moisture content: 15.9 ± 1.9%

Table B10 Carbofuran. Sampling date 12.2 92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.158	13.5
2	0.134	15.5
3	0.191	19.3
4	0.103	19.5
5	0.105	18.9
6	0.205	18.2
7.1	0.702	22.9
7.2	0.115	19.3
7.3	0.104	16.7
7.4	0.136	14.8
8	0.101	15.8
9	0.075	16.9
10	0.110	18.6

Mean conc: 0.145 ± 0.059 ppm Mean moisture content: 17.5 ± 2.0%

Table B11 Carbofuran. Sampling date 4.3.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.074	16.6
2	0.088	14.9
3	0.045	18.8
4	0.186	18.4
5	0.071	18.2
6.1	0.069	21.6
6.2	0.024	14.2
6.3	0.006	11.6
6.4	0.009	14.6
7	0.078	15.6
8	0.098	15.6
9	0.088	16.5
10	0.112	15.3

Mean conc: 0.087 ± 0.043 ppm Mean moisture content: 16.5 ± 1.4%

Results of aldicarb analysis

Soil levels of aldicarb sulphone in Foxbridge and Longlands following Spring 1992 application.

Samples were treated to oxidise all aldicarb residues to aldicarb sulphone. Values are averages over top 1 m except for those marked 3.1, 3.2 etc, which are succesive 25 cm increments down to 1 m. Concentrations are reported as ppm (mg/kg) on a wet weight basis; moisture contents are percentage by weight.

Table B12 Aldicarb Sampling date 13.2.92 Background samples

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	<0.002	14.8
2	<0.002	17.7
3	<0.002	22.6
4	<0.002	23.3
5	<0.002	22.6

Table B13 Aldicarb Sampling date 5.3.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.020	19.0
2	0.035	17.4
3	0.009	15.6
4	0.004	22.6
5.1	0.010	23.7
5.2	0.007	22.1
5.3	0.032	17.8
5.4	0.014	16.4
6	0.017	13.0
7	0.027	15.3
8	0.085	14.6
9	0.067	23.9
10	0.014	21.1

Mean conc: 0.029 ± 0.026 ppm Mean moisture content: 18.3 ± 3.7%

Table B14 Aldicarb Sampling date 19.3.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.011	18.8
2	0.078	10.7
3	0.058	10.5
4	0.016	18.6
5	0.037	20.4
6.1	0.280	17.5
6.2	0.055	18.9
6.3	0.062	14.4
6.4	0.126	14.5
7	0.066	18.8
8	0.155	18.9
9	0.008	17.4
10	0.351*	21.7

Mean conc: 0.091 ± 0.104 ppm Mean moisture content: 17.2 ± 3.8%

Excluding * as more than 2 SD from the mean: 0.062 ± 0.052 ppm

Table B15 Aldicarb Sampling date 1.4.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.021	16.0
2	0.055	15.9
3	0.064	15.5
4	0.003	18.5
5.1	0.081	21.8
5.2	0.025	21.0
5.3	0.055	19.4
5.4	0.010	18.0
6	0.114	19.6
7	0.067	17.6
8	0.031	18.7
9	0.085	18.1
10	0.013	22.8

Mean conc: 0.050 ± 0.034 ppm Mean moisture content: 18.3 ± 2.2%

Table B16 Aldicarb Sampling date 15.4.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.018	17.7
2	0.016	13.2
3	0.003	16.5
4	0.042	17.6
5	0.015	14.1
6	0.035	20.2
7	0.019	19.3
8.1	0.003	20.7
8.2	0.003	18.6
8.3	<0.002	18.4
8.4	<0.002	15.3
9	<0.002	23.3
10	0.003	21.4

Mean conc: 0.015 ± 0.0014ppm Mean moisture content: 18.2 ± 3.1%

Below detection limit treated as half detection limit in calculating mean.

Table B17 Aldicarb Sampling date 6.5.92

Sample No.	Concentration (ppm wet weight)	Moisture content (% weight)
1	0.006	16.2
2	0.056	10.0
3	0.012	18.1
4	0.007	16.4
5	0.030	16.5
6	0.054	18.5
7	0.124*	18.0
8.1	0.003	20.1
8.2	0.003	16.2
8.3	0.010	14.5
8.4	0.006	14.8
9	0.002	23.2
10	0.023	21.1

Mean conc: 0.030 ± 0.039 ppm Mean moisture content: 17.4 ± 3.5%

Excluding * as more than 2 SD from mean: 0.020 ± 0.022 ppm

APPENDIX X

Table A1 Winter 1991/92 Event: 17 December 1992
Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	IPU (µg/l)	Carbofuran (µg/l)	Rain (mm)	Flow (l/s)
	21:00					4	1.25
	22:00					0	2.56
	23:00					0	1.22
18-Dec-91	00:00	0.28	0.18	7.2	1	0	0.48
	01:00	0.06	1.09	8.5	1.1	0	0.48
	02:00			15.1	3.9	0	0.26
	03:00	0.27	0.99	11.4	35.5	0	0.48
	04:00					1	
	05:00	0.25	0.62	8.4	3.2		0.48
	06:00	0.35	0.68	8.3	3.8		
	07:00	0.25	0.38	6.1	2.3		
	08:00	0.25	0.31	5.2	1.9		0.04
	09:00	0.75	0.42	14.9	2.4		0.48
	10:00	0.57	0.32	3.9	2.7		
	11:00	0.8	0.29	5.6	2.2		
	12:00	0.64	0.07	4.6	2.2		0.48
	13:00	1.79	1.17	2.7	1.9		0.48
	14:00			4.4	3		0.04
	15:00			5.9	3.2		
	16:00	0.6	0.26	4.3	1		0.48
	17:00	0.57	0.55	5.3	2.8		
	18:00	0.51	0.25	1	1		
	19:00	0.85	0.24	3.9	1.5		
	20:00	0.82	0.26	6.3	2		
	21:00	0.85	0.42	2.45	3.1	0.5	
	22:00	0.64	0.29	2.9	2.5		
	23:00	0.24	0.13	2.48	2.47		

Table A2. Winter 1991/92 Event: 9th January 1992
Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Atrazine (μg/l)	Simazine (μg/l)	IPU (μg/l)	Carbofuran (μg/l)	Rain (mm)	Flow (l/s)
	17:00	0.33	0.59	<0.02	<1		24.73
11-Jan-92	18:00	0.37	0.23	<0.02	<1		24.21
	19:00	0.36	0.20	<0.02	<1		21.61
	20:00	0.18	0.13	<0.02	<1		21.58
	21:00			<0.02	<1		21.08
	22:00	0.17	0.12	<0.02	<1		21.08
	23:00			<0.02	<1		20.56
12-Jan-92	00:00			<0.02	<1		20.56
	01:00	0.30	0.21	<0.02	<1		20.56
	02:00	0.28	0.17	<0.02	<1		20.56
	03:00	0.22	0.16	2.9	<1		20.06
	04:00			4.8	<1		20.56
	05:00	0.31	0.13	3.3	<1		19.57
	06:00	0.21	0.11	34.5	<1		20.06
	07:00	0.21	0.13	4.4	<1		20.06
	08:00	0.20	0.11	2	<1		19.09
	09:00	0.22	0.12	4.2	<1		16.65
	10:00	0.19	0.12	44.9	<1		19.57
	11:00	0.18	0.10	4.5	<1		16.65
	12:00	0.17	0.11	2.6	<1		17.61
	13:00	0.15	0.15	1.7	<1		16.65
	14:00	0.20	0.16	1.3	<1		16.65
	15:00	0.20	0.10	18.3	<1		16.65
	16:00	0.21	0.36	7.9			16.65

Note: LOD < 0.02 μg/l

Table A3. Winter 1991/92 Event: 4th January 1992
Longlands drain site @ Grid Ref; SO 5688 4849

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	Carbofuran (µg/l)	Rain (mm)	Flow (l/s)
	22:15				1	0.024
	23:15				1	0.062
	00:15				0.5	0.062
05-Jan-92	01:15	22.6		<1	0.5	0.062
	02:15				1	0.062
	03:15				0	0.062
	04:15	20.25	0.49	<1	0	0.062
	05:15	53.3	10.3	1.8	0	0.062
	06:15	56.5	0.1	<1	0	0.062
	07:15	21.6	0.05	<1	0	0.062
	08:15	33.87	0.08	<1	0	0.024
	09:15	20.5	0.07	<1	0	0.024
	10:15	45.11	0.09	<1	0	0.024
	11:15	42.6	0.15	<1	0	0.024
	12:15	51.06	1.24	<1	0	0.024
	13:15	28.2	0.13	<1	0	0.024
	14:15	48.63	0.09	<1	0	0.024
	15:15	44.4	<0.04	<1	0	0.024
	16:15	46.4	0.05	2.1	0	0.024
	17:15	26.3	0.62	<1	0	0.024
	18:15	39.4	0.08	<1	0	0.024
	19:15			<1	0	0.024
	20:15	33.8	<0.04	<1	0	0.024
	21:15	23.2	<0.04	<1	0	0.024
	22:15	21.9	<0.04	3.2	0	0.024
	23:15	26.4	<0.04	<1	0	0.024
06-Jan-92	00:15	52.1	<0.04	<1	0	0.024

Table A4. Winter 1991/92 Event: 8th January 1992
Longlands Drain Site @ Grid Ref; SO 5688 4849

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	Carbofuran (µg/l)	Rain (mm)	Flow (l/s)
08-Jan-92	11:00	3.2	<0.04	<1		0.024
	12:00	6.6	<0.04	<1		0.024
	13:00	10.7	0.2			0.024
	14:00	11.1	0.19	<1	0.5	0.024
	15:00	9.2	0.14	<1	2	0.062
	16:00	10.4	0.14	<1	1.5	0.062
	17:00	7.4	0.17	<1	2	0.108
	18:00	4.3	0.07	<1	2.5	0.160
	19:00	10.9	0.13	<1	2	0.160
	20:00			<1	2	0.401
	21:00	8.7	0.15	<1	1.5	0.686
	22:00	7.7	0.12	<1	2.5	0.762
	23:00	41	<0.04	3	4	1.002
	00:00	40.1	<0.04	<1	4.5	4.016
	01:00	81.4	<0.04	<1	1.5	3.343
	02:00	10.9	<0.04	<1	1	3.234
	03:00	11.1	<0.04	8	4	3.017
	04:00	16.7	<0.04	2.9	4.5	6.452
	05:00	16	<0.04	<1	6.5	8.853
09-Jan-92	06:00	15.9	<0.04	<1	6.0	10.405
	07:00	9.1	<0.04	<1	7	10.405
	08:00	12.2	<0.04	3	5	10.693
	09:00	6.4	<0.04	<1	3	10.261
	10:00	6.7	<0.04	<1	3.5	9.834

Table A5. Winter 1991/92 Event: 8th January 1992
Longlands Drains Site @ Grid Ref; SO 5688 4849

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	Carbofuran (µg/l)	Rain (mm)	Flow (l/s)
	16:20			<1.0		0.40
10-Jan-92	17:20	3.36	0.048	<1.0		0.46
	18:20					0.40
	19:20	7.72	0.050	<1.0		0.33
	20:20	3.31	0.045	<1.0		0.33
	21:20	4.07	0.062	<1.0		0.33
	22:20	4.32	0.039	<1.0		0.27
	23:20	4.39	0.044	<1.0		0.33

Table A6. Spring 1992 Event: 15th April 1992
Longlands Drains Site @ Grid Ref; SO 5688 4849

Date	Time	Simazine (µg/l)	Atrazine (µg/l)	Sulphoxide (µg/l)	Sulphone (µg/l)	Rain (mm)	Flow (l/s)
14-Apr-92	12:00					1	<0.024
	13:00					1	<0.024
	14:00					1	<0.024
	15:00						<0.024
	16:00					1.5	<0.024
	17:00					1	<0.024
	18:00						<0.024
	19:00					1.5	<0.024
	20:00					3	<0.024
	21:00					2	<0.024
	21:46	8.3	11.4	<.15	<.05		0.024
	22:00					3	<0.024
	22:46	13.4	16.2	0.59	0.67		<0.024
	23:00					1.5	0.024
	23:46	9.5	15.3	1.38	1.77		<0.024
15-Apr-92	00:00						0.024
	00:46	6.5	13.7	0.95	1.29		0.024
	01:00					0.5	0.024
	01:46	5.2	13	0.68	0.94		<0.024
	02:00					0.5	<0.024
	02:46	4.7	13	0.69	0.84		<0.024
	03:46	3.9	12.2	0.47	0.67		<0.024
	04:46	3.6	11.1	0.44	0.62		<0.024
	05:46	3.2	11.3	0.44	0.59		<0.024
	06:46	2.6	11.3	0.36	0.56		<0.024
	07:46	2.3	10.4	0.35	0.45		<0.024
	08:46	2.1	11.3	0.31	0.42		<0.024
	09:46	1.97	10.9	0.25	0.33		<0.024
	10:46	1.83	10.8	0.26	0.32		<0.024
	11:46	1.79	10.7	0.21	0.29		0.024
	12:46	1.53	10.2	0.19	0.26		<0.024
	13:46	1.56	10.7	0.19	0.21		<0.024
	14:46	1.45	10.3	0.16	0.2		<0.024
	15:46	1.39	9.9	0.21	0.14		<0.024
	16:46	1.46	8.7	0.15	0.18		<0.024
	17:46	1.42	9.5		0.15		<0.024
	18:46	1.31	8.8		0.14		<0.024
	19:46	1.27	8.7		0.08		<0.024
	20:00						<0.024
	20:46	1.21	9.2		0.11		<0.024

Table A7. Routine Samples Autumn 1991 to Spring 1992
Longlands Drains Site @ Grid Ref; SO 5688 4849

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	IPU (µg/l)	Aldecarb (µg/l)	Sulphone (µg/l)	Sulphoxide (µg/l)
31-Oct-91		<0.05	<0.05	<0.2			
26-Nov-91	18:15	<0.05	<0.05	<0.2			
10-Dec-91	17:38						
17-Dec-91	14:20	160.0	2.10	<0.2			
07-Jan-92	18:00	34.0	0.39	<0.2			
23-Jan-92	15:24	7.2	0.06	<0.2			
04-Feb-92	09:55	7.7	0.09	<0.2			
18-Feb-92	17:42	9.6	0.09	<0.1			
03-Mar-92	14:25	7.4	0.06		<0.2	<0.15	<0.05
17-Mar-92	17:55	7.1	0.09		<0.2	<0.15	<0.05
31-Mar-92	17:10	6.3	0.11		<0.2	<0.15	<0.05
14-Apr-92	16:40						
09-Jun-92	17:12						

Table A8. Routine Samples Spring 1991 to Spring 1992
Main Gauging Site @ Grid Ref; SO 5598 4789

Date	Time	Atrazine (µg/l)	Simazine (µg/l)	IPU (µg/l)	Aldecarb (µg/l)	Sulphoxide (µg/l)	Sulphone (µg/l)
27-Mar-91		0.37	0.395	5.25			
08-May-91		1.05	0.46	7.05			
22-May-91		1.335	0.345	10.5			
04-Jun-91		2.2	1.45	8.85			
19-Jun-91		2.15	1.975	19.2			
03-Jul-91		2	2.1	11.85			
13-Aug-91	10:15	2.95	0.945	20			
28-Aug-91		3.25	0.545	19.05			
11-Sep-91	10:50	3.2	0.59	17.5			
26-Sep-91	09:00	2.45	0.55	10.7			
08-Oct-91		0.82	0.325	3.55			
12-Oct-91		1.9	0.9	16			
22-Oct-91		2.3	0.515	13.15			
12-Nov-91		0.63	0.325	4.25			
26-Nov-91	16:45	1.3	0.6	7.25			
10-Dec-91	15:10						
07-Jan-92	15:42	1.26	0.26	5.5			
23-Jan-92	16:40	0.74	0.24	4.5			
04-Feb-92	09:15	0.65	0.2	4.2			
18-Feb-92	15:40	1.05	0.67	2.4			
03-Mar-92	15:40	0.86	3.3	29	0.44	0.47	0.22
17-Mar-92	15:55	0.92	0.58	5.1	<0.2	<0.15	0.105
31-Mar-92	14:53	0.82	0.36	3.6	<0.2	<0.15	0.07
14-Apr-92	14:45						
28-Apr-92	15:30						
12-May-92	15:30						
27-May-92	15:00						
09-Jun-92	15:30	0.97	0.44	0.71	<0.2		
23-Jun-92	16:00	1.31	1.22	10.7	<0.2		
07-Jul-92	14:20						

Table A9. Spring 1992 Event: 28 May 1992
Main Gauging Station @ grid ref; SO 5598 4789

Date	Time (l/s)	Flow (mm)	Rain (µg/l)	IPU (µg/l)	Simazine (µg/l)	Atrazine (µg/l)	Aldicarb (µg/l)	Sulphoxide (µg/l)	Sulphone (µg/l)
	03:45	6.91	4						
	04:45	11.38							
	05:45	9.81							
	06:45	6.91							
	07:45	5.60							
	08:45	6.91							
	09:45	6.91							
	10:45	6.91							
	11:45	6.91							
	12:45	5.60							
	13:45	6.91							
	14:45	6.91	10.5						
	15:45	43.02							
	16:45	22.36		7.8	3.5	1.76	lt 0.2	lt 0.15	lt 0.05
	17:45	16.56		1.51	0.71	0.97	0.5	lt 0.15	lt 0.05
	18:45	11.38		1.11	0.62	0.65	lt 0.2	lt 0.15	lt 0.15
	19:45	9.81		1.62	0.44	0.47	lt 0.2	lt 0.15	lt 0.05
	20:45	9.81		1.71	0.74	0.57	lt 0.2	lt 0.15	0.18
	21:45	8.32		2	0.61	0.55	lt 0.2	lt 0.15	0.21
	22:45	6.91		2.4	0.71	0.67	lt 0.2	lt 0.15	0.19
	23:45	5.60		4.1	2.5	1.07	lt 0.2	lt 0.15	lt 0.05
29 May 93									
	00:45	6.91		4.3	2.9	1.01	lt 0.2	lt 0.15	0.18
	01:45	6.91		4.9	1.97	0.99	lt 0.2	lt 0.15	0.13
	02:45	6.91		4.3	1.37	0.91	lt 0.2	lt 0.15	0.12
	03:45	6.91		5.1	1.32	0.98	lt 0.2	lt 0.15	0.18
	04:45	5.60		5	1.55	1.13	lt 0.2	lt 0.15	0.17
	05:45	5.60		7.4	1.44	1.17	lt 0.2	lt 0.15	0.12
	06:45	5.60		5.7	1.15	1.02	lt 0.2	lt 0.15	0.11
	07:45	6.91		5.7	1.08	1.16	lt 0.2	lt 0.15	0.09
	08:45	6.91		6	1.15	1.19	lt 0.2	lt 0.15	0.06
	09:45	6.91		6.5	0.97	1.19	lt 0.2	lt 0.15	0.07
	10:45	6.91	0.5	6.7	1.19	1.43	lt 0.2	lt 0.15	lt 0.05
	11:45	5.60	1	6.7	0.96	1.34	lt 0.2	lt 0.15	lt 0.05
	12:45	6.91	1.5	6.1	1.13	1.4	lt 0.2	lt 0.15	lt 0.05
	13:45	9.81	0.5	7.2	1.42	1.49	lt 0.2	lt 0.15	lt 0.05
	14:45	11.38		6.8	1.46	1.46	lt 0.2	lt 0.15	lt 0.05
	15:45	9.81		6.7	1.08	1.37	lt 0.2	lt 0.15	lt 0.05

Table A10 Spring 1992 Event: 07 June 1992
Main Gauging Station@ grid ref; SO 5598 4789

Date	Time	Rain (mm)	Flow (l/s)	Isoproturon (µg/l)	simazine (µg/l)	atrazine (µg/l)	aldicarb (µg/l)	sulphoxide (µg/l)	sulphone (µg/l)
07-Jun-92	01:00	0.0	3.84						
	02:00	0.0	2.79						
	03:00	0.0	2.79						
	04:00	4.5	2.79						
	05:00	0.5	3.84						
	06:00	0.0	13.94	7.5	0.62	1.40	lt 0.2	lt 0.15	lt 0.05
	07:00	0.0	6.28	1.8	0.56	0.95	0.2	0.20	lt 0.05
	08:00	0.0	3.84	1.2	0.46	0.75	0.5	lt 0.15	lt 0.05
	09:00	0.0	3.84	1.7	0.43	0.81	0.2	lt 0.15	lt 0.05
	10:00	0.0	3.84	2.4	0.50	0.98	lt 0.2	lt 0.15	lt 0.05
	11:00	0.0	3.84	3.2	0.44	1.05	lt 0.2	lt 0.15	lt 0.05
	12:00	0.0	3.84	4.1	0.54	1.24	lt 0.2	lt 0.15	lt 0.05
	13:00	0.0	3.84	5.2	0.46	1.19	lt 0.2	lt 0.15	lt 0.05
	14:00	0.0	3.84	5.2	0.53	1.19	lt 0.2	lt 0.15	lt 0.05
	15:00	0.0	5.01	3.4	0.49	0.91	lt 0.2	lt 0.15	lt 0.05
	16:00	0.0	3.84	10.0	1.59	3.00		lt 0.15	lt 0.05
	17:00	0.0	3.84	5.5	0.91	1.27	lt 0.2	lt 0.15	lt 0.05
	18:00	0.0	3.84	6.9	0.93	1.33		lt 0.15	lt 0.05
	19:00	2.5	3.84	7.7	1.01	1.35	lt 0.2	lt 0.15	lt 0.05
	20:00	0.5	13.94	8.0	1.05	1.41		lt 0.15	lt 0.05
	21:00	0.0	9.09	2.8	0.78	1.11	lt 0.2	2.20	0.15
	22:00	0.0	6.28	2.1	0.59	0.78		1.10	0.13
	23:00	0.0	6.28	2.6	0.55	0.78	lt 0.2	1.50	0.12
08-Jun-92	00:00	0.0	6.28	1.1	0.49	0.60		0.20	lt 0.05
	01:00	0.0	6.28	3.0	0.52	0.71		1.10	0.17
	02:00	0.0	6.28	3.2	0.58	0.71	lt 0.2	1.80	lt 0.05
	03:00	0.0	5.01	3.2	0.56	0.68	lt 0.2	2.50	0.14
	04:00	0.0	3.84	3.1	0.64	0.69	lt 0.2	1.61	lt 0.05
	05:00	0.0	5.01	3.8	0.49	0.69	lt 0.2	0.88	lt 0.05

Appendix XI

MANUAL WATER SAMPLES

Table W1 Winter 1991/92 . Atrazine / Carbofuran experiment .

Date	Time		Site 1			Site 2			Site 3			Site 4			Site 5			Site 6	
		Stream flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)	Drain flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)	Drain flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)	Drain flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)	Drain flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)	Drain flow rate (l / sec)	Carbofuran conc. (ug / l)	Atrazine conc. (ug / l)
5.11.91		0	nd	nd		nd	nd	0	nd	nd	-	-	-	dripping	nd	nd	.	.	.
21.11.91		1.11	nd	nd		nd	nd	0.033	nd	nd	0.028	nd	nd	0.068	nd	nd	0.068	nd	nd
02.12 91		0.081	nd	nd		0.01	0.1	0	0.04	0.08		.	.		-	.		.	.
18.12.91		0	0.35	1.48		0.04	0.21		0.69	0.4		.	.		0.01	.		.	.
09.1.92		64.86	25.8	6.14		17.7	2.26	9.26	4.86	0.56		5.52	0.1		nd	nd		0.01	0.04
13.1.92		1.3	0.28	0.08		3.38	1.42	0.14	.	.	0.37	-	0.04	0.96	.	.		.	.
31.1.92		0.791	0.04	0.09		13.9	4.87		1.5	1.18		0.02	0.01		0.25	14.06		.	.
28.2.92		0.45	0.06	0.13		0.5	0.14	0	0.79	0.6		0.03	0.01		nd	5.36		.	.
27.3.92		0.45	nd	nd		nd	nd	0	nd	0.06		nd	nd		nd	3.98		.	.
1[illegible].4.92		0.55	0.03	0.1		nd	0.07	0	0.03	0.47		nd	nd		-	.		nd	6.25

Automatic Water Samples.
Table W2: Winter 1991/92, Carbofuran/atrazine experiment.
Stream at grid ref: SO 5665 4841 (Site 1).

Date	Time	Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
08-Jan	00:00	0	0.42		
08-Jan	01:00	0.5	0.42		
08-Jan	01:00	0	0.42		
08-Jan	03:00	0	0.42		
08-Jan	04:00	0	0.42		
08-Jan	05:00	0.5	0.67		
08-Jan	06:00	0	0.54		
08-Jan	07:00	0	0.54		
08-Jan	08:00	0	0.42		
08-Jan	09:00	0	0.54		
08-Jan	10:00	0	0.67		
08-Jan	11:00	0	0.54	0.6	0.02
08-Jan	12:00	0	0.54	0.07	0.01
08-Jan	13:00	0	0.54	0.08	0.03
08-Jan	14:00	0.5	0.54	0.18	0.25
08-Jan	15:00	2	0.67	1.23	0.84
08-Jan	16:00	1.5	0.67	2.13	0.77
08-Jan	17:00	2	1.13	4.42	1.08
08-Jan	18:00	2.5	1.13	3.44	0.62
08-Jan	19:00	2	1.48	5.95	0.95
08-Jan	20:00	2	2.06	14.84	2.77
08-Jan	21:00	1.5	2.06	9.5	1.4
08-Jan	22:00	2.5	2.92	6.13	0.8
08-Jan	23:00	4	3.38	14.04	2.48
09-Jan	00:00	4.5	4.38	24.32	4.71
09-Jan	01:00	1.5	10.86	14.22	3.17
09-Jan	02:00	1	19.04	23.3	5.67
09-Jan	03:00	4	18.62	16.48	3.76
09-Jan	04:00	4.5	16.55	15.32	4.08
09-Jan	05:00	6.5	26.23	8.25	2.53
09-Jan	06:00	6	50.15	3.63	1.05
09-Jan	07:00	7	80.10	4.12	1.14
09-Jan	08:00	5	92.04	6.32	1.95
09-Jan	09:00	3	112.09	6.47	2.38
09-Jan	10:00	3.5	115.17	3.4	1.18
09-Jan	11:00	2.5	108.28		
09-Jan	12:00	1.5	93.48		
09-Jan	13:00	0	78.74		
09-Jan	14:00	0.5	64.86		
09-Jan	15:00	0	47.82	26.78	3.42
09-Jan	16:00	0	37.28		
09-Jan	17:00	0	29.60		
09-Jan	18:00	0	24.82		
09-Jan	19:00	0	20.77	19.9	3.13
09-Jan	20:00	0	18.20		
09-Jan	21:00	0	16.55		
09-Jan	22:00	0	14.18		
09-Jan	23:00	0	13.04	14.31	1.84

10-Jan	00:00	0	12.30		
10-Jan	01:00	0	11.21		
10-Jan	02:00	0	10.86		
10-Jan	03:00	0	9.48	16.96	2.37
10-Jan	04:00	0	9.15		
10-Jan	05:00	0	8.49		
10-Jan	06:00	0	7.85		
10-Jan	07:00	0	7.23	11.53	1.94
10-Jan	08:00	0	6.62		
10-Jan	09:00	0	6.03		
10-Jan	10:00	0	6.03		
10-Jan	11:00	0	6.03	12.92	2.57
10-Jan	12:00	0	5.46		
10-Jan	13:00	0	5.18		
10-Jan	14:00	0	4.91		
10-Jan	15:00	0	4.64	6.64	2.11
10-Jan	16:00	0	4.64		
10-Jan	17:00	0	4.38		
10-Jan	18:00	0	4.12		
10-Jan	19:00	0	3.87	5.27	1.32
10-Jan	20:00	0	3.87		
10-Jan	21:00	0	3.87		
10-Jan	22:00	0	3.62		
10-Jan	23:00	0	3.38	6.7	1.91
11-Jan	00:00	0	3.38		
11-Jan	01:00	0	3.15		
11-Jan	02:00	0	2.92		
11-Jan	03:00	0	2.92	7.32	1.64
11-Jan	04:00	0	2.92		
11-Jan	05:00	0	2.92		
11-Jan	06:00	0	2.92		
11-Jan	07:00	0	2.69	4.53	1.09
11-Jan	08:00	0	2.69		
11-Jan	09:00	0	2.47		
11-Jan	10:00	0	2.47		
11-Jan	11:00	0	2.47	3.78	1.18
11-Jan	12:00	0	2.47		
11-Jan	13:00	0	2.69		
11-Jan	14:00	0	2.69		
11-Jan	15:00	0	2.47	3.1	1.05
11-Jan	16:00	0	2.47		
11-Jan	17:00	0	2.47		
11-Jan	18:00	0	2.47		
11-Jan	19:00	0	2.06	3.18	1.09
11-Jan	20:00	0	2.26		
11-Jan	21:00	0	2.26		
11-Jan	22:00	0	2.06		
11-Jan	23:00	0	2.06	4.37	1.61
12-Jan	00:00	0	2.06		
12-Jan	01:00	0	2.06		
12-Jan	02:00	0	2.06		
12-Jan	03:00	0	2.06	2.01	1.05
12-Jan	04:00	0	2.06		
12-Jan	05:00	0	1.86		
12-Jan	06:00	0	2.06		
12-Jan	07:00	0	2.06	1.65	0.92

12-Jan	08:00	0	2.06		
12-Jan	09:00	0	1.67		
12-Jan	10:00	0	2.06		
12-Jan	11:00	0	1.67	2.84	1.64
12-Jan	12:00	0	1.67		
12-Jan	13:00	0	1.67		
12-Jan	14:00	0	1.67		
12-Jan	15:00	0	1.67	2.15	1.58
12-Jan	16:00	0	1.67		
12-Jan	17:00	0	1.67		
12-Jan	18:00	0	1.48		
12-Jan	19:00	0	1.48	1.65	1.12
12-Jan	20:00	0	1.48		
12-Jan	21:00	0	1.67		
12-Jan	22:00	0	1.48		
12-Jan	23:00	0	1.48	2.7	1.51
13-Jan	00:00	0	1.48		
13-Jan	01:00	0	1.30		
13-Jan	02:00	0	1.48		
13-Jan	03:00	0	1.48	2.6	2.04
13-Jan	04:00	0	1.48		
13-Jan	05:00	0	1.48		
13-Jan	06:00	0	1.30		
13-Jan	07:00	0	1.48	2.41	1.97
13-Jan	08:00	0	1.30		
13-Jan	09:00	0	1.30		
13-Jan	10:00	0	1.30		
13-Jan	11:00	0	1.30	1.89	1.35

Total rainfall = 72.5 mm

Automatic Water Samples.
Table W3: Winter 1991/92, Carbofuran/atrazine experiment.
Field drain at grid ref: SO5672 4842 (Site 3).

Date	Time	Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
08-Jan	00:00	0	0.00		
08-Jan	01:00	0.5	0.00		
08-Jan	02:00	0	0.00		
08-Jan	03:00	0	0.00		
08-Jan	04:00	0	0.00		
08-Jan	05:00	0.5	0.00		
08-Jan	06:00	0	0.00		
08-Jan	07:00	0	0.00		
08-Jan	08:00	0	0.00		
08-Jan	09:00	0	0.00		
08-Jan	10:00	0	0.00		
08-Jan	11:00	0	0.00	-	-
08-Jan	12:00	0	0.01	-	-
08-Jan	13:00	0	0.02	-	-
08-Jan	14:00	0.5	0.05	-	-
08-Jan	15:00	2	0.12	264.03	35
08-Jan	16:00	1.5	0.21	260.12	51.3
08-Jan	17:00	2	0.33	140.18	33.9
08-Jan	18:00	2.5	0.62	74.39	19.6
08-Jan	19:00	2	1.45	64.04	23.3
08-Jan	20:00	2	2.73	54.23	21.6
08-Jan	21:00	1.5	4.52	52.48	20.5
08-Jan	22:00	2.5	6.87	33.96	16.4
08-Jan	23:00	4	7.92	17.75	9.1
09-Jan	00:00	4.5	6.31	21.5	10.7
09-Jan	01:00	1.5	5.68	34.25	15.3
09-Jan	02:00	1	8.67	40.87	21.2
09-Jan	03:00	4	17.74	41.05	18.8
09-Jan	04:00	4.5	22.27	42.65	20.3
09-Jan	05:00	6.5	22.27	34.74	16.2
09-Jan	06:00	6	22.27	28.89	13.7
09-Jan	07:00	7	22.18	19.34	10.2
09-Jan	08:00	5	19.92	18.98	10.2
09-Jan	09:00	3	17.80	18.75	10.6
09-Jan	10:00	3.5	15.83	12.01	6.1
09-Jan	11:00	2.5	13.99		
09-Jan	12:00	1.5	12.29		
09-Jan	13:00	0	10.71		
09-Jan	14:00	0.5	9.26		
09-Jan	15:00	0	7.94	39.75	7.06
09-Jan	16:00	0	6.74		
09-Jan	17:00	0	5.73		
09-Jan	18:00	0	5.20		
09-Jan	19:00	0	4.70	27.42	1.76
09-Jan	20:00	0	4.24		
09-Jan	21:00	0	3.80		
09-Jan	22:00	0	3.39		
09-Jan	23:00	0	3.01	23.59	1.23

10-Jan	00:00	0	2.65		
10-Jan	01:00	0	2.49		
10-Jan	02:00	0	2.34		
10-Jan	03:00	0	2.19	28.43	1.95
10-Jan	04:00	0	2.05		
10-Jan	05:00	0	1.92		
10-Jan	06:00	0	1.79		
10-Jan	07:00	0	1.67	9.73	0.67
10-Jan	08:00	0	1.55		
10-Jan	09:00	0	1.43		
10-Jan	10:00	0	1.37		
10-Jan	11:00	0	1.32	13.83	1.36
10-Jan	12:00	0	1.27		
10-Jan	13:00	0	1.23		
10-Jan	14:00	0	1.18		
10-Jan	15:00	0	1.14	16.29	1.58
10-Jan	16:00	0	1.09		
10-Jan	17:00	0	1.05		
10-Jan	18:00	0	1.01		
10-Jan	19:00	0	0.97	6.26	0.35
10-Jan	20:00	0	0.93		
10-Jan	21:00	0	0.09		
10-Jan	22:00	0	0.85		
10-Jan	23:00	0	0.82	5.12	0.66
11-Jan	00:00	0	0.78		
11-Jan	01:00	0	0.75		
11-Jan	02:00	0	0.73		
11-Jan	03:00	0	0.71	5.5	0.38
11-Jan	04:00	0	0.70		
11-Jan	05:00	0	0.68		
11-Jan	06:00	0	0.66		
11-Jan	07:00	0	0.65		
11-Jan	08:00	0	0.63		
11-Jan	09:00	0	0.61		
11-Jan	10:00	0	0.60		
11-Jan	11:00	0	0.58		
11-Jan	12:00	0	0.57		
11-Jan	13:00	0	0.55		
11-Jan	14:00	0	0.54		
11-Jan	15:00	0	0.52		
11-Jan	16:00	0	0.51		
11-Jan	17:00	0	0.50		
11-Jan	18:00	0	0.48		
11-Jan	19:00	0	0.47		
11-Jan	20:00	0	0.46		
11-Jan	21:00	0	0.44		
11-Jan	22:00	0	0.43		
11-Jan	23:00	0	0.42		1.8
12-Jan	00:00	0	0.41		
12-Jan	01:00	0	0.40		
12-Jan	02:00	0	0.38		
12-Jan	03:00	0	0.37	6.36	1.62
12-Jan	04:00	0	0.36		
12-Jan	05:00	0	0.35		
12-Jan	06:00	0	0.34		
12-Jan	07:00	0	0.33	5	1.36

12-Jan	08:00	0	0.33		
12-Jan	09:00	0	0.31		
12-Jan	10:00	0	0.30		
12-Jan	11:00	0	0.29	4.64	1.46
12-Jan	12:00	0	0.29		
12-Jan	13:00	0	0.28		
12-Jan	14:00	0	0.27		
12-Jan	15:00	0	0.26	4.57	2.14
12-Jan	16:00	0	0.25		
12-Jan	17:00	0	0.25		
12-Jan	18:00	0	0.24		
12-Jan	19:00	0	0.23	3.96	1.18
12-Jan	20:00	0	0.23		
12-Jan	21:00	0	0.22		
12-Jan	22:00	0	0.21		
12-Jan	23:00	0	0.20	3.63	1.63
13-Jan	00:00	0	0.20		
13-Jan	01:00	0	0.19		
13-Jan	02:00	0	0.19		
13-Jan	03:00	0	0.18	3.91	1.56
13-Jan	04:00	0	0.17		
13-Jan	05:00	0	0.17		
13-Jan	06:00	0	0.16		
13-Jan	07:00	0	0.16	2.24	1.13
13-Jan	08:00	0	0.15		
13-Jan	09:00	0	0.15		
13-Jan	10:00	0	0.14		
13-Jan	11:00	0	0.14	2.67	1.4

Total rainfall=72.5 mm

Automatic Water Samples.
Table W4: Winter 1991/92, Carbofuran/atrazine experiment.
Stream at grid ref: SO 5665 4841 (site 1).

		Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
25-Jan	09:00	0	0.454		
25-Jan	09:30		0.454		
25-Jan	10:00	0	0.454		
25-Jan	10:30		0.454	0.14	0.05
25-Jan	11:00	1	0.454		
25-Jan	11:30		0.454	37.45	7.55
25-Jan	12:00	1.5	0.454		
25-Jan	12:30		0.454	49.4	13.3
25-Jan	13:00	2.5	0.454		
25-Jan	13:30		0.454	26.85	5.57
25-Jan	14:00	3	0.791		
25-Jan	14:30		0.791	18.16	3.95
25-Jan	15:00	0.5	1.245		
25-Jan	15:30		1.826	13.14	3.97
25-Jan	16:00	0	2.545		
25-Jan	16:30		2.545	0.67	0.15
25-Jan	17:00	0	1.826		
25-Jan	17:30		1.826	6.44	2.85
25-Jan	18:00	0	1.245		
25-Jan	18:30		1.245	0.18	0.05
25-Jan	19:00	0.5	1.245		
25-Jan	19:30		1.245	6.91	2.38
25-Jan	20:00	0	1.245		
25-Jan	20:30		1.245	6.48	3.25
25-Jan	21:00	0	0.791		
25-Jan	21:30		0.791	3.18	1.5
25-Jan	22:00	0	0.791		
25-Jan	22:30		0.791	2.38	1.15
25-Jan	23:00	0	0.791		
25-Jan	23:00		0.791	1.64	0.69
26-Jan	00:00	0	0.791		
26-Jan	00:30		0.791	1.52	0.83
26-Jan	01:00	0	0.791		
26-Jan	01:30		0.791	1.48	0.79
26-Jan	02:00	0	0.791		
26-Jan	02:30		0.791	1.14	0.7
26-Jan	03:00	0	0.791		
26-Jan	03:30		0.791	0.48	0.23
26-Jan	04:00	0	0.791		
26-Jan	04:30		0.791	0.69	0.49
26-Jan	05:00	0	0.791		
26-Jan	05:30		0.791	0.41	0.34
26-Jan	06:00	0	0.791		
26-Jan	06:30		0.791	0.06	nd
26-Jan	07:00	0	0.791		
26-Jan	07:30		0.791	1.06	nd
26-Jan	08:00	0	0.791		
26-Jan	08:30		0.791	0.04	nd
26-Jan	09:00	0	0.791		
26-Jan	09:30		0.791	0.18	0.07

Total rainfall = 9.0 mm

Automatic Water Samples
Table W5: Winter 1991/92, Carbofuran/atrazine experiment.
Field drain at grid ref: SO 5672 4842 (Site 3)

		Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/sec)	Atrazine conc (ug/sec)
25-Jan	09:00	0	0.293		
25-Jan	09:30		0.415		
25-Jan	10:00	0	0.367		
25-Jan	10:30		0.28	58.39	6.99
25-Jan	11:00	1	0.206		
25-Jan	11:30		0.146	30.39	4.56
25-Jan	12:00	1.5	0.115		
25-Jan	12:30		0.092	17.7	5.29
25-Jan	13:00	2.5	0.071		
25-Jan	13:30		0.054	14.1	4.87
25-Jan	14:00	3	0.04		
25-Jan	14:30		0.028	10.62	4.34
25-Jan	15:00	0.5	0.022		
25-Jan	15:30		0.017	10.32	3.88
25-Jan	16:00	0	0.014		
25-Jan	16:30		0.011	5.86	2.38
25-Jan	17:00	0	0.008		
25-Jan	17:30		0.006	40.11	8.86
25-Jan	18:00	0	0.004		
25-Jan	18:30		0.003	27	3.36
25-Jan	19:00	0.5	0.002		
25-Jan	19:30		0.002	20.94	4.6
25-Jan	20:00	0	0.001		
25-Jan	20:30		0.001	18.83	5.57
25-Jan	21:00	0	0		
25-Jan	21:30		0	17.62	5
25-Jan	22:00	0	0		
25-Jan	22:30		0	16.47	4.61
25-Jan	23:00	0	0		
25-Jan	23:00		0	10.61	2.95
26-Jan	00:00	0	0		
26-Jan	00:30		0	8.07	2.27
26-Jan	01:00	0	0		
26-Jan	01:30		0	11.85	7.07
26-Jan	02:00	0	0		
26-Jan	02:30		0	9.66	2.15
26-Jan	03:00	0	0		
26-Jan	03:30		0	6.13	2.53
26-Jan	04:00	0	0		
26-Jan	04:30		0	7.21	1.8
26-Jan	05:00	0	0		
26-Jan	05:30		0	6.71	1.02
26-Jan	06:00	0	0		
26-Jan	06:30		0	12.17	3.87
26-Jan	07:00	0	0		
26-Jan	07:30		0	-	-
26-Jan	08:00	0	0		
26-Jan	08:30		0	9.05	2.46
26-Jan	09:00	0	0		
26-Jan	09:30		0	7.19	1.69

Total rainfall = 9.0 mm
Note: Drainflow did not cease entirely, but dropped below 0.001 l/sec.

Automatic Water Samples
Table W8: Winter 1991/92, Carbofuran/atrazine experiment
Stream at grid ref: SO 5665 4841 (Site 1)

		Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
14-Apr	09:00	0	0.57		
14-Apr	10:00	0	0.51		
14-Apr	11:00	1	0.57		
14-Apr	12:00	1	0.54		
14-Apr	13:00	1	0.67		
14-Apr	14:00	0			
14-Apr	15:00	1.5			
14-Apr	16:00	1	0.71		
14-Apr	17:00	0	0.93		
14-Apr	18:00	1.5	1.06		
14-Apr	19:00	3	0.86		
14-Apr	20:00	2	1.69		
14-Apr	21:00	3	1.67		
14-Apr	22:00	1.5	2.22	0.43	0.05
14-Apr	23:00	0	2.69	0.65	0.06
15-Apr	00:00	0.5	1.86	2.35	0.15
15-Apr	01:00	0.5	1.57	0.26	0.23
15-Apr	02:00	0	1.35	-	-
15-Apr	03:00	0	1.22	0.42	0.22
15-Apr	04:00	0	1.01	0.67	0.15
15-Apr	05:00	0	0.89	-	-
15-Apr	06:00	0	0.78	-	-
15-Apr	07:00	0	0.67	0.22	0.12
15-Apr	08:00	0	0.71	0.28	0.11
15-Apr	09:00	0	0.67	-	-
15-Apr	10:00	0	0.67	0.18	0.1
15-Apr	11:00	0	0.71	0.12	0.11
15-Apr	12:00	0	0.67	0.16	0.17
15-Apr	13:00	0	0.67	0.07	0.05
15-Apr	14:00	0	0.67	-	-
15-Apr	15:00	0	0.67	0.08	0.07
15-Apr	16:00	0	0.67	-	-
15-Apr	17:00	0	0.64	0.04	0.02
15-Apr	18:00	0	0.67	0.02	0.02
15-Apr	19:00	1.5	0.61	0.03	0.03
15-Apr	20:00	0	0.51	0.01	0.02
15-Apr	21:00	0	0.67	-	-

Total rainfall = 19.0 mm

Automatic Water Samples
Table W7: Winter 1991/92, Carbofuran/atrazine experiment
Field drain at grid ref: SO 5672 4842 (Site 3)

		Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
14-Apr	09:00	0	0		
14-Apr	10:00	0	0		
14-Apr	11:00	1	0		
14-Apr	12:00	1	0		
14-Apr	13:00	1	0		
14-Apr	14:00	0	0		
14-Apr	15:00	1.5	0		
14-Apr	16:00	1	0		
14-Apr	17:00	0	0		
14-Apr	18:00	1.5	0		
14-Apr	19:00	3	0		
14-Apr	20:00	2	0		
14-Apr	21:00	3	0.007		
14-Apr	22:00	1.5	0.044	9.87	0.56
14-Apr	23:00	0	0.125	0.55	0.57
15-Apr	00:00	0.5	0.26	1.92	0.42
15-Apr	01:00	0.5	0.456	0.7	0.43
15-Apr	02:00	0	0.557	1.59	0.46
15-Apr	03:00	0	0.529	0.35	0.45
15-Apr	04:00	0	0.382	1.13	0.38
15-Apr	05:00	0	0.262	0.3	0.39
15-Apr	06:00	0	0.168	0.84	0.55
15-Apr	07:00	0	0.098	0.15	0.57
15-Apr	08:00	0	0.049	0.53	0.65
15-Apr	09:00	0	0.025	0.15	0.6
15-Apr	10:00	0	0.012	0.23	0.45
15-Apr	11:00	0	0.005	0.08	0.45
15-Apr	12:00	0	0.002	0.07	0.24
15-Apr	13:00	0	0.001	0.07	0.37
15-Apr	14:00	0	0.001	0.05	0.3
15-Apr	15:00	0	0	0.02	0.25
15-Apr	16:00	0	0	0.05	0.3
15-Apr	17:00	0	0	0.01	0.09
15-Apr	18:00	0	0	0.05	0.23
15-Apr	19:00	1.5	0	0.01	0.18
15-Apr	20:00	0	0	nd	0.21
15-Apr	21:00	0	0	0.02	0.12

Total rainfall = 19.0 mm

Automatic Water Samples
Table W8: Winter 1991/92, Carbofuran/atrazine experiment
Stream at grid ref: SO 5665 4841 (Site 1)

Date	Time	Rainfall	Flow	Carbofuran	Atrazine
28-May	00:00	0	0.791		
28-May	00:30	0	0.791		
28-May	01:00	0	0.791		
28-May	01:30	0	0.791		
28-May	02:00	0	0.791		
28-May	02:30	0	0.791		
28-May	03:00	4	0.791		
28-May	03:30	0	1.245		
28-May	04:00	0	0.791		
28-May	04:30	0	0.791		
28-May	05:00	0	0.791		
28-May	05:30	0	0.791		
28-May	06:00	0	0.791		
28-May	06:30	0	0.791		
28-May	07:00	0	0.454		
28-May	07:30	0	0.454		
28-May	08:00	0	0.454		
28-May	08:30	0	0.454		
28-May	09:00	0	0.454		
28-May	09:30	0	0.454		
28-May	10:00	0	0.454		
28-May	10:30	0	0.454		
28-May	11:00	0	0.222		
28-May	11:30	0	0.222		
28-May	12:00	0	0.222		
28-May	12:30	0	0.222		
28-May	13:00	0	0.222		
28-May	13:30	0	0.222		
28-May	14:00	10.5	0.222		
28-May	14:30	0	0.454		
28-May	15:00	0	2.545	0.01	nd
28-May	15:30	0	8.507		
28-May	16:00	0	2.545	0.01	0.13
28-May	16:30	0	2.545		
28-May	17:00	0	2.545	-	0.1
28-May	17:30	0	1.826		
28-May	18:00	0	1.826	-	-
28-May	18:30	0	1.245		
28-May	19:00	0	1.245	0.01	-
28-May	19:30	0	1.245		
28-May	20:00	0	1.245	0.02	0.09
28-May	20:30	0	1.245		
28-May	21:00	0	1.245	0.01	0.09
28-May	21:30	0	1.245		
28-May	22:00	0	1.245	0.01	0.04
28-May	22:30	0	1.245		
28-May	23:00	0	1.245	-	0.07
28-May	23:30	0	1.245		
29-May	00:00	0	1.245		-
29-May	00:30	0	1.245		
29-May	01:00	0	1.245	nd	-
29-May	01:30	0	1.245		
29-May	02:00	0	1.245	nd	0.05
29-May	02:30	0	1.245		
29-May	03:00	0	1.245	nd	0.05
29-May	03:30	0	1.245		
29-May	04:00	0	0.791	nd	0.05
29-May	04:30	0	0.791		
29-May	05:00	0	0.791	nd	-
29-May	05:30	0	0.791		
29-May	06:00	0	0.791	nd	0.04
29-May	06:30	0	0.791		
29-May	07:00	0	0.791	nd	0.03
29-May	07:30	0	0.791		
29-May	08:00	0	0.791	-	0.03
29-May	08:30	0	0.791		
29-May	09:00	0	0.454	nd	-
29-May	09:30	0	0.454		
29-May	10:00	0.5	0.454	nd	nd
29-May	10:30		0.454		
29-May	11:00	1	0.454	nd	nd
29-May	11:30		0.454		
29-May	12:00	1.5	0.454	nd	nd
29-May	12:30		0.454		
29-May	13:00	0.5	0.454	nd	nd

Total rainfall = 18.0 mm

Automatic Water Samples.
Table W9: Winter1991/92, Carbofuran/atrazine experiment.
Field drain at grid ref: SO 5672 4842 (Site 3).

Date	Time	Rainfall (mm)	Flow (l/sec)	Carbofuran conc (ug/l)	Atrazine conc (ug/l)
28-May	00:00	0	0		
28-May	00:30		0		
28-May	01:00	0	0		
28-May	01:30		0		
28-May	02:00	0	0		
28-May	02:30		0		
28-May	03:00	4	0		
28-May	03:30		0		
28-May	04:00	0	0		
28-May	04:30		0		
28-May	05:00	0	0		
28-May	05:30		0		
28-May	06:00	0	0		
28-May	06:30		0		
28-May	07:00	0	0		
28-May	07:30		0		
28-May	08:00	0	0		
28-May	08:30		0		
28-May	09:00	0	0		
28-May	09:30		0		
28-May	10:00	0	0		
28-May	10:30		0		
28-May	11:00	0	0		
28-May	11:30		0		
28-May	12:00	0	0		
28-May	12:30		0		
28-May	13:00	0	0		
28-May	13:30		0		
28-May	14:00	10.5	0		
28-May	14:30		0		
28-May	15:00	0	0	0.02	0.68
28-May	15:30		0		
28-May	16:00	0	0	0.18	1.02
28-May	16:30		0.197		
28-May	17:00	0	0.132	0.12	1.73
28-May	17:30		0.082		
28-May	18:00	0	0.045	0.06	1.57
28-May	18:30		0.021		
28-May	19:00	0	0.007	0.03	1.46
28-May	19:30		0.001		
28-May	20.00	0	0	0.03	1.28
28-May	20:30		0		
28-May	21:00	0	0	0.02	1.09
28-May	21:30		0		
28-May	22:00	0	0	0.02	0.7
28-May	22:30		0		
28-May	23:00	0	0	0.01	0.58
28-May	23:30		0		
29-May	00:00	0	0	0.02	0.59
29-May	00:30		0		
29-May	01:00	0	0	0.01	0.21
29-May	01:30		0		
29-May	02:00	0	0	nd	0.16
29-May	02:30		0		
29-May	03:00	0	0	nd	0.11
29-May	03:30		0		
29-May	04:00	0	0	nd	0.19
29-May	04:30		0		
29-May	05:00	0	0	nd	0.09
29-May	05:30		0		
29-May	06:00	0	0	nd	0.09
29-May	06:30		0		
29-May	07:00	0	0	nd	0.08
29-May	07:30		0		
29-May	08:00	0	0	nd	0.07
29-May	08:30		0		
29-May	09:00	0	0	nd	0.04
29-May	09:30		0		
29-May	10:00	0.5	0	nd	0.04
29-May	10:30		0		
29-May	11:00	1	0	nd	0.04
29-May	11:30		0		
29-May	12:00	1.5	0	nd	0.03
29-May	12:30		0		
29-May	13:00	0.5	0	nd	0.04

Total rainfall = 18.0 mm

Note: Drainflow did not cease entirely, but dropped below 0.001 l/sec.

MANUAL WATER SAMPLES

Table W10. Spring 1992. Trietazine / terbutryn / aldicarb experiment.

	Trietazine				Terbutryn				Aldicarb sulphoxide				Aldicarb sulphone			
Date	27.3.92		15.4.92		27.3.92		15.4.92		27.3.92		15.4.92		27.3.92		15.4.92	
	Flow rate (l / sec)	Conc (ug/ l)	Flow rate (l / sec)	Conc (ug/ l)	Flow rate (l / sec)	Conc (ug/ l)	Flow rate (l / sec)	Conc (ug/ l)	Flow rate (l / sec)	Conc. (ug/ l)	Flow rate (l / sec)	Conc. (ug/ l)	Flow rate (l / sec)	Conc. (ug/ l)	Flow rate (l / sec)	Conc. (ug/ l)
Stream (site 1)	0.45	nd	0.55	0.21	0.45	nd	0.55	0.03	0.45	nd	0.55	0.3	0.45	0.2	0.55	0.3
Ditch (site 2)		nd		0.04		nd		0.01		nd		nd		nd		nd
Drain (site 3)	0	nd	0	2.06	0	nd	0	0.17	0	nd	0	0.7	0	nd	0	0.8
Drain (site 4)		nd		0.05		nd		nd		nd		0.1		nd		nd
Drain (site 5)		0.07		-		0.01		-		0.1		-		nd		-
Drain (site 6)		-		2.9		-		0.31		-		0.3		-		0.2

Note : Aldicarb parent compound was not detected in any sample .

Automatic Water Samples.
Table W11: Spring 1992, Trietazine/terbutryn/aldicarb experiment.
Stream at grid ref: SO 5665 4841 (Site 1).

		Rainfall (mm)	Flow (l/sec)	Trietazine (ug/l)	Turbutryn (ug/l)	Aldicarb sulphoxide (ug/l)	Aldicarb sulphone (ug/l)	Mercury treatment ?
14-Apr	09:00	0	0.57					
14-Apr	10:00	0	0.51					
14-Apr	11:00	1	0.57					
14-Apr	12:00	1	0.54					
14-Apr	13:00	1	0.67					
14-Apr	14:00	0						
14-Apr	15:00	1.5						
14-Apr	16:00	1	0.71					
14-Apr	17:00	0	0.93					
14-Apr	18:00	1.5	1.06					
14-Apr	19:00	3	0.86					
14-Apr	20:00	2	1.69					
14-Apr	21:00	3	1.67					
14-Apr	22:00	1.5	2.22	0.06	0.01	nd	nd	Y
14-Apr	23:00	0	2.69	0.51	0.04	nd	nd	N
15-Apr	00:00	0.5	1.86	0.97	0.14	0.5	0.4	Y
15-Apr	01:00	0.5	1.57	1.27	0.16	0.4	0.4	N
15-Apr	02:00	0	1.35	-	-	-	-	-
15-Apr	03:00	0	1.22	1	0.12	0.4	0.5	N
15-Apr	04:00	0	1.01	0.79	0.1	0.4	0.3	N
15-Apr	05:00	0	0.89	-	-	-	-	-
15-Apr	06:00	0	0.78	-	-	-	-	-
15-Apr	07:00	0	0.67	0.52	0.06	0.3	0.2	N
15-Apr	08:00	0	0.71	0.48	0.09	0.4	0.5	N
15-Apr	09:00	0	0.67	-	-	-	-	-
15-Apr	10:00	0	0.67	0.37	0.04	nd	nd	Y
15-Apr	11:00	0	0.71	0.32	0.04	nd	nd	N
15-Apr	12:00	0	0.67	0.36	0.04	-	-	Y
15-Apr	13:00	0	0.67	0.26	0.03	nd	nd	N
15-Apr	14:00	0	0.67	-	-	-	-	-
15-Apr	15:00	0	0.67	0.26	0.03	-	-	Y
15-Apr	16:00	0	0.67	-	-	-	-	-
15-Apr	17:00	0	0.64	0.21	0.02	-	-	N
15-Apr	18:00	0	0.67	0.08	nd	-	-	Y
15-Apr	19:00	1.5	0.61	0.05	0.01	nd	nd	N
15-Apr	20:00	0	0.51	0.13	nd	-	-	Y
15-Apr	21:00	0	0.67	-	-	-	-	-

Total rainfall = 19.0 mm
Note: No unchanged aldicarb was detected.

Automatic Water Samples.
Table W12: Spring 1992, Trietazine/terbutryn/aldicarb experiment.
Field drain at grid ref: SO 5672 4842 (Site 3).

		Rainfall (mm)	Flow (l/sec)	Trietazine (ug/l)	Turbutryn (ug/l)	Aldicarb sulphoxide (ug/l)	Aldicarb sulphone (ug/l)	Mercury treatment ?
14-Apr	09:00	0	0					
14-Apr	10:00	0	0					
14-Apr	11:00	1	0					
14-Apr	12:00	1	0					
14-Apr	13:00	1	0					
14-Apr	14:00	0	0					
14-Apr	15:00	1.5	0					
14-Apr	16:00	1	0					
14-Apr	17:00	0	0					
14-Apr	18:00	1.5	0					
14-Apr	19:00	3	0					
14-Apr	20:00	2	0					
14-Apr	21:00	3	0.007					
14-Apr	22:00	1.5	0.044	3.59	0.24	0.6	0.6	Y
14-Apr	23:00	0	0.125	3.24	0.15	1	1.1	N
15-Apr	00:00	0.5	0.26	2.15	0.11	0.7	0.6	Y
15-Apr	01:00	0.5	0.456	1.97	0.16	0.9	0.8	N
15-Apr	02:00	0	0.557	2.19	0.15	0.9	0.8	Y
15-Apr	03:00	0	0.529	1.6	0.15	0.9	0.8	N
15-Apr	04:00	0	0.382	1.46	0.12	0.9	0.8	Y
15-Apr	05:00	0	0.262	1.61	0.12	0.8	0.8	N
15-Apr	06:00	0	0.168	1.69	0.17	1	1	Y
15-Apr	07:00	0	0.098	1.91	0.2	0.9	0.7	N
15-Apr	08:00	0	0.049	2.02	0.17	0.9	0.9	Y
15-Apr	09:00	0	0.025	1.95	0.2	0.9	1	N
15-Apr	10:00	0	0.012	1.49	0.13	1.1	0.9	Y
15-Apr	11:00	0	0.005	1.48	0.18	0.7	0.8	N
15-Apr	12:00	0	0.002	1.13	0.14	0.9	1	Y
15-Apr	13:00	0	0.001	1.54	0.16	0.7	0.7	N
15-Apr	14:00	0	0.001	1.3	0.12	0.8	0.9	Y
15-Apr	15:00	0	0	1.18	0.11	0.5	0.5	N
15-Apr	16:00	0	0	1.06	0.1	0.9	0.9	Y
15-Apr	17:00	0	0	0.64	0.06	0.4	0.5	N
15-Apr	18:00	0	0	0.86	0.08	0.5	0.6	Y
15-Apr	19:00	1.5	0	0.72	0.07	0.6	0.6	Y
15-Apr	20:00	0	0	0.65	0.07	0.3	0.4	Y
15-Apr	21:00	0	0	0.47	0.05	0.4	0.5	N

Total rainfall = 19.0 mm
Note: No unchanged aldicarb was detected.

Automatic Water Samples.
Table W13: Spring 1992, Trietazine/terbutryn/aldicarb experiment.
Stream at grid ref: SO 5665 4841 (Site 1).

Date	Time	Rainfall	Flow	Trietazine	Terbutryn
28-May	00:00	0	0.791		
28-May	00:30		0.791		
28-May	01:00	0	0.791		
28-May	01:30		0.791		
28-May	02:00	0	0.791		
28-May	02:30		0.791		
28-May	03:00	4	0.791		
28-May	03:30		1.245		
28-May	04:00	0	0.791		
28-May	04:30		0.791		
28-May	05:00	0	0.791		
28-May	05:30		0.791		
28-May	06:00	0	0.791		
28-May	06:30		0.791		
28-May	07:00	0	0.454		
28-May	07:30		0.454		
28-May	08:00	0	0.454		
28-May	08:30		0.454		
28-May	09:00	0	0.454		
28-May	09:30		0.454		
28-May	10:00	0	0.454		
28-May	10:30		0.454		
28-May	11:00	0	0.222		
28-May	11:30		0.222		
28-May	12:00	0	0.222		
28-May	12:30		0.222		
28-May	13:00	0	0.222		
28-May	13:30		0.222		
28-May	14:00	10.5	0.222		
28-May	14:30		0.454		
28-May	15:00	0	2.545	nd	nd
28-May	15:30		8.507		
28-May	16:00	0	2.545	0.52	0.06
28-May	16:30		2.545		
28-May	17:00	0	2.545	0.37	0.04
28-May	17:30		1.826		
28-May	18:00	0	1.826	-	-
28-May	18:30		1.245		
28-May	19:00	0	1.245	-	-
28-May	19:30		1.245		
28-May	20:00	0	1.245	0.29	0.03
28-May	20:30		1.245		
28-May	21:00	0	1.245	0.27	0.02
28-May	21:30		1.245		
28-May	22:00	0	1.245	0.14	0.01

28-May	22:30		1.245		
28-May	23:00	0	1.245	0.23	0.02
28-May	23:30		1.245		
29-May	00:00	0	1.245	-	-
29-May	00:30		1.245		
29-May	01:00	0	1.245	-	-
29-May	01:30		1.245		
29-May	02:00	0	1.245	0.16	0.01
29-May	02:30		1.245		
29-May	03:00	0	1.245	0.14	0.01
29-May	03:30		1.245		
29-May	04:00	0	0.791	0.14	0.01
29-May	04:30		0.791		
29-May	05:00	0	0.791	-	-
29-May	05:30		0.791		
29-May	06:00	0	0.791	0.09	nd
29-May	06:30		0.791		
29-May	07:00	0	0.791	0.07	nd
29-May	07:30		0.791		
29-May	08:00	0	0.791	0.06	nd
29-May	08:30		0.791		
29-May	09:00	0	0.454	-	-
29-May	09:30		0.454		
29-May	10:00	0.5	0.454	0.03	nd
29-May	10:30		0.454		
29-May	11:00	1	0.454	0.02	nd
29-May	11:30		0.454		
29-May	12:00	1.5	0.454	0.02	nd
29-May	12:30		0.454		
29-May	13:00	0.5	0.454	0.01	nd
29-May	13:30		0.454		
29-May	14:00	0	0.454	0.01	nd

Total rainfall = 18.0 mm

Note: No residues of aldicarb or its two primary degradation products (sulphoxide and sulphone) were detected in any sample.

Automatic Water Samples.
Table W14: Spring 1992, Trietazine/terbutryn/aldicarb experiment.
Field drain at grid ref; SO 5672 4842 (Site 3).

Date	Time	Rainfall (mm)	Flow (l/sec)	Trietazine (ug/l)	Terbutryn (ug/l)	Aldicarb Sulphoxide (ug/l)	Aldicarb sulphone (ug/l)
28-May	00:00	0	0				
28-May	00:30		0				
28-May	01:00	0	0				
28-May	01:30		0				
28-May	02:00	0	0				
28-May	02:30		0				
28-May	03:00	4	0				
28-May	03:30		0				
28-May	04:00	0	0				
28-May	04:30		0				
28-May	05:00	0	0				
28-May	05:30		0				
28-May	06:00	0	0				
28-May	06:30		0				
28-May	07:00	0	0				
28-May	07:30		0				
28-May	08:00	0	0				
28-May	08:30		0				
28-May	09:00	0	0				
28-May	09:30		0				
28-May	10:00	0	0				
28-May	10:30		0				
28-May	11:00	0	0				
28-May	11:30		0				
28-May	12:00	0	0				
28-May	12:30		0				
28-May	13:00	0	0				
28-May	13:30		0				
28-May	14:00	10.5	0				
28-May	14:30		0				
28-May	15:00	0	0	nd	nd	0.1	0.3
28-May	15:30		0				
28-May	16:00	0	0	0.52	0.06	0.5	1.2
28-May	16:30		0.197				
28-May	17:00	0	0.132	0.37	0.04	0.4	1.2
28-May	17:30		0.082				
28-May	18:00	0	0.045	-	-	0.7	1.5
28-May	18:30		0.021				
28-May	19:00	0	0.007	-	-	0.6	1.4
28-May	19:30		0.001				
28-May	20:00	0	0	0.29	0.03	0.5	0.3
28-May	20:30		0				
28-May	21:00	0	0	0.27	0.02	0.5	1.1
28-May	21:30		0				
28-May	22:00	0	0	0.14	0.01	-	-

28-May	22:30		0				
28-May	23:00	0	0	0.23	0.02	0.3	0.7
28-May	23:30		0				
29-May	00:00	0	0	-	-	0.4	0.4
29-May	00:30		0				
29-May	01:00	0	0	-	-	nd	0.8
29-May	01:30		0				
29-May	02:00	0	0	0.16	0.01	nd	0.8
29-May	02:30		0				
29-May	03:00	0	0	0.14	0.01	0.3	0.5
29-May	03:30		0				
29-May	04:00	0	0	0.14	0.01	nd	nd
29-May	04:30		0				
29-May	05:00	0	0	-	-	nd	nd
29-May	05:30		0				
29-May	06:00	0	0	0.09	nd	nd	0.3
29-May	06:30		0				
29-May	07:00	0	0	0.07	nd	nd	nd
29-May	07:30		0				
29-May	08:00	0	0	0.06	nd	nd	nd
29-May	08:30		0				
29-May	09:00	0	0	-	-	nd	nd
29-May	09:30		0				
29-May	10:00	0.5	0	0.03	nd	nd	nd
29-May	10:30		0				
29-May	11:00	1	0	0.02	nd	nd	nd
29-May	11:30		0				
29-May	12:00	1.5	0	0.02	nd	nd	nd
29-May	12:30		0				
29-May	13:00	0.5	0	0.01	nd	nd	nd
29-May	13:30	0	0				
29-May	14:00	0	0	0.01	nd	nd	nd

Total rainfall =18 mm
Note: No unchanged aldicarb was detected.

Soil Water Samples.

Table W15. Winter 1991/92. Atrazine / Carbofuran experiment. Foxbridge and Longlands. Atrazine residues (ug/l). Atrazine was applied on 27.11.91.

Sample	Depth (cm)	6.11.91	4.12.91	8.1.92	14.1.92	6.2.92	6.3.92
1	50	-	0.01	0.03	1.09	-	0.12
4	50	-	0.01	0.04	0.56	-	-
7	50	nd	0.01	-	2.3	2.22	1.17
10	50	-	nd	0.02	0.45	0.87	-
2	100	-	0.02	0.01	5.51	5.28	2
5	100	-	0.02	0.02	0.83	1.06	0.42
8	100	-	0.02	-	0.32	0.77	0.33
11	100	-	nd	0.23	0.05	0.87	0.32
3	150	-	0.08	0.04	2.69	-	0.36
6	150	-	0.04	0.01	0.82	1.07	0.52
9	150	-	0.4	0.34	0.66	0.81	0.43
12	150	-	-	0.05	1.41	0.07	nd
16	50	-	-	0.026	14.38	-	7.3
19	50	-	0.02	0.14	1.16	3.66	7.59
22	50	nd	-	4.97	9.4	27.34	0.85
25	50	nd	-	0.98	16.61	11.22	28.26
17	100	nd	-	0.08	8.03	7.36	1.91
20	100	-	nd	0.03	6.47	1.35	0.61
23	100	nd	-	0.4	1.9	2.17	0.62
26	100	-	-	0.16	10.69	5.31	12.41
18	150	-	-	0.04	10.57	2.98	1.15
21	150	nd	nd	0.21	7.22	3.78	0.85
24	150	-	-	1.24	12.3	-	2.95
27	150	-	-	0.04	3.84	1.92	1.11

Table W15. (Continued)

Sample	Depth (cm)	24.3.92	8.4.92	17.4.92	8.5.92	13.5.92
1	50	0.12	0.14	0.19	0.15	-
4	50	-	-	-	-	-
7	50	0.53	0.63	0.88	0.34	-
10	50	-	-	-	-	-
2	100	1.49	0.79	1.5	1.02	0.7
5	100	0.26	0.23	0.36	0.12	0.14
8	100	0.25	0.1	0.2	0.13	0.08
11	100	nd	0.03	0.16	-	0.1
3	150	0.38	0.24	0.74	0.23	-
6	150	0.39	0.23	0.64	0.32	0.26
9	150	0.6	0.13	0.54	0.44	0.25
12	150	-	-	-	-	-
16	50	8.06	-	-	3.44	1.96
19	50	-	2.46	4.96	2.92	2.08
22	50	-	-	-	5.93	-
25	50	13.04	6.91	6.93	-	3.71
17	100	0.16	0.66	1.9	0.81	0.33
20	100	0.49	0.39	4	1.29	0.77
23	100	0.51	0.38	0.72	0.41	0.27
26	100	4.09	5.99	-	-	-
18	150	0.78	0.35	1.26	0.34	0.22
21	150	0.59	0.29	0.79	0.3	0.17
24	150	2.66	1.97	4.87	3.31	2.26
27	150	0.63	0.5	1.52	0.7	0.7

Soil Water Samples.
Table W16.

Winter 1991/92. Atrazine / Carbofuran experiment.
Foxbridge and Longlands. Carbofuran residues (ug/l).
Carbofuran was applied on 3.12.91.

Sample	Depth (cm)	6.11.91	4.12.91	8.1.92	14.1.92	6.2.92	6.3.92
1	50	-	nd	0.01	nd	-	nd
4	50	-	nd	nd	nd	-	-
7	50	nd	nd	-	nd	0.01	nd
10	50	-	nd	nd	nd	0.01	-
2	100	-	nd	0.02	0.03	0.01	0.08
5	100	-	nd	nd	nd	nd	nd
8	100	-	nd	-	0.02	nd	nd
11	100	-	nd	0.02	nd	0.01	nd
3	150	-	0.01	0.05	0.02	-	nd
6	150	-	0.03	nd	nd	nd	nd
9	150	-	nd	nd	0.01	nd	nd
12	150	-	-	nd	nd	0.04	nd
16	50	-	-	nd	1	-	0.43
19	50	-	nd	nd	0.12	0.33	0.7
22	50	nd	-	0.03	2.58	nd	0.08
25	50	nd	-	nd	nd	nd	0.62
17	100	nd	-	nd	0.08	0.03	0.1
20	100	-	nd	0.01	0.04	nd	nd
23	100	nd	-	nd	0.01	nd	nd
26	100	-	-	0.02	nd	nd	0.32
18	150	-	-	nd	0.72	0.14	0.05
21	150	nd	nd	nd	1.89	0.45	0.08
24	150	-	-	0.01	nd	-	0.05
27	150	-	-	nd	nd	nd	nd

Table W16. (Continued)

Sample	Depth (cm)	24.3.92	8.4.92	17.4.92	8.5.92	13.5.92
1	50	nd	nd	nd	nd	-
4	50	-	-	-	-	-
7	50	nd	0.04	0.03	nd	-
10	50	-	-	-	-	-
2	100	0.04	nd	nd	nd	nd
5	100	0.01	0.01	nd	nd	nd
8	100	nd	nd	nd	nd	nd
11	100	nd	nd	nd	-	nd
3	150	nd	nd	0.05	nd	-
6	150	nd	nd	0.03	nd	nd
9	150	nd	nd	nd	nd	nd
12	150	-	-	-	-	-
16	50	0.06	-	-	0.03	0.04
19	50	-	nd	0.29	nd	0.04
22	50	-	-	-	0.04	-
25	50	0.33	0.22	0.22	-	0.05
17	100	nd	nd	0.18	nd	nd
20	100	nd	nd	0.14	0.02	nd
23	100	0.01	0.04	0.04	nd	nd
26	100	0.02	0.17	-	-	-
18	150	0.05	nd	0.06	0.02	nd
21	150	nd	nd	0.04	nd	nd
24	150	0.09	nd	0.1	0.02	0.03
27	150	0.07	nd	0.05	nd	nd

Soil Water Samples.
Table W17.

Spring 1992 . Trietazine / Terbutryn / Aldicarb experiment .
Foxbridge and Longlands . Trietazine residues (ug/l) .
Trietazine was applied on 27.2.92 .

Sample	Depth (cm)	24.3.92	8.4.92	17.4.92	8.5.92	13.5.92
1	50	0.01	nd	nd	nd	-
4	50	-	-	-	-	-
7	50	nd	nd	nd	nd	-
10	50	-	-	-	-	-
2	100	0.01	nd	nd	nd	nd
5	100	0.01	nd	nd	nd	nd
8	100	nd	nd	nd	nd	nd
11	100	nd	nd	nd	-	nd
3	150	0.03	nd	nd	nd	-
6	150	0.01	nd	nd	nd	nd
9	150	nd	nd	nd	nd	nd
12	150	-	-	-	-	-
16	50	nd	-	-	nd	nd
19	50	-	nd	nd	nd	nd
22	50	-		-	nd	-
25	50	0.01	nd	0.15	-	nd
17	100	nd	nd	0.17	0.04	nd
20	100	nd	nd	0.03	nd	nd
23	100	nd	nd	nd	nd	nd
26	100	nd	nd	-	-	-
18	150	nd	nd	0.17	nd	nd
21	150	nd	nd	0.09	0.09	nd
24	150	nd	nd	0.05	0.21	0.07
27	150	0.03	nd	0.12	0.03	nd

Soil Water Samples.
Table W18.

Spring 1992. Trietazine / Terbutryn / Aldicarb experiment. Foxbridge and Longlands. Terbutryn residues (ug/l). Terbutryn was applied on 5.3.92.

Sample	Depth (cm)	24.3.92	8.4.92	17.4.92	8.5.92	13.5.92
1	50	nd	nd	nd	nd	-
4	50	-	-	-	-	-
7	50	nd	nd	nd	nd	-
10	50	-	-	-	-	-
2	100	0.01	nd	nd	nd	nd
5	100	0.01	nd	nd	0.04	0.06
8	100	nd	nd	nd	0.13	nd
11	100	nd	nd	nd	-	nd
3	150	0.03	nd	nd	nd	-
6	150	nd	nd	nd	nd	nd
9	150	nd	nd	nd	nd	nd
12	150	-	-	-	-	-
16	50	nd	-	-	0.03	0.03
19	50	-	nd	nd	0.17	0.06
22	50	-	-	-	0.05	-
25	50	nd	nd	nd	-	0.01
17	100	nd	nd	nd	0.02	nd
20	100	nd	nd	nd	0.03	0.07
23	100	nd	nd	nd	nd	0.03
26	100	nd	nd	-	-	-
18	150	nd	nd	nd	0.02	0.04
21	150	nd	nd	nd	0.13	0.04
24	150	nd	nd	nd	0.11	0.06
27	150	nd	nd	nd	0.09	0.04

Table W19. (Continued .)

Sample	8.4.92			17.4.92		
	sulphoxide	sulphone	aldicarb	sulphoxide	sulphone	aldicarb
1	nd	nd	nd	nd	nd	nd
4	-	-	-	-	-	-
7	nd	nd	nd	nd	nd	nd
10	-	-	-	-	-	-
2	nd	nd	nd	nd	nd	nd
5	nd	nd	nd	nd	nd	nd
8	nd	nd	nd	nd	nd	nd
11	x	x	x	nd	nd	nd
3	nd	nd	nd	nd	nd	nd
6	x	x	x	nd	nd	nd
9	nd	nd	nd	nd	nd	nd
12	-	-	-	-	-	-
16	-	-	-	-	-	-
19	x	x	x	nd	nd	nd
22	-	-	-	nd	nd	nd
25	nd	nd	nd	0.1	0.2	nd
17	nd	nd	nd	0.8	1.8	
20	nd	nd	nd	1.8	3.5	
23	x	x	x	nd	nd	nd
26	nd	nd	nd	-	-	-
18	nd	nd	nd	nd	nd	nd
21	x	x	x	1.9	2.6	nd
24	x	x	x	nd	nd	nd
27	nd	nd	nd	4.2	4.2	nd

Soil Water Samples
Table W19.

Spring 1992. Trietazine / Terbutryn / Aldicarb experiment. Foxbridge and Longlands. Aldicarb residues (ug/l). Aldicarb was applied on 27.2.92.

Sample	6.3.92			24.3.92		
	sulphoxide	sulphone	aldicarb	sulphoxide	sulphone	aldicarb
1	x	x	x	nd	nd	nd
4	x	x	x	-	-	-
7	nd	nd	nd	x	x	x
10	x	x	x	-	-	-
2	x	x	x	nd	nd	nd
5	nd	nd	nd	nd	nd	nd
8	x	x	x	x	x	x
11	x	x	x	x	x	x
3	x	x	x	nd	nd	nd
6	x	x	x	nd	nd	nd
9	nd	nd	nd	nd	nd	nd
12	x	x	x	-	-	-
16	x	x	x	nd	nd	nd
19	nd	nd	nd	nd	nd	nd
22	x	x	x	-	-	-
25	x	x	x	nd	nd	nd
17	x	x	x	x	x	x
20	x	x	x	x	x	x
23	x	x	x	x	x	x
26	x	x	x	x	x	x
18	nd	nd	nd	x	x	x
21	x	x	x	nd	nd	nd
24	x	x	x	nd	nd	nd
27	x	x	x	x	x	x

Table W19. (Continued .)

Sample	8.5.92 sulphoxide	8.5.92 sulphone	8.5.92 aldicarb	13.5.92 sulphoxide	13.5.92 sulphone	13.5.92 aldicarb
1	nd	nd	nd	-	-	-
4	-	-	-	-	-	-
7	nd	nd	nd	nd	nd	nd
10	-	-	-	-	-	-
2	nd	nd	nd	nd	nd	nd
5	nd	nd	nd	nd	nd	nd
8	nd	nd	nd	nd	nd	nd
11	nd	nd	nd	nd	nd	nd
3	nd	nd	nd	-	-	-
6	nd	nd	nd	nd	nd	nd
9	nd	nd	nd	nd	nd	nd
12	-	-	-	-	-	-
16	nd	0.5	nd	0.9	0.3	nd
19	nd	nd	nd	nd	nd	nd
22	nd	nd	nd	-	-	-
25	-	-	-	nd	nd	nd
17	0.5	0.1	nd	0.2	0.8	nd
20	3.6	6.7	nd	1.9	4.3	nd
23	nd	nd	nd	nd	nd	nd
26	-	-	-	-	-	-
18	nd	nd	nd	nd	nd	nd
21	0.5	0.8	nd	nd	nd	nd
24	9.1	12.8	nd	1.4	1.7	nd
27	0.8	0.5	nd	0.2	0.3	nd

For sample depth information corresponding to these results , refer to soil water result tables for the other compounds.

Samples denoted by ' x ' were not analysed .

Appendix XII

[1]USE OF A *GAMMARUS PULEX* BIOASSAY TO MEASURE THE EFFECTS OF TRANSIENT CARBOFURAN RUNOFF FROM FARMLAND

Peter Matthiessen*, David Sheahan*, Roy Harrison#, Mark Kirby*, Richard Rycroft*,
Alan Turnbull#, Conrad Volkner§ and Richard Williams§

* *Ministry of Agriculture, Fisheries & Food, Directorate of Fisheries Research, Fisheries Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex CM0 8HA, UK.*
\# *University of Birmingham, Department of Biological Sciences, Edgbaston, Birmingham B15 2TT, UK.*
§ *Institute of Hydrology, Wallingford, Oxfordshire OX10 8BB, UK.*

There is now much information on the presence of pesticides in surface waters, but very little about their actual effects on aquatic life. This paper reports on the transient concentrations of a carbamate insecticide, carbofuran, which were observed in a headwater stream draining treated farmland, and describes the resulting effects on a bioassay organism. One month after an application of 3 kg carbofuran/ha as broadcast granules to an oilseed rape crop, carbofuran concentrations of up to 26 µg/l were measured in a nearby headwater stream after heavy rainfall. The majority of the carbofuran was translocated via field drains (where concentrations up to 264 µg/l were detected), although the possibility of some surface runoff cannot be ruled out. Peak carbofuran concentrations only persisted for about 24 hours after the rainfall event, although measurable levels could be detected for at least 4 days. An *in-situ* bioassay of streamwater which monitored the feeding rate of the gammarid amphipod crustacean *Gammarus pulex* showed that feeding stopped completely during the rainfall event, and was rapidly followed by death of all the caged organisms. Subsequent laboratory studies of toxicity showed that the peak concentrations of carbofuran had exceeded the *G. pulex* 24 h LC50 of 21 µg/l, and that concentrations as low as 4 µg/l could reduce feeding rate. These findings are discussed with reference to regulatory risk evaluation procedures.

INTRODUCTION

Until recently, pesticide regulatory authorities have been hampered in their efforts to assess the risks for aquatic organisms associated with pesticides, primarily due to the difficulty of predicting exposure. Thus, although there is good understanding of the factors which predispose a chemical to leach through an idealised soil (mainly high water solubility, low soil adsorbance and long persistence), our knowledge of the way pesticides behave in agricultural fields is more limited. Leaching studies with soil columns and even lysimeters tend to be interpreted on the assumption that fields behave like homogeneous chromatographic media, but this is not generally true. In particular, it has been shown that solutes are often not in equilibrium with stationary soil particles due to the phenomenon of preferential or by-pass flow in which soil water can take the line of least resistance down so-called macropores which can range in size from relatively small intergranular spaces up to large cracks and root or worm holes (eg. Bouwer, 1989; Jury *et al.*, 1986; Rao *et al.*, 1974; White *et al.* 1986). Modelling such processes is difficult, although some progress is being made (Harrison *et al.*, 1992).

At least for some soils, there is therefore a tendency to underestimate the pesticide concentrations which may appear in ground and surface waters, and the speed with which such waters may become contaminated. The widespread use of field drains in intensive agricultural systems has tended to maximise the translocation of these contaminated soil waters into streams and rivers, and it is therefore not surprising that many surface waters contain pesticides at measurable concentrations. For example, surface waters used as a source for drinking water in the United Kingdom can be contaminated with a suite of up to 15 or more pesticides (mainly water-soluble herbicides at individual concentrations up to 16 µg/l), many of which exceed the European Community Drinking Water Directive maximum admissible concentration (MAC) of 0.1 µg/l (Council of the European Communities, 1980). This MAC is precautionary rather than based on toxicological data, and none of the concentrations found in drinking water sources are a significant risk to human consumers (Clark *et al.*, 1991; Croll, 1991; Gomme, J.W. *et al.*, 1991; Lees & McVeigh, 1988; Royal Commission on Environmental Pollution, 1992). Furthermore, it is fortunate that few if any are of concern from the viewpoint of aquatic organisms.

However, it must be remembered that in most cases the pesticides seen in major rivers at or near drinking water intakes have been significantly diluted and degraded since they leached from their areas of use. In particular, small headwater streams in agricultural regions are likely to experience higher concentrations. For example, recent studies in a stream arising in a small arable catchment in the west of England (ADAS Rosemaund) have revealed that relatively high concentrations of herbicides and insecticides can, after heavy rainfall, appear transiently in stream water, having been transported via the field drains (Brooke & Matthiessen, 1991; Matthiessen *et al.*, 1992; Williams *et al.*, 1991a; Williams *et al.*, 1991b). It has been shown at Rosemaund that translocation is assisted by preferential flow, and most soil water eventually moves laterally into the stream due to essentially impermeable subsoil. Although peak concentrations of individual pesticides in the Rosemaund stream have been found to exceed 60 µg/l on occasions, the products studied to date have not generally been of ecotoxicological significance due to either low toxicity or transience. Indeed, the prime purpose of the Rosemaund work is to provide validation data for runoff models and not to measure environmental impacts.

The purpose of this paper is to describe a recent rainfall event at Rosemaund during which concentrations of an insecticide, carbofuran, increased in the stream to the point at which toxic effects were experienced by a bioassay organism, the amphipod crustacean *Gammarus pulex*. The significance of these observations for pesticide risk assessment procedures will be discussed.

MATERIALS AND METHODS

The catchment at Rosemaund Farm (which is run by ADAS) has been described in detail by Matthiessen *et al.* (1992) and Williams *et al.* (1991b). The farm, although dedicated to agricultural research, is run as a profit-making operation and the principles of good agricultural practice are followed as closely as possible.

On 3 December 1991, the Bayer product Yaltox (5% w/w carbofuran granule) was applied broadcast to part of a field known as Stoney & Brushes which had previously been sown with oilseed rape. Yaltox is approved in the U.K. for the control of cabbage stem flea beetle, rape winter stem weevil and cabbage root fly in winter rape. The field lies nearly at the top end of the catchment, and 3 ha of it received carbofuran active ingredient (ai) at the maximum recommended rate of 3.0 kg ai/ha. No carbofuran had been applied in the upper 180 ha of the Rosemaund catchment for at least the preceding 6 years.

Automatic suction samplers for water were placed at Site 1 on the main stream, and Site 3 on a field drain which issues from part of Stoney & Brushes. Site 1 is approximately 150 m downslope from the nearest treated part of the field and receives drainage water from the top 35 ha of the catchment. Some water samples were also obtained from a point on the stream 1 km below site 1. The samplers were triggered by a float switch at a V-notch weir in the stream at Site 1, at a flow rate which corresponded to a rainfall intensity of about 10 mm in 24 h. The samplers transferred water by peristaltic pump into 24 x 1 l brown glass bottles, and were programmed to sample at 1-hourly or 4-hourly intervals. Water flow rates, water quality parameters, and meteorological data were recorded automatically on data loggers.

Raw water samples were stored in the dark at 4°C for a maximum of 10 days, and then extracted with solid phase extraction (SPE) cartridges (Analytichem 'Bond Elute' 0.5g, C18 LRC, Jones Chromatography) without prior treatment. A 250 ml aliquot of each sample was filtered through a 12.5 cm Whatman glass fibre (GF/C) filter and then passed through a preconditioned SPE cartridge at approximately 10 ml/min using a water jet vacuum pump. The cartridges were preconditioned by pumping through 5 ml ethyl acetate followed by 5 ml methanol and lastly 10 ml distilled deionised water (DDW). Carbofuran was eluted from the SPE cartridges by approximately 0.5 ml ethyl acetate (determined gravimetrically). The extracts were stored at approximately -20°C to await analysis. The % recovery of this extraction method was 98 ± 8%, and results were not corrected for this.

Carbofuran analysis was by gas chromatography / mass spectrometry (GC/MS). The instrument used was a Hewlett Packard 5890 GC with a Hewlett Packard 5791A Mass Selective Detector (MSD) operating in single ion mode. The column used was a 25 m x 0.2 mm Hewlett Packard HP-5 (5% phenyl methyl silicone bonded phase). The chromatography conditions were as follows:-

Initial oven temperature	55°C
Temperature ramp A	12°C/min
Final temperature	220°C
Hold time	0 min
Temperature ramp B	25°C/min
Final temperature	280°C
Hold time	4 min

Quantification was achieved by external calibration standards 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 0.01 μg/l.

The bioassay organism was the gammarid amphipod crustacean *Gammarus pulex* (L.). Male and female animals of mean size 44.5 ± 1.5 mg wet wt. were obtained from an unpolluted tributary of the River Stort, U.K. and used for both field and laboratory experiments. The methods adopted in the field trials were based on those of Maltby *et al.* (1990 a & b). One hundred animals were allocated to individual cages (made from short sections of 50 mm diameter PVC tubing with mesh-covered ends) which were then divided between 3 holding baskets. The holding baskets were deployed in the Rosemaund stream at Site1. Each animal was provided with 4 conditioned alder (*Alnus glutinosa*) leaf discs (1.5 cm diameter) of known dry weight. A total of 10 cages containing leaf discs alone were also divided between the 3 holding baskets in order to assess changes in leaf weight resulting from microbial degradation or accumulation of microbial biomass. The animals were maintained on site for a period of 11 weeks from 25 October 1991 during which time leaf discs and dead animals were replaced weekly, and uneaten leaf weights measured.

For the acute toxicity studies in the laboratory, groups of 10 animals maintained in nylon mesh pots were exposed to a range of carbofuran concentrations in 10 l glass aquaria which received constant aeration. The test solutions were renewed every 24 h. At regular intervals during the test, any animals which failed to respond to gentle mechanical stimulation were scored as dead and removed. LC50 values were calculated by the graphical method of Litchfield & Wilcoxon (1949). Water quality during the acute toxicity experiments (95% confidence limits) was as follows:- pH 7.1-7.2, temperature 7.3-7.5°C, dissolved oxygen 84-87% saturation.

Feeding trials were also conducted under laboratory conditions. 10-15 animals were placed in individual cages (as described above) and maintained in 10 l glass aquaria. Each aquarium was supplied with one of a range of nominal carbofuran concentrations (0.75, 1:25, 2.25, 4.0, 7.0 and 12.0 μg/l) or with uncontaminated water at a rate of 500 ml/min. Animals were supplied with alder leaf discs (of known weight) at the start of the 7 day exposure period and the remaining uneaten discs weighed at the end. Water quality during the growth experiments (95% confidence limits) was as follows:- pH 7.5-7.9, temperature 8.0-13.5°C, dissolved oxygen 80-84% saturation.

RESULTS

Before the rainfall event which is the subject of this paper (8-9 January 1992), most of the rainfall which occurred after application of carbofuran (3 December 1991) was fairly evenly spread between 15 and 22 December. This amounted to 18.5 mm, 8.5 mm of which fell on 17/18 December. A further 7.5 mm fell between 3 and 5 January. These intermediate events caused only modest elevations in stream flow (up to 2.5 l/sec at the sampling point 1 km below Site 1), but a series of 23 streamwater samples taken at 1 h intervals on 18 December at the 1 km point was nevertheless analysed for carbofuran. Excluding one outlier (35.5 µg/l) the mean concentration was 2.3 µg/l (standard deviation 0.86). Previous experience at Rosemaund (Brooke & Matthiessen, 1991; Matthiessen *et al.*, 1992; Williams *et al.*, 1991 a&b) has shown that rainfall with an intensity below 10 mm/24 h does not often produce major elevations in pesticide concentrations in the stream, so one can be confident that the monitoring programme did not miss any larger intermediate pesticide runoff events.

The main rainfall event occurred between 14.00 on 8 January and 14.00 on 9 January, consisting of a total of 71.5 mm. That this rainfall intensity is rare can be judged from the fact that the mean monthly rainfall for January (1951-1991) at Rosemaund is only 61 mm. Records and calculations show that the return period of an event of this magnitude is approximately 50 years. Most of the soil became fully saturated within 2 h of the start of rainfall and overland flow was observed, although little if any of this water reached the stream due to interception by vegetation and more permeable soil. Figures 1 and 2 present rainfall, water flow rates and carbofuran concentrations for the Site 3 field drain and Site 1 main stream respectively. The field drain was not flowing just before the start of the event but flow increased rapidly to a peak of 22 l/sec after 14 h. The drain flow then declined almost equally steeply, although flow did not cease completely for at least 4 days. The earliest significant flow (0.1-0.2 l/sec) was accompanied by a peak carbofuran level of 260-264 µg/l which rapidly declined to a mean level of about 33 µg/l (sd 15). After a short delay, sampling was resumed at 4-hourly intervals, which revealed that the concentration had risen again to 40 µg/l at the end of the rainfall event, declining gradually over the ensuing 3 days to about 2 µg/l.

In many respects, the picture in the main stream at Site 1 (Fig. 2) resembled that in the field drain, although carbofuran concentrations were proportionately lower due to the considerable dilution provided by runoff from the 35 ha of the upper catchment which were not treated. Stream flow increased from a background level of approximately 0.4 l/sec up to 115 l/sec after 20 h, and then declined smoothly to 1.3 l/sec after 4 days.

Carbofuran concentrations peaked initially at 24 µg/l about 10 h after rainfall began (and before the main water flowrate peak), but had risen to 27 µg/l when sampling was resumed. Concentrations then gradually declined over 4 days to about 1.9 µg/l. The entire amount of carbofuran mobilised into the stream between the onset of rain on 8 January and cessation of sampling on 13 January was approximately 48 g or 0.5% of the total applied.

Some subsequent rainfall events (25 January 1992, 9 mm; 14 April, 17.5 mm; 28 May, 14.5 mm) were also monitored in detail, but will not be described here in full because bioassays were not in place. It is, however, of interest to report that peak concentrations of carbofuran in streamwater at Site 1 during these subsequent events were 49.4, 2.3 and 0.02 µg/l respectively (mean values 7.5, 0.35 and 0.007 µg/l - values below detection limit taken as 0.005 for calculation of the means). In the first 2 cases, concentrations declined to <0.05 µg/l within about 24 h of the onset of rainfall, whereas on 28 May levels became undetectable (<0.01 µg/l) after 8 h.

Mean dissolved oxygen levels during the field experiments ranged from 48 to 59% saturation, and mean pH values (7.4-7.9) were also well within the acceptable range for *Gammarus* species. Water temperatures were generally in the range 5-11°C, although they dipped to less than 2°C between 6 and 13 December and some ice formed on the water surface during that week. Mean mortality rates of the *G. pulex* deployed at Site 1 were 9%, but the transient ice formation caused 53% mortality (all dead animals were replaced). The *G. pulex* feeding rates (corrected for weight changes in leaf-only cages) shown in Fig. 3 generally reflect the variable and rather low temperatures, but it will be noted that feeding largely ceased during the week ending 10 January when the first large rainfall event took place. The water temperatures at that time were adequate, ranging from 6.5 to 11.2 °C, so it is possible that the cessation of feeding was related to carbofuran. The precise reduction in feeding rate was, however, obscured by the fact that all animals were found to be dead on 10 January at the time of peak carbofuran concentrations (Fig. 2).

The laboratory toxicity experiments were conducted under similar water quality conditions to those seen in the field in order to check whether carbofuran was a likely cause of the observed biological effects. Such a check was considered essential because upstream controls were not possible (the stream rises below the treated field). The acute experiments showed that carbofuran is very toxic to *G. pulex* with 24, 48 and 96 h LC50 values (95% confidence limits in parentheses) of 21.0 (14.7-30.0), 12.5 (5.7-27.5) and 9.0 (5.8-13.9) µg/l, respectively. The horizontal broken line in Fig.

2 shows the position of the 24 h LC50, and it is apparent that carbofuran levels in the stream exceeded this value for several hours. It is therefore likely that at least a proportion of the mortalities observed at Site 1 were caused by carbofuran. The laboratory feeding experiments (Fig. 4) confirm that a 7-day exposure to carbofuran concentrations in excess of about 3 µg/l reduces *G. pulex* feeding rates to zero, a result which is also consistent with the hypothesis that carbofuran was at least partly responsible for the observed effects. The only other pesticides to have been applied to parts of the upper catchment in late 1991 (on 27 November) were products containing the herbicides atrazine, benazolin, clopyralid and cycloxydim. All of these are of low acute toxicity to aquatic animals (Ivens [ed.], 1993; Macek *et al.*, 1976) and are therefore very unlikely to have contributed significantly to the observed effects.

DISCUSSION

That carbofuran should be found in streamwater derived largely from field drains is scarcely surprising, although the concentrations and effects found in this study were unexpected. Carbofuran's key properties with respect to potential leaching are shown in Table 1 and it can be seen that its high water solubility, fairly long soil halflife, poor adsorptive properties and low vapour pressure all combine to encourage its appearance in the soil's aqueous phase and its translocation in drainage water. Indeed, some of the data in Table 1 can be used in a simple 'model world' based on fugacity theory (Mackay, 1979; Mackay & Paterson, 1981) to predict which environmental compartment will receive the greatest loading of carbofuran. Mackay's Level 1 model predicts that >93% will enter the aqueous phase at equilibrium, ignoring degradation losses. Looking at the data in a different way, carbofuran's Groundwater Ubiquity Score (GUS) which is a function of the soil degradation halflife and the soil organic carbon partition coefficient (Koc), has been calculated as 3.54, a value which categorises it as a moderate to high leacher (Gustafson, 1989).

Table 1. Properties of carbofuran which can lead to leaching.

Water solubility (mg/l)	Soil halflife (days)	Soil organic carbon adsorption coefficient, Koc (cc/g)	Log octanol-water partition coefficient (Kow)	Vapour pressure (mm Hg)	Reference (mainly review articles)
257	-	-	-	-	Seiber (1987)
700	37	55	-	-	Gustafson (1989)
700	-	-	1.6-2.3	$1.12x10^{-5}$ at 20°C	Suntio *et al.* (1988)
-	-	25-117	-	-	Sukop & Cogger (1992)
700	50	29	-	$1.1x10^{-5}$	Wauchope *et al*(1992)
320	30-60	-	1.2-1.4	$2.02x10^{-5}$ at 33°C	Anon. (1991)
700	26-110	14-160	2.32	$8.3x10^{-6}$ at 25°C	Howard (1991)

It is, of course, a large step from this very generalised modelling to the prediction of likely environmental concentrations. Although more sophisticated models are being developed which take account of degradation rates and bulk transport (e.g. Mackay *et al.*, 1985; Williams *et al.*, 1991b), none have been adequately validated with environmental data. In any event, such models were not available when carbofuran was first introduced in 1967. It would be fair to say, however, that the biologically active concentrations seen in the Rosemaund stream would not have been predicted by the regulatory procedures in place at the time, even though some leaching was to be expected.

Carbofuran has been observed in rainwater (Richards *et al.*, 1987), groundwater (Krawchuk & Webster, 1987; Ritter, 1990; Shirmohammadi *et al.*, 1989) and surface waters (Bailey, 1985; Frank et al., 1982). The highest concentration seen in surface waters (as opposed to soil drainage) has been 1.8 µg/l, while up to 158 µg/l has been found in groundwater. Not unnaturally, much higher concentrations (up to 7.8 mg/l) have been seen in field drains and stormwater runoff, especially in North America where carbofuran is used much more extensively than in the United Kingdom (Achik & Schiavon, 1989; Bush *et al.*, 1986; Caro *et al.*, 1973). However, it is important to recognise that headwater streams like that at Rosemaund, although consisting largely of undiluted field drainage, may nevertheless be of considerable wildlife significance, and should therefore be protected from harmful concentrations of pesticides.

The toxicity of carbofuran to aquatic life has been reviewed by Eisler (1985) and by the Canadian Water Quality Guidelines (Anon., 1989). 24-48 h LC50 values for fish range between 280 and 8500 µg/l (Bakthavathsalam & Reddy,1982; Carter & Graves, 1972; Davey *et al.*, 1976; Hejduk & Svobodova, 1980; Stephenson *et al.*, 1984; Verma *et al.*, 1981 & 1982), while amphibians, molluscs, oligochaetes, plants and algae are generally less sensitive than this (Dad et al., 1982; Hartman & Martin, 1985; Kar & Singh, 1979; Khangarot et al., 1985; Pawar & Katdare, 1983). On the other hand, crustacea and insect larvae are among the most susceptible groups of organisms, with acute toxicities in the range 1.6-500 µg/l (Chitra & Pillai, 1984; Hartman & Martin, 1985; Johnson, 1986; Karnak & Collins, 1974; Parsons & Surgeoner, 1991; Pawar & Katdare, 1983). In particular, field trials with (*inter alia*) amphipod crustacea in cages have observed mortalities in this group over 3-4 days at initial carbofuran exposure concentrations in the range 9-32 µg/l (Wayland & Boag, 1990), making them some of the most sensitive taxa known. Furthermore, it has been shown that sediment in storm runoff collected at the edge of American fields treated with carbofuran and atrazine was acutely toxic to chironomid insect larvae, and laboratory experiments showed that all the toxicity was probably attributable to the carbofuran (Douglas *et al.*, 1993). The experiments reported in the present paper support the view that arthropods are at high risk. On the basis of acute toxicity tests with *Daphnia pulex* (48 h EC50 = 35 µg/l; Hartman & Martin, 1985), the Canadian Water Quality Guidelines (Anon., 1989) have set an aquatic life Guideline value of 1.75 µg/l for continuous exposures, a level which appears to have been exceeded in the Rosemaund stream for periods of at least a few consecutive days.

CONCLUSIONS

It should be remembered that although the *G. pulex* bioassays were deployed during a storm of exceptional intensity, carbofuran concentrations in the stream during the subsequent, much smaller, rainfall event would also have been expected to kill many aquatic arthropods. There is consequently little doubt that crustacea and insect larvae in some headwater streams are at risk from the agricultural use of carbofuran at currently approved rates. These risks are probably highest on soils in which by-pass flow is an important component of the hydrological regime (approximately 28% of UK soils - J. Hollis, pers. comm. 1993), and will be exacerbated by the presence of field drains and impermeable subsoil. More generally, the conduct of pesticide risk assessments should in future take account of organisms in these types of headwater streams which will tend to be exposed to transiently high concentrations of certain products. If such habitats are protected, then it follows that larger rivers and lakes downstream will also be safe.

ACKNOWLEDGEMENTS

The authors thank the following for their advice and assistance:- UK National Rivers Authority (NRA), Martin Mills (NRA Welsh Region), John Hollis (Soil Survey & Land Research Centre), Lisa Stewart and John Bell (Institute of Hydrology), Paula Neall (MAFF Fisheries Laboratory, Burnham-on-Crouch), Bob Clare and Caroline Hack (ADAS Rosemaund).

REFERENCES

Achik, J. & Schiavon, M. (1989). Carbofuran transfer and persistence in drained agricultural soils related to their structure and adsorption properties. *Ecotoxicol. Environ. Saf.* **18**, 83-92.

Anon. (1989). *Canadian Water Quality Guidelines*: Updates (September 1989). Appendix V.2, Carbofuran, pp. V1-V7, Canadian Council of Resource and Environment Ministers, Environment Canada, Ottawa.

Anon. (1991). *The Agrochemicals Handbook* 3rd edition. Royal Society of Chemistry, Cambridge.

Bailey, H.S. (1985). 1983 *Toxic Chemical Survey: a survey of nine impoundments in the Saint John River basin.* Water Quality Branch, Atlantic Region, Inland Waters Directorate, Environment Canada, Moncton, New Brunswick. IWD-AR-WQB-85-88.

Bakthavathsalam. R. & Reddy, Y.S. (1982). Toxicity and behavioural responses of *Anabas testudineus* (Bloch) exposed to pesticides. *Ind. J. Environ. Hlth* **24**, 65-68.

Bouwer, H. (1989). Agricultural contamination: problems and solutions. *Wat. Environ. Technol.*, October 1989, 292-297.

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

Bush, P.B., Neary, D.G., Taylor, J.W. & Nutter, W.L. (1986). Effects of insecticide use in a pine seed orchard on pesticide levels in fish. *Water Resour. Bull.* **22**, 817-827.

Caro, J.H., Freeman, H.P., Glotfelty, D.W., Turner, B.J. & Edwards, W.M. (1973). Dissipation of soil-incorporated carbofuran in the field. *J. Agric. Fd Chem.* **21**, 1010-1015.

Carter, F.L. & Graves, J.B. (1972). Measuring effects of insecticides on aquatic animals. *Louisiana Agric.* **16**, 14-15.

Chitra, S. & Pillai, M.K.K. (1984). Development of organophosphorus and carbamate-resistance in Indian strains of *Anopheles stephensi* Liston. *Proc.Ind. Acad. Sci. (Anim. Sci.)* **93**, 159-170.

Clark, L., Gomme, J. & Hennings, S. (1991). Study of pesticides in waters from a chalk catchment, Cambridgeshire. *Pestic. Sci.* **32**, 15-33.

Council of the European Communities (1980). Directive relating to the quality of water intended for human consumption, 80/778/EEC.

Croll, B.T. (1991). Pesticides in surface waters and groundwaters. *J. Inst. Wat. Environ. Manag.* **5**, 389-395.

Dad, N.K., Qureshi, S.A. & Pandya, V.K. (1982). Acute toxicity of two insecticides to tubificid worms, *Tubifex tubifex* and *Limnodrilus hoffmeisteri*. *Environ. Int.* **7**, 361-363.

Davey, R.B., Meisch, M.V. & Carter, F.L. (1976). Toxicity of five ricefield pesticides to the mosquitofish, *Gambusia affinis*, and green sunfish, *Lepomis cyanellus*, under laboratory and field conditions. *Environ. Entomol.* **5**, 1053-1056.

Douglas, W.S., McIntosh, A. & Clausen, J.C. (1993). Toxicity of sediments containing atrazine and carbofuran to larvae of the midge *Chironomus tentans*. *Environ. Toxicol. Chem.* **12**, 847-853.

Eisler, R. (1985). *Carbofuran hazards to fish, wildlife and invertebrates: a synoptic review.* U.S. Department of the Interior, Fish & Wildlife Service, Laurel, Maryland. Contaminant Hazard Review Report No. 3, Biological Report 85 (1.3).

Frank, R., Braun, H.E., Van Hove Holdrinet, M., Sirons, G.J. & Ripley, B.D. (1982). Agriculture and water quality in the Canadian Great Lakes basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. *J. Environ. Qual.* **11**, 497-505.

Gomme, J.W., Shurvell, S., Hennings, S.M. & Clark, L. (1991). Hydrology of pesticides in a chalk catchment: surface waters. *J. Inst. Wat. Environ. Manag.* **5**, 546-552.

Gustafson, D.I. (1989). Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **8**, 339-357.

Harrison, B., Sudicky, E.A. & Cherry, J.A. (1992). Numerical analysis of solute migration through fractured clayey deposits into underlying aquifers. *Wat. Resources Res.* **28**, 515-526.

Hartman, W.A. & Martin, D.B. (1985). Effects of four agricultural pesticides on *Daphnia pulex*, *Lemna minor*, and *Potamogeton pectinatus*.*Bull. Environ.Contam. Toxicol.* **35**, 646-651.

Hejduk, J. & Svobodova, Z. (1980). Acute toxicity of carbamate-based pesticides for fish. *Acta Vet. Brno* **49**, 251-257.

Howard, P.H. (ed.) (1991). *Handbook of environmental fate and exposure data. Volume 3, Pesticides*. Lewis Publishers, Michigan, 684 pp.

Ivens, G.W. (ed.) (1993). *The UK Pesticide Guide*. C.A.B. International and the British Crop Protection Council, Wallingford & Farnham, 565 pp.

Johnson, B.T. (1986). Potential impact of selected agricultural chemical contaminants on a northern prairie wetland: a microcosm evaluation. *Environ. Toxicol. Chem.* **5**, 473-485.

Jury, W.A., El Abd, H., Clending, L.D. & Resketo, M. (1986). Evaluation of pesticide screening models under field conditions. In: *ACS Symposium Series*, 315, American Chemical Society, Washington D.C., p 384.

Karnak, R.E. & Collins, W.J. (1974). The susceptibility to selected insecticides and acetylcholinesterase activity in a laboratory colony of midge larvae, *Chironomus tentans* (Diptera: Chironomidae). *Bull. Environ. Contam. Toxicol.* **12**, 62-69.

Kar, S. & Singh, P.K. (1979). Effect of pH, light intensity and population on the toxicity of the pesticide carbofuran to the blue-green alga *Nostoc muscorum*. *Microbios* **21**, 177-184.

Khangarot, B.S., Sehgal, A. & Bhasin, M.K. (1985). 'Man and Biosphere' - studies on the Sikkim Himalayas. Part 6: Toxicity of selected pesticides to frog tadpole *Rana hexadactyla* (Lesson). *Acta Hydrochim. Hydrobiol.* **13**, 391-394.

Krawchuk, B.P. & Webster, G.R.B. (1987). Movement of pesticides to groundwater in an irrigated soil. *Wat. Pollut. Res. J. Can.* **22**, 129-146.

Lees, A. & McVeigh, K. (1988). *An investigation of pesticide pollution in drinking water in England and Wales*. Friends of the Earth, London, 8 pp.

Litchfield, J.. & Wilcoxon, F. (1949). A simplified method of evaluating dose-effect experiments. *J. Pharmacol. exp. Therapeut.* **96**, 99-113.

Macek, K.J., Buxton, K.S., Sauter, S., Gnilka, S. & Dean, J.W. (1976). *Chronic toxicity of atrazine to selected aquatic invertebrates and fish*. US Environmental Protection Agency report number EPA-600/3-76-047.

Mackay, D. (1979). Finding fugacity feasible. *Environ. Sci. Technol.* **13**, 1218-1223.

Mackay, D. & Paterson, S. (1981). Calculating fugacity. *Environ. Sci. Technol.* **15**, 1006-1014.

Mackay, D., Paterson, S., Cheung, B. & Neely, W.B. (1985). Evaluating the environmental behavior of chemicals with a Level III fugacity model. *Chemosphere* **14**, 335-374.

Maltby, L., Naylor, C. & Calow, P. (1990a). Effect of stress on a freshwater benthic detritivore: scope for growth in *Gammarus pulex*. *Ecotoxicol. Environ. Saf.* **19**, 285-291.

Maltby, L., Naylor, C. & Calow, P. (1990b). Field deployment of a scope for growth assay involving *Gammarus pulex*, a freshwater benthic invertebrate. *Ecotoxicol. Environ. Saf.* **19**, 292-300.

Matthiessen, P., Allchin, C., Williams, R.J., Bird, S.C., Brooke, D. & Glendinning, P.J. (1992). The translocation of some herbicides between soil and water in a small catchment. *J. Inst. Wat. Environ. Manag.* **6**, 496-504.

Parsons, J.T. & Surgeoner, G.A. (1991). Effect of exposure time on the acute toxicities of permethrin, fenitrothion, carbaryl and carbofuran to mosquito larvae. *Environ. Toxicol. Chem.* **10**, 1219-1227.

Pawar, K.R. & Katdare, M. (1983). Acute toxicity of Sumithion, BHC and Furadan to some selected fresh water organisms. *Biovigyanam* **9**, 67-72.

Rao, P.S.C., Green, R.E., Balasubramaniam, V. & Kanchiro, Y. (1974). Field study of solute movement in a highly aggregated Oxisol with intermittent flooding. II. Picloram. *J. Environ. Qual.* **3**, 197-202.

Richards, R.P., Kramer, J.W., Baker, D.B. & Krieger, K.A. (1987). Pesticides in rainwater in the northeastern United States. *Nature* **327**, 129-131.

Ritter, W.F. (1990). Pesticide contamination of groundwater in the United States - a review. *J. Environ. Sci. Hlth* **B25**, 1-29.

Royal Commission on Environmental Pollution (1992). *Sixteenth Report, Freshwater Quality*. Her Majesty's Stationery Office, London, 122-133.

Seiber, J.N. (1987). Principles governing environmental mobility and fate. In: Ragsdale N.N. & Kuhr, R.J. (eds), *Pesticides: Minimising Risks*, ACS Symposium Series 336, pp 88-105, American Chemical Society, Washington D.C., 183 pp.

Shirmohammadi, A., Magette, W.L., Brinsfield, R.B. & Staver, K. (1989). Ground water loading of pesticides in the Atlantic coastal plain. *Ground Wat. Monit. Rev.* **9**, 141-148.

Stephenson, R.R., Choi, S.Y. & Olmos-Jerez, A. (1984). Determining the toxicity and hazard to fish of a rice insecticide. *Crop Prot.* **3**, 151-165.

Sukop, M. & Cogger, C.G. (1992). Adsorption of carbofuran, metalaxyl and simazine: Koc evaluation and relation to soil transport. *J. Environ. Sci. Hlth* **B27**, 565-590.

Suntio, L.R., Shiu, W.Y., Mackay, D., Seiber, J.N. & Glotfelty, D. (1988). Critical review of Henry's Law constants for pesticides. *Rev. Environ. Contam. Toxicol.* **103**, 1-59.

Verma, S.R., Rani, S., Bansal, S.K. & Dalela, R.C. (1981). Evaluation of the comparative toxicity of Thiotox, dichlorvos and carbofuran to two fresh water teleosts *Ophiocephalus punctatus* and *Mystus vittatus*. *Acta Hydrochim. Hydrobiol.* **9**, 119-129.

Verma, S.R., Bansal, S.K., Gupta, A.K., Pal, N., Tyagi, A.K., Bhatnagar, M.C., Kumar, V. & Dalela, R.C. (1982). Bioassay trials with twenty-three pesticides to a fresh water teleost, *Saccobranchus fossilis*. *Wat. Res.* **16**, 525-529.

Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn Beckers, P.W.M. & Burt, J.P. (1992). The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.* **123**, 1-164.

Wayland, M. & Boag, D.A. (1990). Toxicity of carbofuran to selected macroinvertebrates in prairie ponds. *Bull. Environ. Contam. Toxicol.* **45**, 74-81.

White, R.E., Dyson, J.S., Gerstl, Z. & Yaron, B. (1986). Leaching of herbicide through undisturbed cores of structured clay soil. *Soil Sci. Soc. Am. J.* **50**, 277-283.

Figure 1. Carbofuran event in the site 3 field drain at Rosemaund Farm

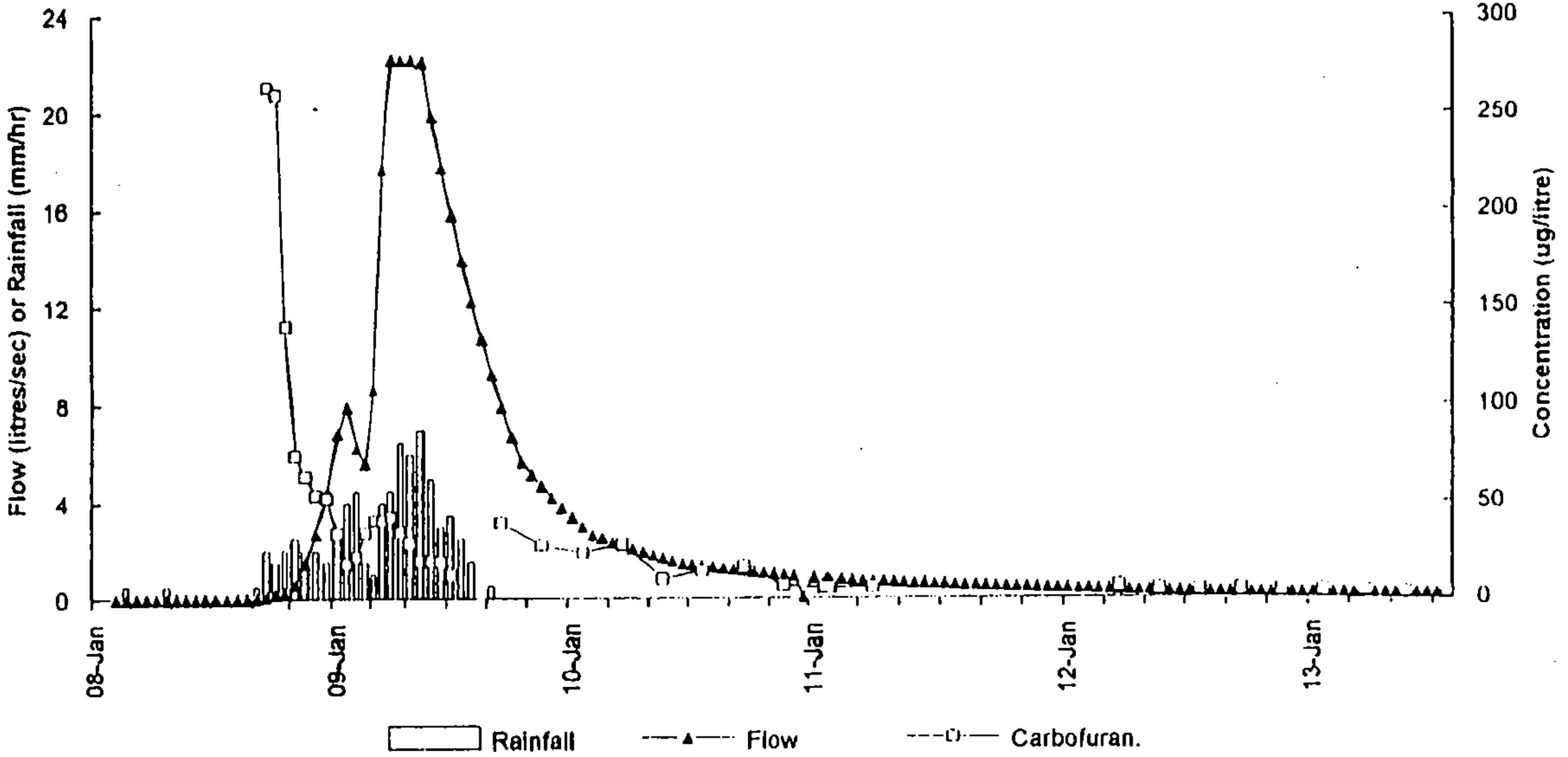


Figure 2. Carbofuran event in the stream at site 1 at Rosemaund Farm

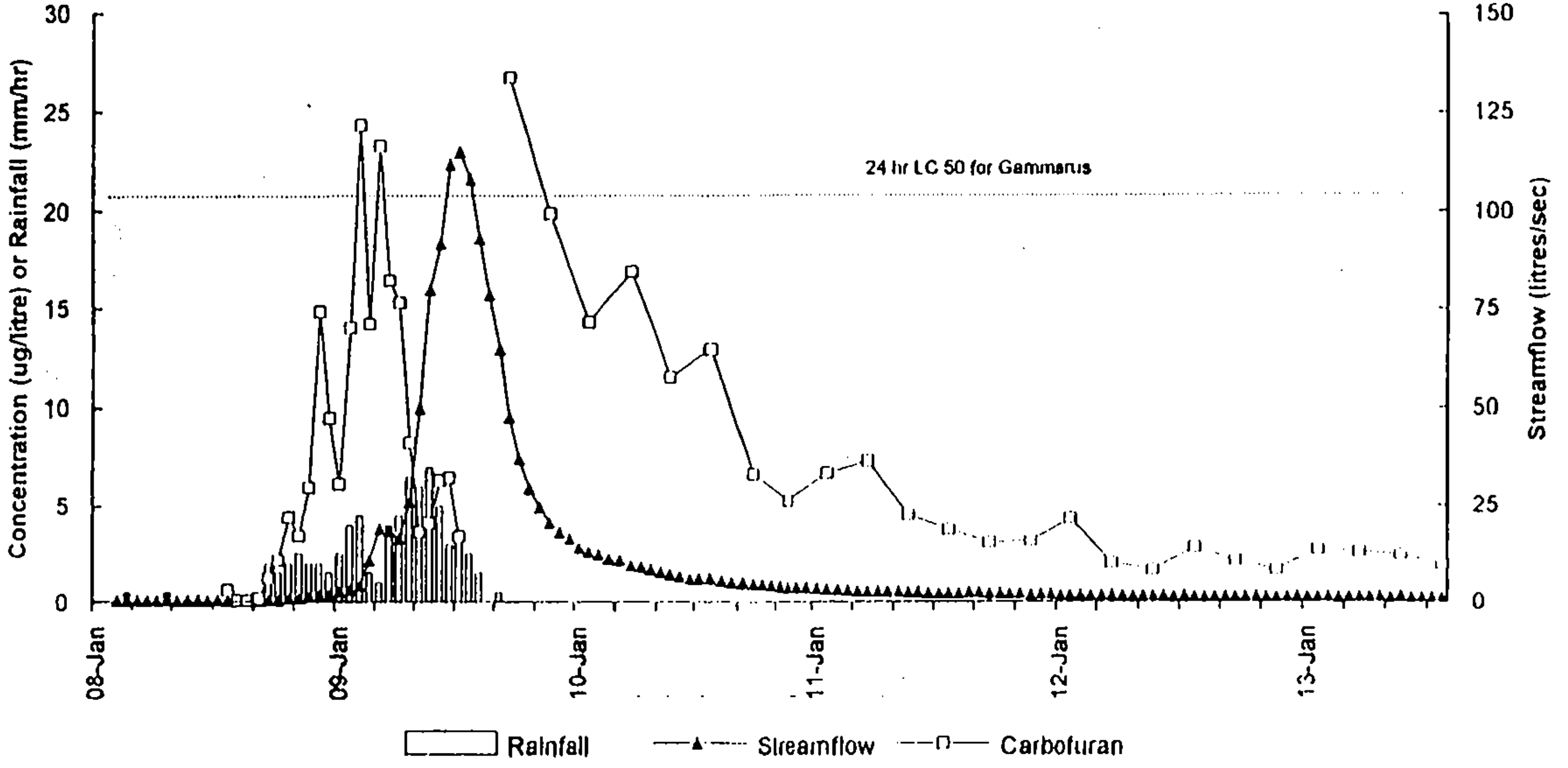


Figure 3.

Gammarus pulex feeding rates, October 1991 to January 1992

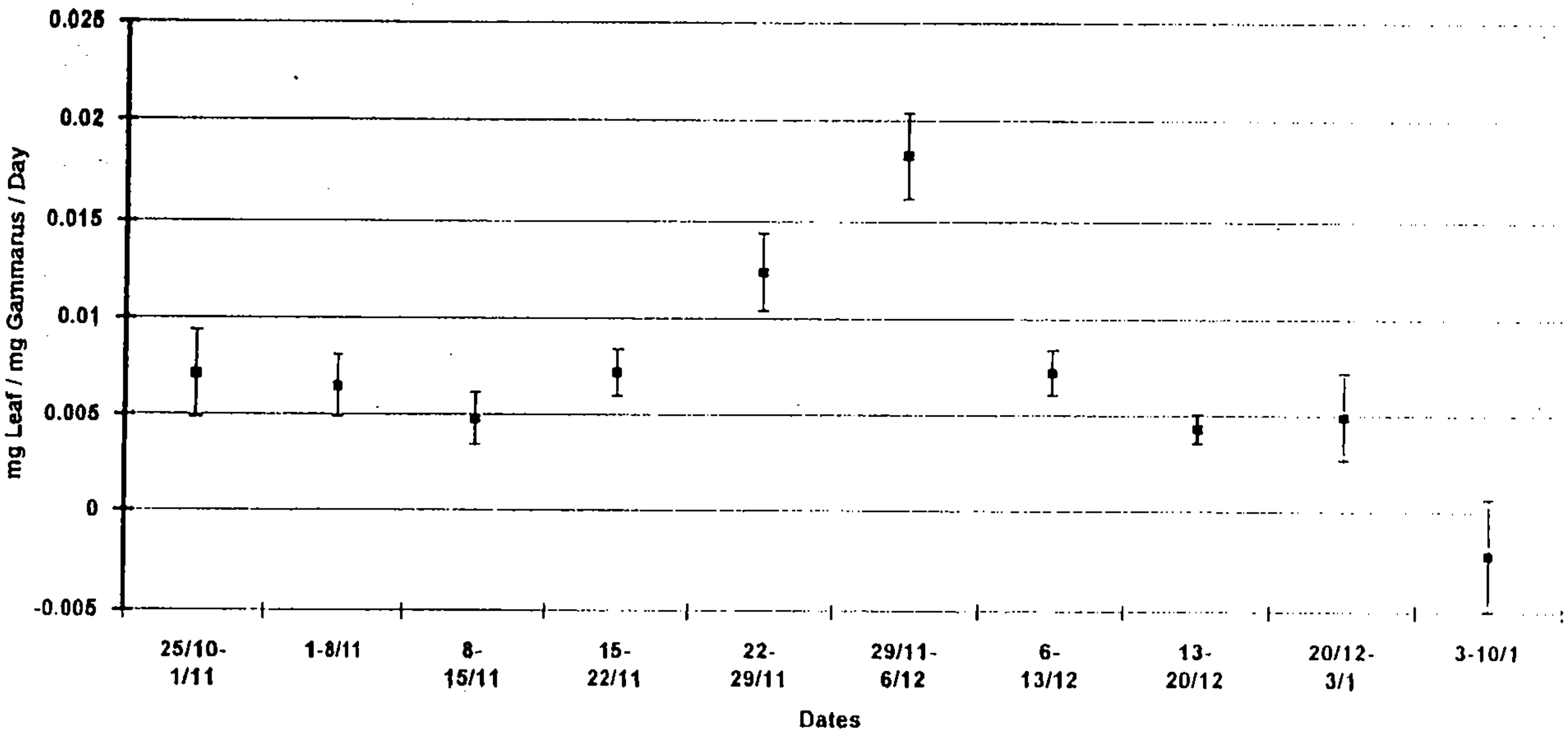


Figure 4.

The feeding rate of Gammarus pulex exposed to a range of carbofuran concentrations for a seven day period (mean values with 95% confidence limits are shown)