

Pesticides in Major Aquifers: Phase 2

WRc plc

Project Record 439/16/A



NRA

National Rivers Authority

PESTICIDES IN MAJOR AQUIFERS: PHASE 2

J Turrell, L Clark, D B Oakes, M Fielding, I Wilson, B Hegarty and R A Kanda

Environment Agency
Information Centre
Head Office

Class No ...Project...439.

Accession No .BBMH.....

Research Contractor:
WRc plc
Henley Road
Medmenham Marlow
Buckinghamshire SL7 2HD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD

Project Record 439/16/A

National Rivers Authority
Rivers House
Waterside Drive
Almondsbury
BRISTOL
BS12 4UD

Tel: 0454 624400

Fax: 0454 624409

© National Rivers Authority 1994

All rights reserved. No part of this document may be reproduced, stored in a retrieval system or transmitted, in any form or by any means, mechanical, photocopying, recording or otherwise without the prior permission of the National Rivers Authority.

Dissemination Status

Internal: Restricted

External: Restricted

Research Contractor

This document was produced under R&D Contract 439 by:

WRc plc
Henley Road
Medmenham Marlow
Buckinghamshire
SL7 2HD

Tel: 0491 571531

Fax: 0491 579094

WRc Reference: NR 3605/1/7077

NRA Project Leader

The NRA's Project Leader for R&D Contract 439:

D Tester - Anglia Region

Additional Copies

Further copies of this document may be obtained from Regional R&D Co-ordinators or the R&D Section of NRA Head Office.

CONTENTS	Page
LIST OF TABLES	ii
LIST OF FIGURES	ii
EXECUTIVE SUMMARY	1
KEY WORDS	1
1. INTRODUCTION	3
2. ANALYTICAL DEVELOPMENT	5
2.1 Methods Developed during Phase 1 of the Project	5
2.2 Development of Method for Acid Herbicides in Sandstone and Chalk Aquifer Material	5
2.3 Development of Method for Triazine Herbicides in Chalk Aquifer Material	6
3. FIELD STUDIES	7
3.1 Background	7
3.2 Selection of Sites	7
3.3 Drilling Programme	22
3.4 Sub-sampling Procedures for GCMS and Immunoassay analysis	22
3.5 Analytical Methodology and Results	23
3.6 Discussion of Profiling	26
4. MODELLING	43
5. CONCLUSIONS	45
6. RECOMMENDATIONS	47
REFERENCES	49
APPENDICES	
A DRILLING RECORDS	51
B PROTOCOL FOR THE EXTRACTION OF POREWATER FROM CORE MATERIAL USING CENTRIFUGATION	59
C ANALYTICAL RESULTS	61

LIST OF TABLES

	Page
3.1 Boreholes required for Phase 2	7
3.2 Herbicide loading data for Field 57, Institute for Animal Health Compton Laboratory, Compton, Berkshire	11
3.3 Herbicide loading data for Bishopfield Farm, Serlby, Bautry, Doncaster	15
3.4 Herbicide loading data for Side Mill Road, Green Hedge Farm, Stapleford, Cambridge	18
3.5 Herbicide loading data for Bottom Birklands Field, Assarts Farm, Warsop, Nottingham	21

LIST OF FIGURES

3.1 Site location AFRC, Compton, Berkshire	9
3.2 Location of boreholes AFRC, Compton, Berkshire	10
3.3 Site location Bishops Field Farm, Serlby, Doncaster	13
3.4 Location of boreholes Bishops Field Farm, Serlby, Doncaster	14
3.5 Site location Green Hedge Farm, Stapleford, Cambridge	16
3.6 Location of boreholes Green Hedge Farm, Stapleford, Cambridge	17
3.7 Site location Assarts Farm, Warsop, Nottingham	19
3.8 Location of boreholes Assarts Farm, Warsop, Nottingham	20
3.9 Concentration of atrazine detected by immunoassay ($\mu\text{g l}^{-1}$) and GC-MS ($\mu\text{g kg}^{-1}$) in the chalk at Compton, Berkshire	27
3.10 Concentration of atrazine detected by GCMS in the chalk at Compton, Berkshire	31
3.11 Concentration of triazine herbicides detected by GCMS in the sandstone at Bishopfield Farm, Doncaster	33
3.12 Concentrations of simazine/trietazine detected by immunoassay ($\mu\text{g l}^{-1}$) and trietazine detected by GCMS ($\mu\text{g kg}^{-1}$) in sandstone at Bishopfield Farm, Borehole 2	35
3.13 Concentration of phenoxyacid herbicides detected in the core profiles by GCMS in the sandstone at Assarts Farm, Nottingham	41

EXECUTIVE SUMMARY

The 'Pesticides in Major Aquifers' project began in 1984 as the Granta Catchment Study in co-operation with the Anglian Water Authority. In 1989 the project continued under the sponsorship of the NRA and the results of Phase 1 of the project (1984-1992) were reported to the NRA in 1992 in R&D Note 72. Phase 2 of the project was authorised by the NRA to complete the work outstanding from Phase 1. This report describes the work done in Phase 2 and marks the completion of the project. A summary of the whole project has been presented to the NRA in a companion volume, R&D Report 17.

Analytical methods for acid herbicides in sandstone and chalk matrices have been completed successfully. The development of a similar method for triazines in chalk has been less successful. The NRA now have methods of analysis reported to SCA format for two major groups of pesticides; the urons and carbamates, and acid herbicides, in sandstone and chalk as well as one for triazines in sandstone.

Profiling of the concentrations of the three major groups of pesticides through the unsaturated zone of the Chalk and Sherwood Sandstone Aquifers has been completed. The acid herbicides, urons and carbamates appear to be attenuated sharply in the soil and unsaturated zone and are rarely detected below 3 m from the surface. Triazines are shown by the profiling to be persistent and mobile beneath crops (Maize) as well as in drainage structures with high hydraulic loading.

The modelling needs of the NRA with respect to pesticide transport in the groundwater system have been reviewed. The need for two kinds of models, screening and catchment models, has been identified. These models will be used to produce a pesticide information and risk assessment tool expert system for use by NRA Head Office and Regional Headquarters Staff. It is suggested that by the use of GIS technology and existing databases, these models could be produced at a relatively small cost.

KEY WORDS

Pesticides, analysis, profiling, ground water, transport, modelling.

1. INTRODUCTION

Research on Pesticides in Major Aquifers started as the Granta Catchment Study in 1984 in co-operation with the Anglian Water Authority and has continued from 1989 with funding by the National Rivers Authority (NRA).

The key objectives of that work were:

- to determine the fate and transport of selected pesticides in surface and groundwater;
- to relate measured levels of pesticides to their patterns of use and physico-chemical properties;
- to develop predictive models of pesticide transport and fate.

The results of Phase 1 of the project, the work programme upto 1992, were presented to the National Rivers Authority in R&D Note 72 (Clark *et al.* 1992).

An important part of that work programme had been the development of analytical methods for the determination of pesticides in aquifer materials and in environmental waters at very low concentrations. A multi-residue method for 20 pesticides had been developed for monitoring pesticides in river, ground and rain waters. A method had been completed for uron and carbamate pesticides in chalk and sandstone to a limit of detection of $0.03 \mu\text{g kg}^{-1}$, and for triazines in sandstone to the same limit. Method development for triazines in chalk had been less successful and methods for acid herbicides in chalk and sandstone were still awaited.

The NRA authorised Phase 2 of the 'Pesticides in Major Aquifers' project to complete the work outstanding from Phase 1. This would be to:

- improve the analytical method for triazines in chalk;
- develop analytical methods for acid herbicides in chalk and sandstone;
- present all the analytical methods developed in Phases 1 and 2 as NRA R&D Notes in the Standing Committee of Analysts (SCA) format;
- drill and core seven boreholes to up to 10 m depth at selected locations. The samples from these boreholes would be analysed to provide examples of the analytical methods in use and to provide profiles of the concentration of the pesticides with depth as follows:

Borehole numbers	Aquifer	Pesticide group to be analysed
1	Chalk	Triazines
2	Sherwood Sandstone	Triazines
2	Chalk	Acid herbicides
2	Sherwood Sandstone	Acid herbicides

The profiles also would be interpreted and compared with previous ones to assess the rate of pesticide transport through the unsaturated zone of the aquifers;

- prepare a review of the current status of models of pesticide transport through soils and groundwater systems. Assess the relationship between GIS and mechanistically-based models and then use the model review and assessment to prepare a specification for a modelling framework which would meet the needs of the NRA.

This report presents the results of Phase 2 of the 'Pesticides in Major Aquifers' project and covers the work done in the calendar year 1993. This work programme is given in the report of Phase 1 of the project but details given in R&D Note 72 are not repeated. Most of the work done in 1993 has been reported in various R&D Notes and these are referred to in the text but are not duplicated.

2. ANALYTICAL DEVELOPMENT

2.1 Methods Developed during Phase 1 of the Project

A multi-residue method for the analysis of 20 pesticides in environmental waters was described in R&D Note 72 (Clark *et al.* 1992) and has been presented to the NRA in SCA format in R&D Note 231 (Shurvell *et al.* 1993). Analytical methods based on Gas Chromatography-Mass Spectrometry (GCMS) techniques for the detection of pesticides in solid materials also had been described in R&D Note 72 including:

- urons and carbamates in chalk and sandstone;
- triazines in sandstone.

A method for triazines in chalk and sandstone using immunoassay techniques has been developed and described by Turrell in R&D Report 72.

The method for urons and carbamates has been issued in SCA format in R&D Note 223 (Forbes *et al.* 1993A), and for triazines in sandstone in SCA format in R&D Note 222 (Forbes *et al.* 1993B).

2.2 Development of Method for Acid Herbicides in Sandstone and Chalk Aquifer Material

In Phase 2 of the 'Pesticides in Major Aquifers' project, a multi-residue method for acid herbicides in chalk and sandstone has been developed and validated. The final method has been described and presented to the NRA as an R&D Note in SCA format (Forbes *et al.* 1994a).

The method is based on aqueous extraction of the acids from the aquifer material (chalk or sandstone) under basic conditions followed by acidification and extraction into dichloromethane. Concentrated organic extracts are methylated and analysed by GCMS. It was found during the method development and validation that the value and the control of pH after acidification plays an important part in ensuring reproducibility of analysis. Initially the pH was brought to 0.5-2.0 and the recovery of internal standard was variable (<50%) and the precision of analysis of the seven acid herbicides was poor. Conducting the acidification under more controlled conditions (final pH 1.2 ± 0.2) gave more reproducible results with lower standard deviations, between and within batches, although recoveries for ioxynil and bromoxynil were lower under these conditions and recoveries of the five other herbicides were higher. It is possible that another value of pH, also controlled precisely, may give optimum recoveries of all seven pesticides.

Two other extraction procedures were investigated for acid herbicides in sandstone, based on literature methods for other sample matrices:

- extraction under acidic conditions (HCl) from the acidic aqueous solution into diethyl ether;

- extraction under acidic conditions (H_2SO_4) with ultrasonic agitation from the acidic aqueous solution into 50:50 acetone:hexane, followed by back-extraction into acidified water and then dichloromethane.

Neither method gave adequate recoveries of the acid herbicides.

Extraction with methanol of chalk samples (spiked with acid herbicides) followed by High-Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) of concentrated extracts was also investigated, as an alternative analytical technique which offered potential advantages over acidic extraction methods for chalk samples. The acid herbicides were not methylated and were thus analysed as the free acids; the resulting polarity apparently lowered the sensitivity of the thermospray/plasma spray ionisation detector for the seven compounds. It was found that although the method appeared to be satisfactory for five of the seven compounds, the detector sensitivity for bromoxynil and ioxynil was approximately 50-fold lower than for the other acid herbicides. As the aim of the work was an analytical method for the seven acid herbicides, this technique was not investigated further.

2.3 Development of Method for Triazine Herbicides in Chalk Aquifer Material

A major problem met in both Phases of the Project has been with the development of a sensitive method based on GCMS techniques for triazines in chalk (Forbes *et al.* 1994). A variety of techniques, based on solid-phase extraction and gel-permeation chromatography, to remove material interfering with the determination were investigated. None were found capable of selectively removing the interferences while adequately recovering the triazines.

Profiling of the atrazine in the Chalk Aquifer has been undertaken (Section 3) using immunoassay techniques with confirmatory analyses of some samples by the GCMS method developed for triazines in sandstone (Figures 3.9 and 3.10).

A High Performance Liquid Chromatography- Mass Spectrometry (HPLC-MS) method of analysis of triazines in chalk was studied (Forbes *et al.* 1994). This method could be conducted under the same conditions as are used successfully for the uron and carbamates. No adverse effects of the co-extracted impurities on the chromatographic performance were observed during analysis of the spiked chalk samples. The preliminary experiments, however, indicated that interfering material was still present in the extracts and affecting the determination of triazines in the chalk. Although the HPLC-MS method has shown more potential than the GCMS method, further development of extraction/clean-up and separation steps is required before the method could be used for triazine analysis in a chalk matrix.

3. FIELD STUDIES

3.1 Background

Although there are numerous instances of pesticides being detected in groundwater, little is understood about the mechanisms by which pesticides enter the groundwater after application for agricultural and non-agricultural weed control. To improve understanding of pesticide transport processes, the NRA contracted WRC to develop a series of analytical methods capable of detecting pesticides at low levels in solid aquifer material. In Phase 1 of the 'Pesticides in Major Aquifers' project, methods for uron herbicides were developed and field profiles obtained for both chalk and sandstone aquifer materials. Following additional development of analytical methods for chlorophenoxy acid and triazine herbicides (Section 2.), the field studies detailed in the following section complete the profiling programme for these herbicides in chalk and sandstone and provide quantitative data on pesticide transport through the unsaturated zone for these groups of compounds.

3.2 Selection of Sites

To complete the field validation started in Phase 1, a total of seven cores were selected in both chalk and sandstone matrices. The breakdown of the drilling programme is shown in Table 3.1.

Table 3.1 Boreholes required for Phase 2

No. of boreholes	Aquifer type to be analysed	Pesticide group
1	Chalk	triazines
2	Sandstone	triazines
2	Chalk	acid herbicides
2	Sandstone	acid herbicides

Note: One profile for triazine herbicides in chalk was completed during Phase 1 of the project so only one additional set of profiling data was required to complete the programme in Phase 2.

Each borehole was selected to provide profile data for one group of herbicides. Sites were selected on a number of criteria:

- availability of reliable herbicide loading data;
- the target group of herbicides had been applied over a period of years;

- the land owner was prepared to grant permission for drilling following the 1993 harvest.

The selection of each drilling location was dictated by the soil types commonly associated with chalk and sandstone outcrops. In the UK, maize crops account for the majority of agriculturally-applied atrazine, however maize is not normally grown on the light sandy soils associated with sandstone areas. To locate a site using triazine herbicides on sandstone, attention was focused on commercial pea and bean growers' crops to which simazine and trietazine are usually applied for weed control. This imposed a slight restriction on the loading frequency which could be expected from any given site; to prevent proliferation of soil-born diseases peas and beans are only grown at five year intervals on the same field. To obtain maximum data from the profiling work, a sandstone site was selected with simazine and trietazine applications and a chalk site selected on the basis of atrazine use.

Likewise, the use of acid herbicides is limited to the heavier valley soils on the Chalk rather than the somewhat thinner soils often associated with the Chalk outcrop. These lighter soils are more suited to a contact type herbicide, whereas the residual herbicides (e.g. acid herbicides) are found to be more effective on the moisture retentive clay soils found in the valleys.

3.2.1 Sites for triazine profiling

(a) Chalk

The site for profiling in the Chalk was selected to compliment the work undertaken by the British Geological Survey (BGS) for the NRA (reported in NRA R&D 113/9 ST). As part of research into 'Diffuse Pollution from Land-use Practices', BGS identified a site in Compton in Berkshire where atrazine herbicide had been used to control weeds in maize crops for two years. WRC revisited AFRC (Agriculture & Food Research Council) at Compton to discuss atrazine use since the 1990/91 study. The Farm Manager was able to confirm that maize cropping in Field 57 had been continuous since 1988 to 1993. The detailed loading data are presented in Table 3.2. Permission was granted for drilling access and a site selected (NGR SU 508 817) for one borehole 10 m deep close to the BGS boreholes. The site at Compton is situated on the outcrop of the Lower Chalk on the flanks of the valley of the River Pang. The borehole was drilled in the corner of the field where drainage and run-off from the surrounding field was most likely to occur. Figures 3.1 and 3.2 show the location of the site and exact drilling location. The drilling log of the borehole is given in Appendix A, Table A.1.

(b) Sandstone

The sandstone site was selected with the assistance of the PGRO (Pulse and Growers Research Organisation). A site at Bishopfield Farm, Serlby, near Bawtry, Doncaster (NGR SK 647 886) was identified on the Sherwood Sandstone where peas had been grown twice in the last five years. Sites for two boreholes, one 10 m deep and one

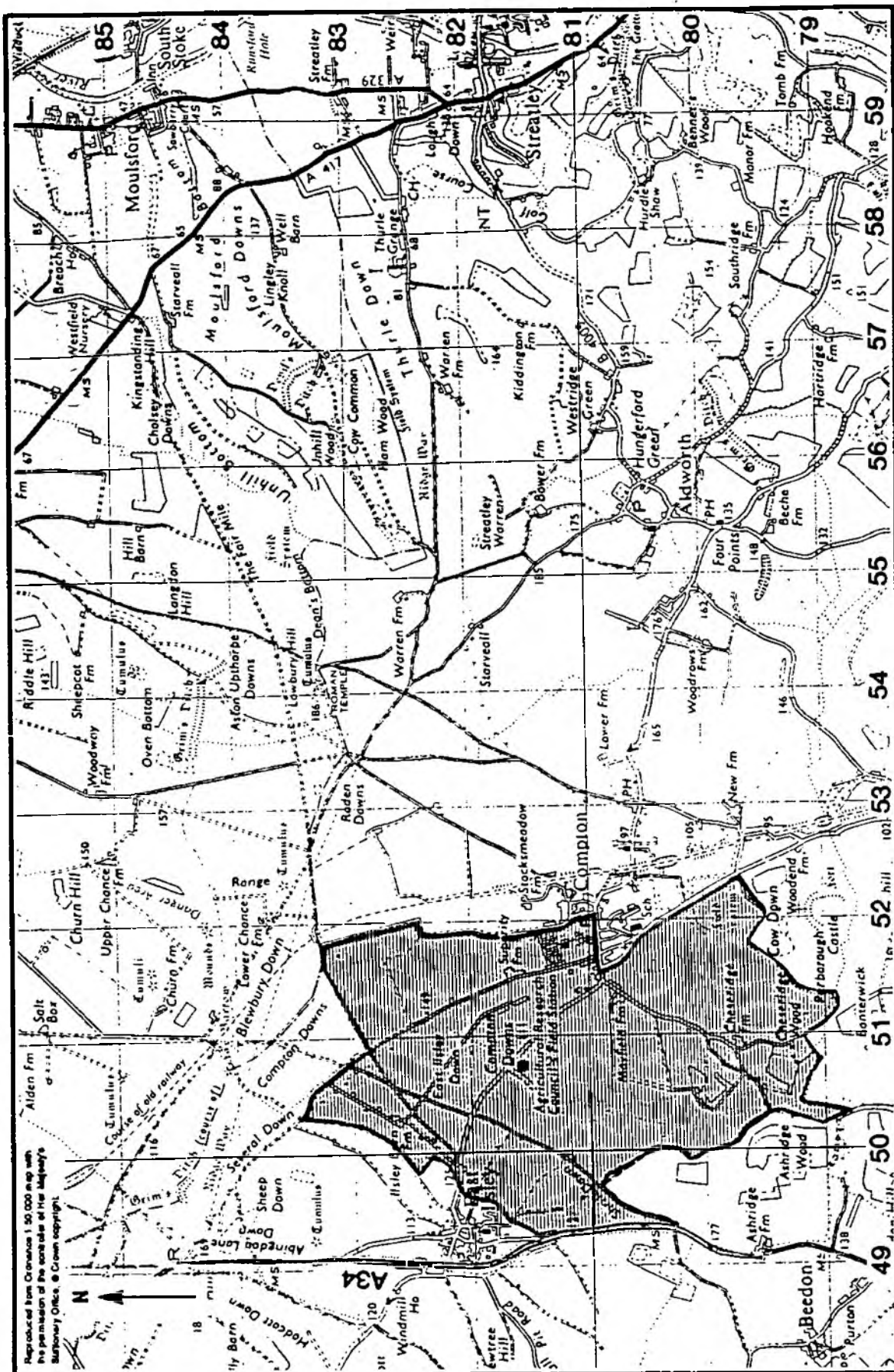


Figure 3.1 Site location AFRC, Compton, Berkshire

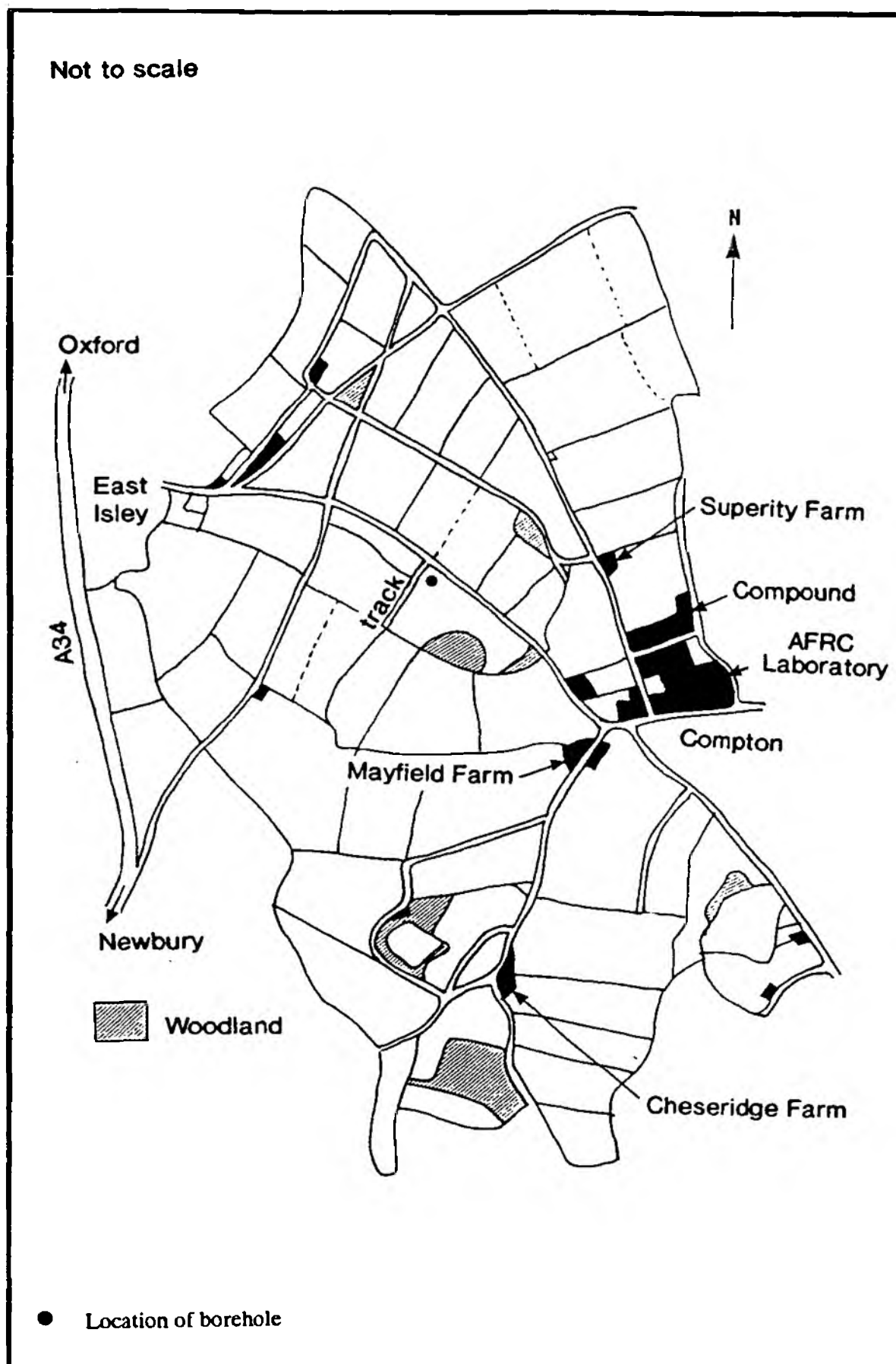


Figure 3.2 Location of boreholes AFRC, Compton, Berkshire

Table 3.2: Herbicide loading data for Field 57, Institute for Animal Health Compton Laboratory, Compton, Berkshire

Harvest Year	Crop	Herbicide Brand name	Manufacturer	Active Ingredients	Quantity active ingredient	Area under crop (and sprayed) (ha)	Loading Rate of herbicide (ha-1)	Amount active ingredient ha-1 (kg)
1989	Maize	Gesaprim 500L	Ciba Geigy	atrazine	500 g l ⁻¹	13.37	3 l	1.5
1990	Maize	Gesaprim 500L	Ciba Geigy	atrazine	500 g l ⁻¹	13.37	3 l	1.5
1991	Maize	Gesaprim 500L Lentagran	Ciba Geigy	atrazine pyridate	500 g l ⁻¹	13.37	1.5 l 1.5 kg	0.75
1992	Maize	Gesaprim 500L Lentagran	Ciba Geigy	atrazine pyridate	500 g l ⁻¹	13.37	1.5 l 1.5 kg	0.75
1993	Maize	Gesaprim 500L Lentagran	Ciba Geigy	atrazine pyridate	500 g l ⁻¹	13.37	1.5 l 1.5 kg	0.75

Note: Detailed loading data is provided for triazine herbicides only

6 m deep, were selected. Figures 3.3 and 3.4 show the location of the site and exact drilling locations. The drilling logs are given in Appendix A (Tables A.2, A.3). The farmer provided loading data (Table 3.3) and agreed to the drilling taking place after harvest of the 1992/93 crop. The farm is located in the valley between the Rivers Ryton and Idle, the topsoil consists of a thin layer of boulder clay over the sandstone outcrop.

Sites for acid herbicide profiling

(a) Chalk

During a preliminary field survey of the Granta catchment, contact was made with a number of farmers willing to take part in the profiling work. Following compilation of herbicide loading data, Green Hedge Farm, lying to the north-east of Stapleford was selected on the basis that mecoprop, MCPA, bromoxynil and ioxynil had been applied at known loading rates in various combinations to Side Mill Road field over a period of seven years. Good recoveries could be expected from the coring work as the field was known to be free of flints. The farm is situated in the valley of the River Granta (NGR TL 481 521), although the field selected for drilling work lay on the flanks of the valley. Two boreholes were drilled to 10 m depth. Figures 3.5 and 3.6 show the exact location of the site and drilling locations, drilling logs are given in Appendix A (Tables A.4, A.5). Drilling was undertaken in a depression down gradient of the access track and field boundary.

(b) Sandstone

Loading data collated as part of the 1991 profiling programme at the end of Phase 1, indicated Assarts Farm, Nottingham, previously used for uron profiling would also provide a suitable site for looking at chlorophenoxy herbicides. The farmer agreed to the proposals for new work and provided additional loading data from 1991 to the present. On this basis Bottom Birklands field was selected for drilling two further boreholes. Table 3.5 presents the detailed loading data for the field; repeated applications of mecoprop, MCPA, bromoxynil and ioxynil have been used on this field over a period of four years.

The farm is located on the Sherwood Sandstone to the north-east of Warsop, Nottinghamshire (NGR SK 594 685). Figures 3.7 and 3.8 show the general location of the site and more detailed drilling locations. The field sloped gently to the south-east and drilling was located in a natural depression approximately 20 metres into the field.

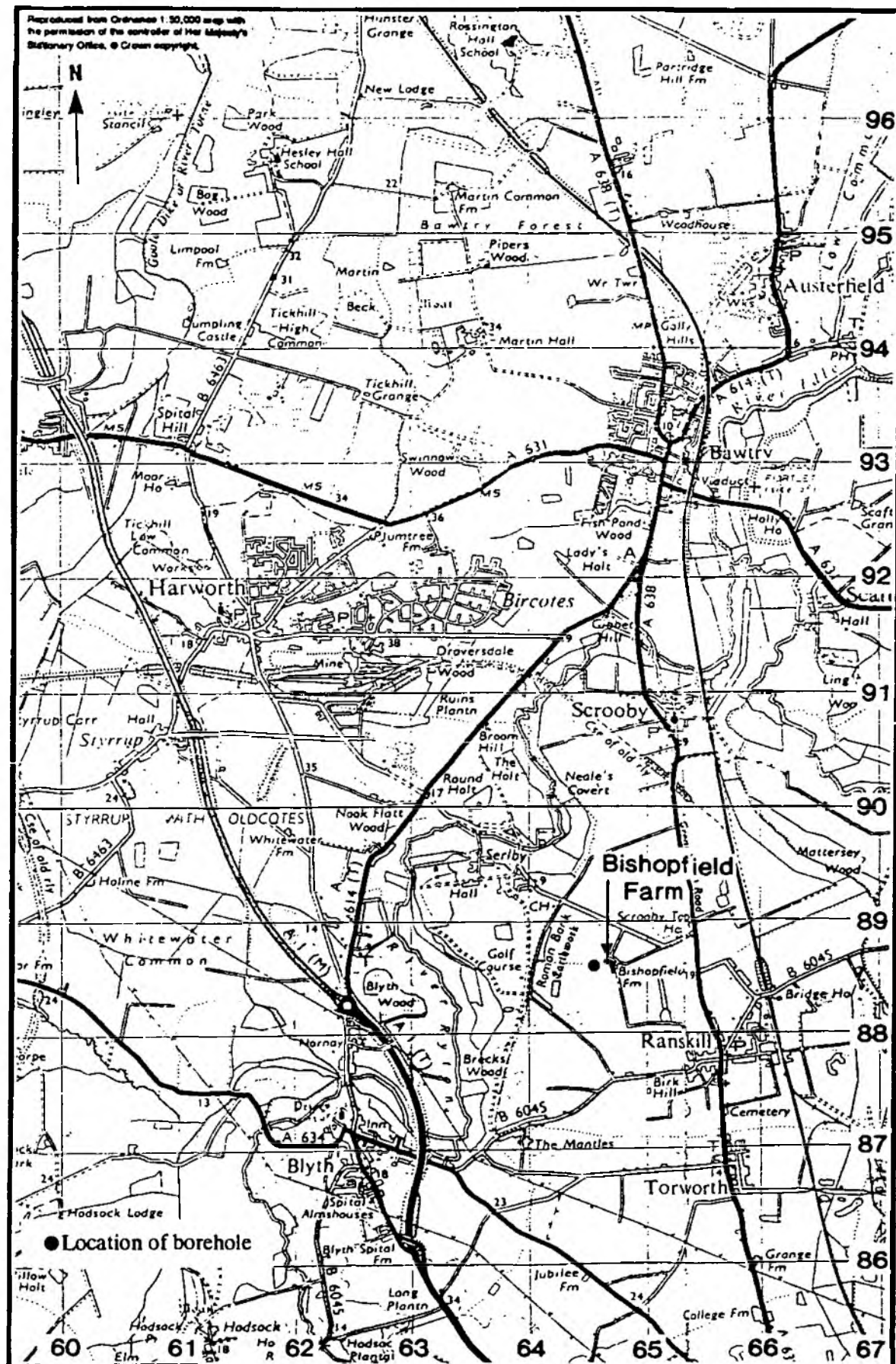


Figure 3.3 Site location Bishop's Field Farm, Serlby, Doncaster

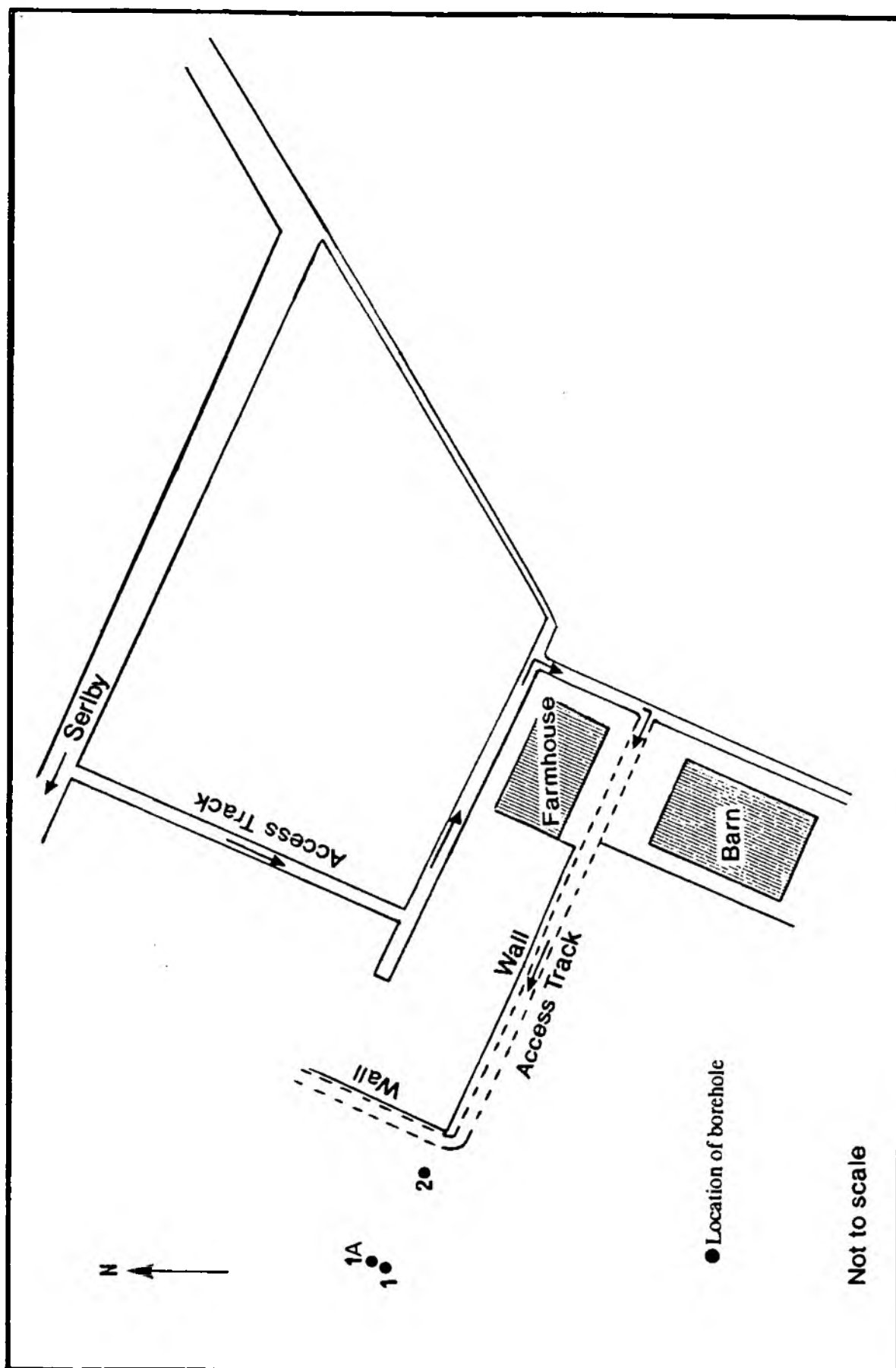


Figure 3.4 Location of boreholes Bishop's Field Farm, Serlby, Doncaster

Table 3.3: Herbicide loading data for Bishopfield Farm, Serlby, Baulby, Doncaster

Harvest Year	Crop	Herbicide Brand name	Manufacturer	Active Ingredients	Quantity active ingredient	Area under crop (and sprayed) (ha)	Loading Rate of herbicide (ha-l)	Amount active ingredient ha ⁻¹ (kg)
1988	Peas	Rental RC	Dow Elanco	simazine: trietazine	57:5 : 402.5 g l-l	13	2.4 l	0.14 : 0.97
1989	Potatoes	-	-	-	-	-	-	-
1990	Winter Barley	-	-	-	-	-	-	-
1991	Winter Barley	-	-	-	-	-	-	-
1992	Sugar Beet	-	-	-	-	-	-	-
1993	Peas	Pulsar Fortrol	BASF Shell	bentazone: MCPB cyanazine	200 : 200 g l-l 500 g l-l	13	4 l 4 l	0.80 : 0.80 2.0

Note: Detailed loading data is provided for triazine herbicides only

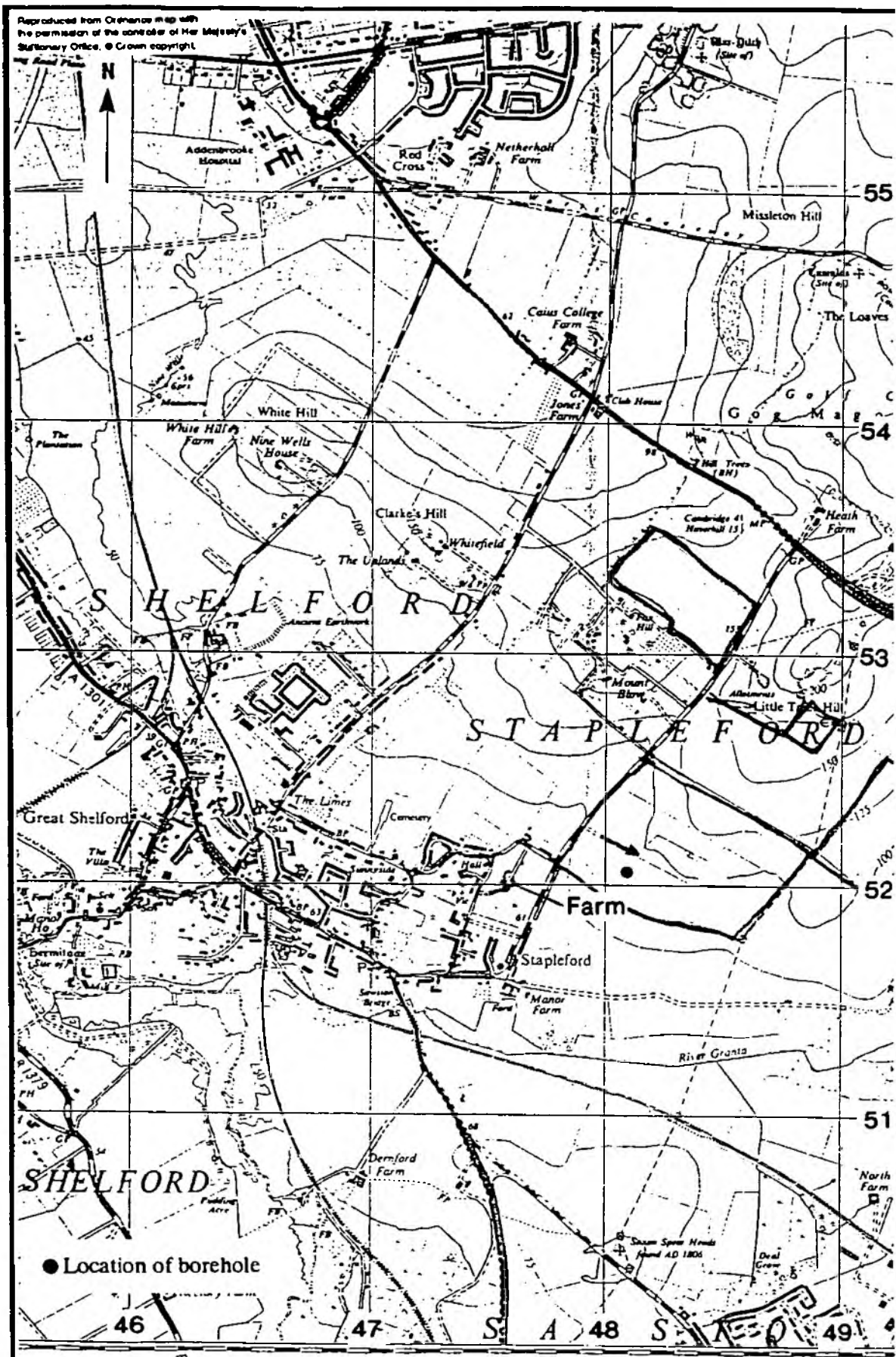


Figure 3.5 Site location Green Hedge Farm, Stapleford, Cambridge

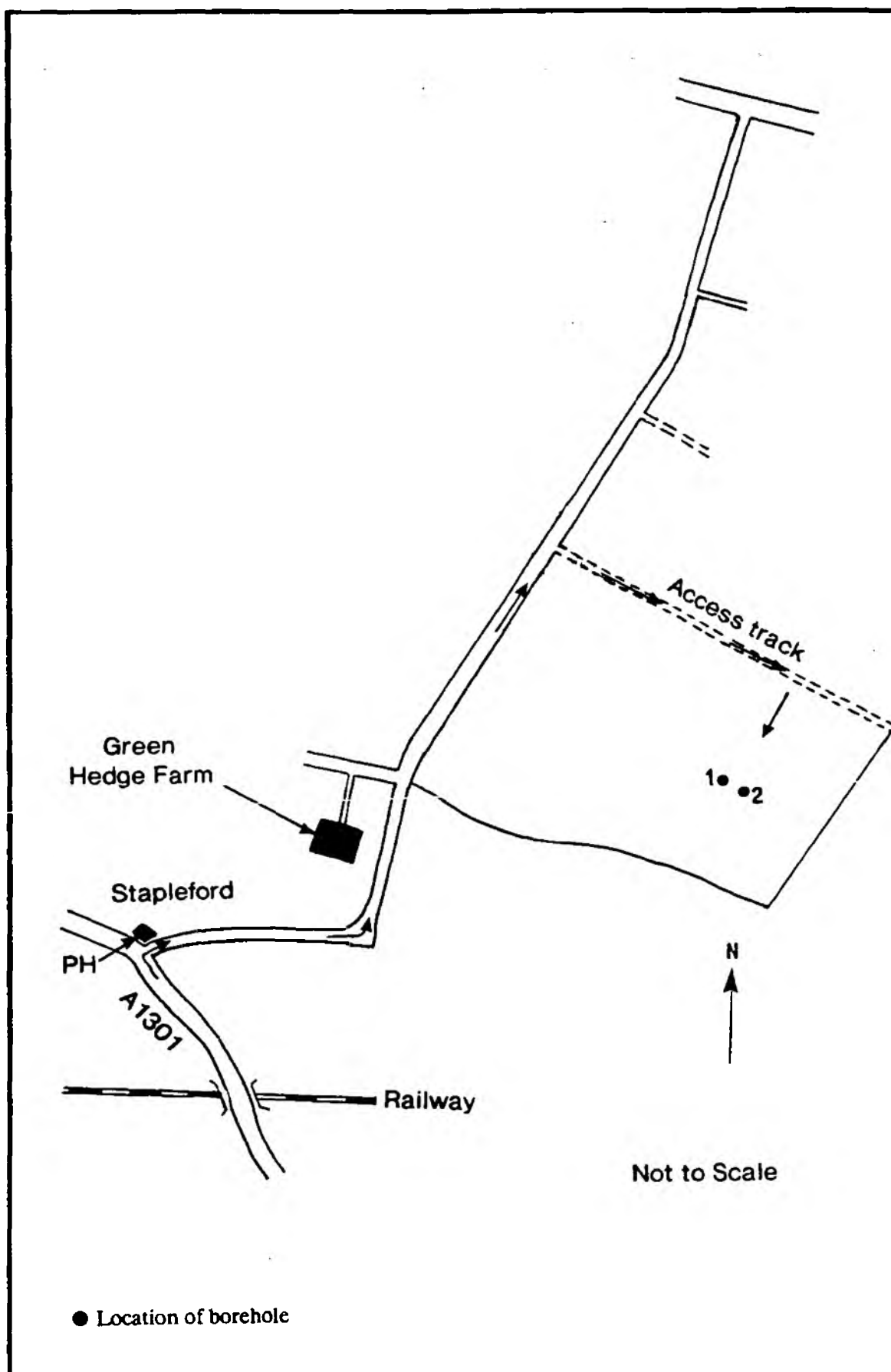


Figure 3.6 Location of boreholes Green Hedge Farm, Stapleford, Cambridge

Table 3.4: Herbicide loading data for Side Mill Road, Green Hedge Farm, Stapleford, Cambridge

Harvest Year	Crop	Herbicide Brand name	Manufacturer	Active Ingredients	Quantity active ingredient	Area under crop (and sprayed) (ha)	Loading Rate of herbicide (ha ⁻¹)	Amount active ingredient ha ⁻¹ (kg)
1985	Winter Barley	Oxytril CM - Agritox 50 -	Rhone Polenc Rhone Polenc	bromoxynil: ioxynil MCPA	200:200 g l ⁻¹ 500 g l ⁻¹	8	2.1 1.4	0.42:0.42 0.70
1986	Winter Barley	Hobane CMPP	Top Farm Top Farm	bromoxynil:ioxynil mecoprop	340:160 g l ⁻¹ 570 g l ⁻¹	4	2.8 1.4	0.95:0.45 0.80
1987	Sugar Beet	-	-	-	-	-	-	-
1988	Winter Wheat	Swipe 560 EC	Ciba-Geigy	bromoxynil:ioxynil:mecoprop	56:56:448 g l ⁻¹	13	3.8	0.21:0.21:1.7
1989	Winter Barley	Swipe 560 EC	Ciba-Geigy	bromoxynil:ioxynil:mecoprop	56:56:448 g l ⁻¹	13	3.8	0.21:0.21:1.7
1990	Spring Barley	Banlenc Plus	Schering	dicamba:MCPA:mecoprop	18:252:84 g l ⁻¹	13	4.1	0.08:1.03:0.34
1991	Sugar Beet	-	-	-	-	-	-	-
1992	Spring Barley	Banlenc Plus	Schering	dicamba:MCPA:mecoprop	18:252:84 g l ⁻¹	13	4.1	0.08:1.03:0.34
1993	Spring Barley	Swipe 560 EC - Banlenc -	Ciba-Geigy	bromoxynil:ioxynil:mecoprop	56:56:448 g l ⁻¹	13	4.1	0.21:0.21:1.7

Note: Detailed loading data is provided for chlorophenoxy acid, ioxynil and bromoxynil herbicides only

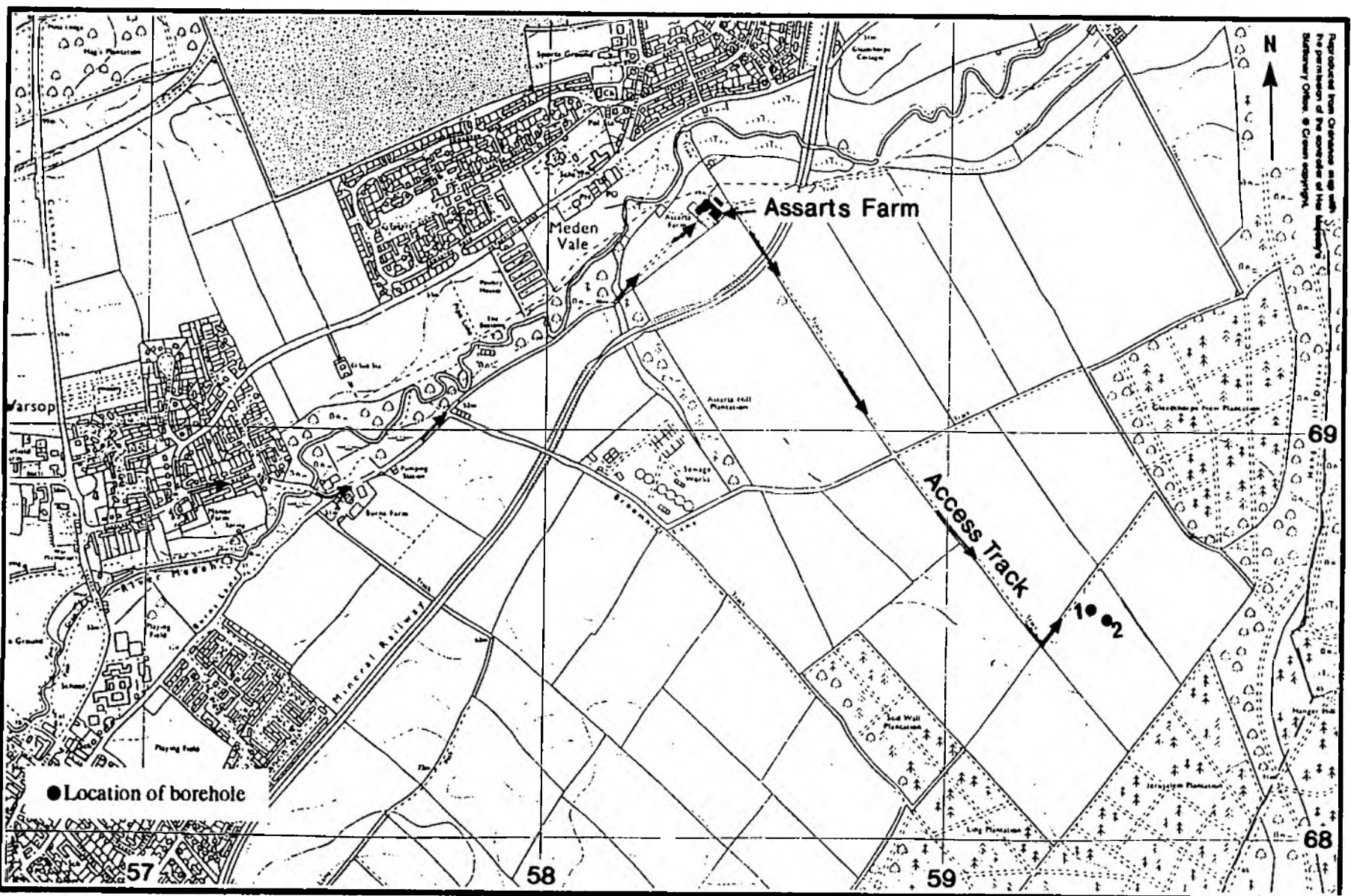


Figure 3.8 Location of boreholes Assarts Farm, Warsop, Nottingham

Table 3.5: Herbicide loading data for Bottom Birklands Field, Assart Farm, Warsop, Nottingham

Harvest Year	Crop	Herbicide Brand name	Manufacturer	Active Ingredients	Quantity active ingredient	Area under crop (and sprayed) (ha)	Loading Rate of herbicide (ha ⁻¹)	Active ingredient applied ha ⁻¹ (kg)
1986	Winter Barley	CMPP Super MCPA	Chafer Ltd. Top Farm	mecoprop MCPA	600gl ⁻¹ 500gl ⁻¹	18	3.5 l	2.1 1.75
1987	Winter Barley	CMPP Super MCPA	Chafer Ltd Top Farm	mecoprop MCPA	600gl ⁻¹ 500gl ⁻¹	18	2.1 l	1.26 1.05
1988	Onions	Totril	RP	ioxynil	275gl ⁻¹	18	3.5 l	0.96
1989	Sugar Beet	-	-	-	-	18	2.1 l	-
1990	Peas/Potatoes	-	-	-	-	18	225 g	-
1991	Spring Barley	CMPP Super MCPA Oxytril CM	Chafer Ltd. Top Farm Ciba Geigy	mecoprop MCPA bromoxynil : ioxynil	600gl ⁻¹ 500gl ⁻¹ 200:200gl ⁻¹	18	2.1 l 1 l 1 l	1.26 0.50 0.20
1992	Winter Rape	-	-	-	-	18	-	-
1993	Winter Barley	Stomp I.P.U	Cyanamid (added in same proportions as pendimethalin	pendimethalin isoproturon	236gl ⁻¹ 236gl ⁻¹	18	-	-

Note: Detailed loading data is provided for chlorophenoxy acid, ioxynil and bromoxynil herbicides only

3.3 Drilling Programme

Drilling work in the Chalk was completed using the unsaturated zone core- profiling techniques adopted for Phase I of the sampling programme. A 'U-100' percussion drilling rig contracted from Smith and Webb Drilling Ltd completed the work at Compton and Stapleford. The 'U-100' rig was used to remove samples, using aluminium core barrel liners to the full depth of each borehole. B&B Drilling Ltd were contracted to undertake drilling in the sandstone using an air flush rotary drilling rig as previous experience has shown 'U-100' percussion drilling is not effective in the 'hard' Sherwood Sandstone. Whilst 100% recovery was required in both drilling contracts, despite the use of temporary casing and a variety of catching techniques, the loose sandstone in this area made it extremely difficult to fulfil this specification. However only two samples were completely lost.

The use of drilling muds and water was avoided to prevent contamination of the recovered material. All drilling equipment and casing was steam cleaned prior to commencing drilling work and subsequently between sites. To reduce the risk of cross-contamination as each sample was cored by the drilling rig it was extruded (where necessary) into a double layer of polythene layflat tubing, sealed and frozen on-site. The samples were subsequently transported to the laboratory for analysis by GCMS and immunoassay techniques.

A replicate borehole was drilled approximately two metres from the first at each location to obtain an indication of the variability in the herbicide concentrations with depth. An exception was at AFRC Compton where only one borehole was required to complete the profiling for triazines in chalk.

At each site, after clearance of surface vegetation, the drilling rigs were used to drill and core borehole upto about 10 m from the surface. The topsoil proved to be fairly shallow at all locations (approximately half a metre) before firm chalk or sandstone was reached. All boreholes were subsequently backfilled on completion of the drilling work. The borehole logs for the 1993 drilling programme are presented in Appendix A (Tables A1 to A7). The drilling programme was completed in September 1993.

3.4 Sub-sampling Procedures for GCMS and Immunoassay analysis

3.4.1 Sub-samples for GCMS analysis

Nine sub-samples were taken from each core for GCMS analysis, with the exception of the chalk cored for atrazine analysis from which only six samples were taken (see 3.5.3). The selected sampling frequency was greatest in the top 5 m of each core where it was anticipated higher concentrations of pesticides would be present. Each core was defrosted for 12 hours, then unwrapped and a sample taken from the inner part of the core. Sampling the outer 2 cm of core, which may have become contaminated during the drilling and extrusion procedures, was avoided.

A blank and two spiked samples were included for Quality Assurance/Quality Control purposes for each borehole. Four duplicate samples taken at random from the seven cores under investigation were analysed.

3.4.2 Sub-samples for immunoassay analysis

The cores required for triazine profiling were sub-sampled for GCMS and immunoassay analysis. Whilst the GCMS extraction is undertaken on a sample of the solid aquifer material, immunoassay requires a sample of porewater to be extracted from the core. The porewater was extracted using centrifugation according to sampling protocol WMEC L19 detailed in Appendix B. Sub-samples were taken for spinning at 33 cm intervals (the length of an aluminium liner) from the chalk core. It was possible to sample at more frequent intervals from the sandstone material. The porewater aliquots were refrigerated in sealed amber vials prior to analysis. A selected number of samples were spun in duplicate to check reproducibility of the spinning procedure.

3.5 Analytical Methodology and Results

3.5.1 GCMS methodology for acid herbicides

Analytical method

The chalk and sandstone cores were analysed according to the method described in Forbes *et al.* 1994a. The sandstone results have been corrected for the recoveries obtained and the chalk results have been corrected for both moisture content and recoveries.

GCMS conditions

GCMS analysis was carried out using a Hewlett Packard 5890 GC equipped with a 30 m x 0.32 mm DB-1 fused silica capillary column and a HP 7673 autosampler. The GC was connected to an Ion Trap Mass Spectrometer. The MS was equipped with and Electron Impact (EI) source which was operated in the Mass Ion Detector (MID) positive EI mode at a temperature of 250 °C. The GC oven temperature was 60 °C, held for three minutes and then linearly programmed at 8 °C minute⁻¹ to 300 °C and held for ten minutes. The sample extract volume analysed in each case was 1 µl using a cool on-column injector.

Results

The recoveries obtained for the spiked samples included with each batch were quite consistent and satisfactory, and the mean of the duplicate recoveries were used to calculate the reported concentrations of the acid herbicides and the limits of detection obtained. The quantification ions for mecoprop, dichlorprop and 2,4DB had some interference present in some of the samples and this has led to a slightly higher limit of

detection for these compounds. The results are all corrected for moisture and this accounts for the slight variation in the detection quoted for individual compounds across a depth profile.

3.5.2 GCMS methodology for triazine herbicides

Analytical method

The method was carried out as described in R&D Note 222 (Forbes *et al.* 1993a). All results were corrected for recoveries obtained. No results were corrected for moisture content, results are therefore on wet weight (or as cored) basis.

GCMS conditions

GCMS analysis was carried out using a Hewlett Packard 5890 GC equipped with a 30 m x 0.32 mm DB-1 fused silica capillary column and a HP 7673 autosampler. The GC was connected to a Trio-1 Mass Spectrometer, operated in MID mode with positive EI, at a source temperature of 200 °C. The GC temperature programme was 60 °C, held for three minutes, ramped at 8 °C minute⁻¹ to 300 °C.

Results

There were a large number of interferences present in the chalk aquifer samples and as a result it was only possible to quantify atrazine. Even for these results, the chromatography was poor and quantification is therefore less accurate than it could have been. Low recoveries were obtained for the spiked samples. For some of the samples the internal standard added prior to extraction was not detectable or quantifiable, therefore external standards were used. This has led to increased analytical error. The reported detection limit for this run was <0.06 µg kg⁻¹.

The method proved to be satisfactory for the two sandstone batches. Better chromatography for the first GCMS scan (borehole 1, Appendix C, Table C2) resulted in the slightly better detection limits reported for these samples (trietazine <0.06, simazine <0.04, and atrazine <0.03 µg kg⁻¹).

3.5.3 Immunoassay methodology for triazine herbicides

The study of the unsaturated zone of an aquifer is of particular importance in understanding the movement and fate of pesticides in groundwater. Recently developed GC-MS techniques for analysing solid materials from cores are, however, time-consuming and expensive. Immunoassay represents a quick, sensitive and less expensive analytical technique than more conventional GC methodology although the method has some limitations.

The profiles produced for this study using immunoassay provide a semi-quantitative measure of the concentration of the triazine group of pesticides in the spun porewater from the chalk and sandstone aquifer material. More precise quantification could be achieved if the immunoassay standards were matrix matched with the aquifer porewater, and spiked samples were included to aid quantification of other background interference effects. Results of previous spiking tests (reported in NRA R&D Note 172) indicate recoveries of triazine pesticides using the Guildhay and Millipore kits are of the order of 90% and the coefficient of variation between five replicates less than 5%. This was felt to be an acceptable level of accuracy for this work.

Where suitable kits are available, immunoassay has an important role to play in providing trends of pesticide movement within the porewater in the unsaturated and saturated zones of an aquifer. Results from immunoassay represent pesticide concentrations in the mobile phase and are reported in $\mu\text{g l}^{-1}$. It should be understood that immunoassay techniques can not quantify the amount of a given pesticide which may be adsorbed onto the walls of the voids. In comparison GC-MS methodology, which involves a solvent extraction on a given weight of the matrix material effectively quantifies the sum of pesticides present in the porewater and adsorbed onto the matrix material. Results are therefore reported as $\mu\text{g kg}^{-1}$ of wet or dry chalk/sandstone. Reference to the moisture content of any given sample will allow some comparison between the two methods. Large differences in the results reported from immunoassay and GC-MS for the same sample could be due to a number of reasons:

- immunoassay results may be significantly suppressed by matrix effects of the porewater;
- if a significant percentage of the pesticide is adsorbed onto the solid material as opposed to being present in the porewater phase, this will lead to proportionally higher GC-MS results to those obtained from immunoassay.

Whilst the immunoassay kits used in this study can not distinguish completely between individual triazines, the sensitivity of the kits to particular triazine do vary. They can therefore be used more selectively in conjunction with accurate loading data. For instance, if atrazine is known to be the only triazine herbicide which has been applied to a particular field, results could be reported as $\mu\text{g l}^{-1}$ atrazine, especially if a kit is selected which is particularly sensitive to atrazine rather than a screen for 'total' triazines. The kits will also give positive results for transformation products of that group, however, sensitivity for these breakdown products is usually considerably less than for the parent compound. Positive results can therefore be attributed largely to the pesticide under investigation.

As a result of continued problems with the development of a reproducible GCMS method for triazines in chalk, the NRA agreed that immunoassay should be used to provide the detailed profile information. GCMS would only be used to provide a limited number of confirmatory analyses to corroborate results obtained by immunoassay. The development and validation of this technique for the analysis of porewater from solid aquifer material is described in R&D Note 72 (Clark *et al.* 1992). There are a number of commercial immunoassay kits available for triazine analysis. The herbicide loading record for AFRC

Compton showed atrazine to be the only triazine herbicide applied to the chosen site. On this basis the Guildhay Aquascreen© Atrazine Elisa kit was chosen to analyse the extracted porewater samples. The kit is very specific to atrazine, and has a quoted lower limit of detection for atrazine of $0.006 \mu\text{g l}^{-1}$.

Due to the availability of a suitable commercial kit, the opportunity was taken to supplement the GCMS analyses of the sandstone cores with immunoassay analyses. Although the GCMS method is satisfactory for sandstone material, immunoassay can provide a greater level of detail in a profile than GCMS for a far smaller cost. Immunoassay analysis has the additional benefit of analysing the porewater rather than producing a total extractable herbicide concentration for the given aquifer material. On the other hand, immunoassay does not measure either adsorbed or total pesticide in a sample. Loading data for the site at Bishopfield Farm Serlby indicated the Millipore Enviro-Gard© Kit would be the most suitable to quantify simazine and trietazine concentrations in the sandstone. The lower level of detection for these two compounds are reported as 0.004 and $0.006 \mu\text{g l}^{-1}$ respectively. Results reported for immunoassay will be the sum of the concentrations of these two compounds. The triazine herbicide cyanazine was also applied to the field in 1993 and although the kit has a lower limit of detection of $0.23 \mu\text{g l}^{-1}$ for this particular compound, it is likely that any higher concentrations detected in the top of the core will, to some extent, reflect the presence of this triazine.

Each spun sample was replicated four times and a mean triazine concentration calculated.

3.6 Discussion of Profiling

3.6.1 Triazine Herbicides

The results of the profiling undertaken by GCMS are detailed in Appendix C in Tables C1 to C3. Moisture determinations are reported in Tables C4 to C7. For easy comparison with borehole depth, GCMS and immunoassay results have been appended to the borehole logs where appropriate (see Appendix A). GCMS analysis was undertaken on each core for atrazine, simazine and trietazine. Although loading data for the sandstone cores showed that cyanazine had also been applied in 1993, quantification was not possible since it was not included as part of the original method development suite. Immunoassay analysis was undertaken on the chalk core for atrazine and one of the sandstone cores from Bishopfield Farm for simazine and trietazine.

The borehole at AFRC Compton was sited at the edge of the field which drains excess runoff and field drainage water. It was expected that recharge pathways to the unsaturated zone should be fairly well developed. The analysis by immunoassay of the porewater extracted from the chalk support such a case. The results provide an extremely detailed picture of atrazine migration from the soil surface through the unsaturated zone and into the groundwater (Figure 3.9). The profile represents five years of repetitive atrazine application, during this time the atrazine has moved through 11 metres of relatively unfractured chalk. The loading data are only available for the last five years but it is possible that atrazine may have been applied prior to 1988. This would suggest that discrete peaks of atrazine may have already penetrated the water table. It is interesting to note that despite receiving large quantities of drainage water from the surrounding field

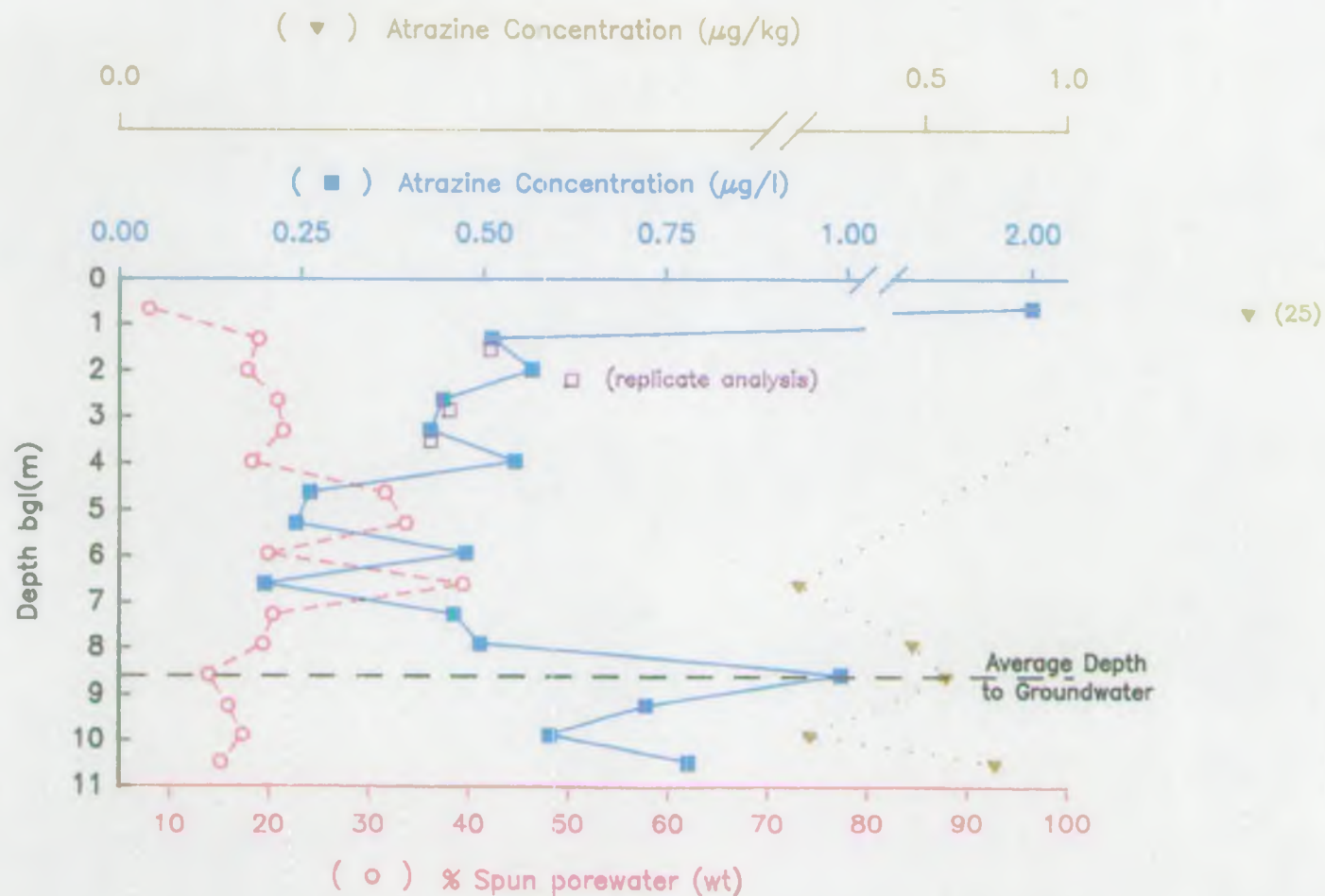


Figure: 3.9 Concentration of atrazine detected by immunoassay ($\mu\text{g}/\text{l}$) and GC-MS ($\mu\text{g}/\text{kg}$) in the chalk at Compton, Berkshire.

atrazine has not been completely leached from the surface and is persisting at levels in excess of $10 \mu\text{g l}^{-1}$ ($25 \mu\text{g kg}^{-1}$). It is likely the atrazine is adsorbed onto organic matter present in the soil horizon. In 1989 and 1990, application rates were double those presently used; the large peaks of atrazine detected near the water table between 8 and 11 metres could well represent the atrazine applied at this time. The data clearly shows that atrazine is persisting in the unsaturated zone and moving through the profile as discrete peaks, adsorption and degradation rates are not sufficient to cause 'smoothing' of the profile. The level of atrazine detected by immunoassay in the top core sample ($>2 \mu\text{g l}^{-1}$) is likely to be considerably higher; the absorbance reading obtained for this sample on the immunoassay plate significantly exceeded that of the $2 \mu\text{g l}^{-1}$ standard. Looking at the result obtained for this sample by GCMS the result is probably nearer $12 \mu\text{g l}^{-1}$. Although the results obtained by GCMS (which represent $\mu\text{g kg}^{-1}$ of solid aquifer material) can not be compared directly with those of immunoassay, the GCMS results mimics the trend of the immunoassay profile (Figures 3.9 and 3.10).

These results show that contamination by pesticides will take place when the pesticides are persistent and applied repeatedly over a period of years. The form of the atrazine profile is reminiscent of those for nitrate under arable land suggesting that the pesticide transport may be by a similar mechanism and at a similar rate to nitrate infiltration.

The GCMS and immunoassay profiles for the sandstone cores from Bishopsfield Farm show a number of positive results for trietazine to the bottom of the borehole (Figures 3.11 and 3.12). No simazine was detected in either of the two cores. This latter may be because simazine was only present in the product applied (Remtal RC) at one-tenth of the quantity of trietazine or it may be it is degraded much quicker than trietazine after application. The limit of detection obtained for the triazine herbicides in sandstone were as follows; atrazine <0.03 ; simazine <0.04 and trietazine $<0.06 \mu\text{g l}^{-1}$ respectively. Significantly higher concentrations of herbicide are detected in the top 0.5 metre of the profile; this duplicates the results obtained for the Chalk. Elevated levels were detected through the full depth of the borehole. Although the concentrations detected by GCMS at similar depths in the two profiles do not correlate exactly despite the fact that they were drilled only a few metres apart, the results obtained from borehole 2 correlate very well with those obtained by immunoassay from borehole 1. The differences between the two cores may reflect lateral inhomogeneity in the sandstone but it is more likely that the results reflect the method of herbicide application. Due to a buried pipe, borehole 2 was sited much closer to the field edge than borehole 1. Visual examination of weed growth through the pea crop during a field visit to the site prior to harvest showed weed growth around the perimeter of the field to be significantly less than that 20 metres in (location of borehole 1). During spraying, turning of the tractor at the field edge will result in a significantly higher loading of herbicide to the margins than the centre of the field. The profiles obtained for the sandstone exhibit less discrete peaks than those obtained for atrazine in chalk, however this could perhaps be expected. The atrazine profile in chalk is a result of repetitive loading of herbicide over a five year period, whereas there is a gap of five years between the two applications of triazines in the sandstone. Although only two applications of triazines have been applied to this field in the past five years, positive detection of trietazine at depth in both would imply that any applications prior to the five years would have moved further down the profile beyond the extent of the present drilling.

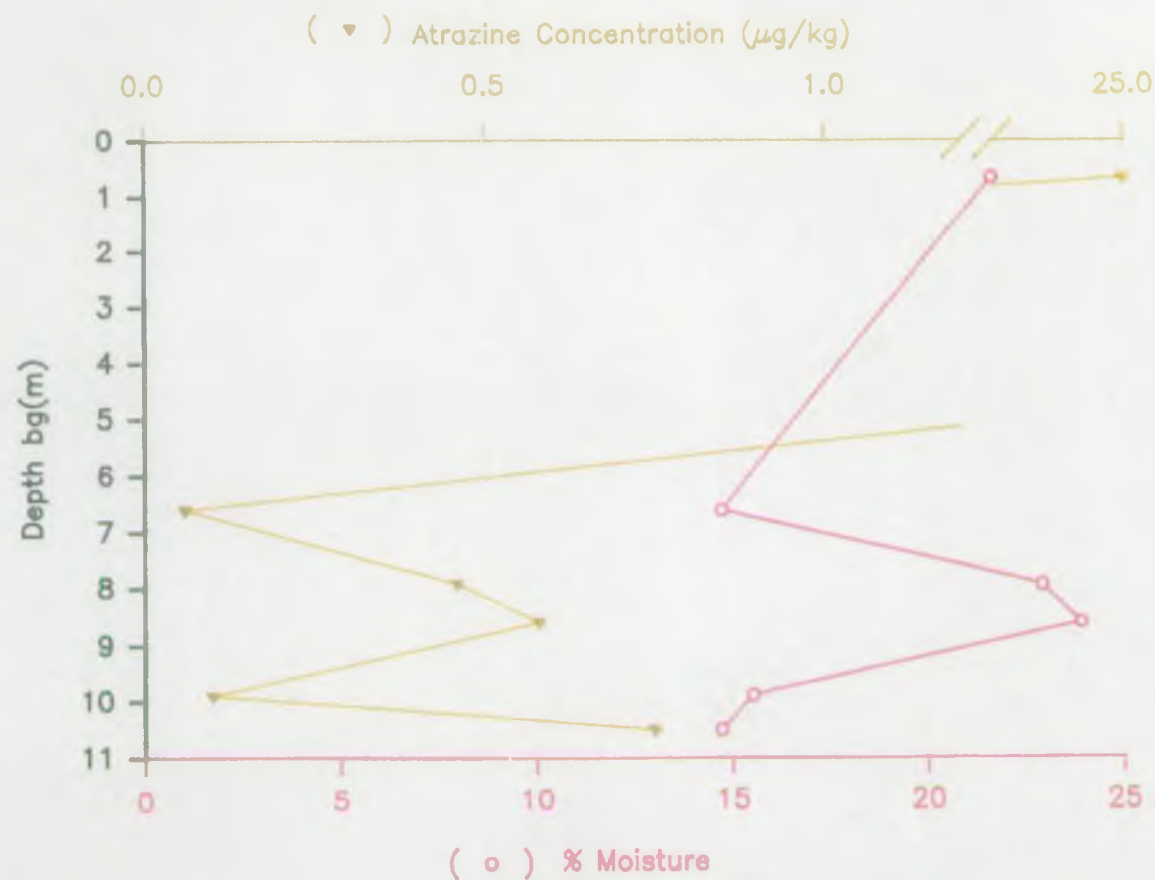
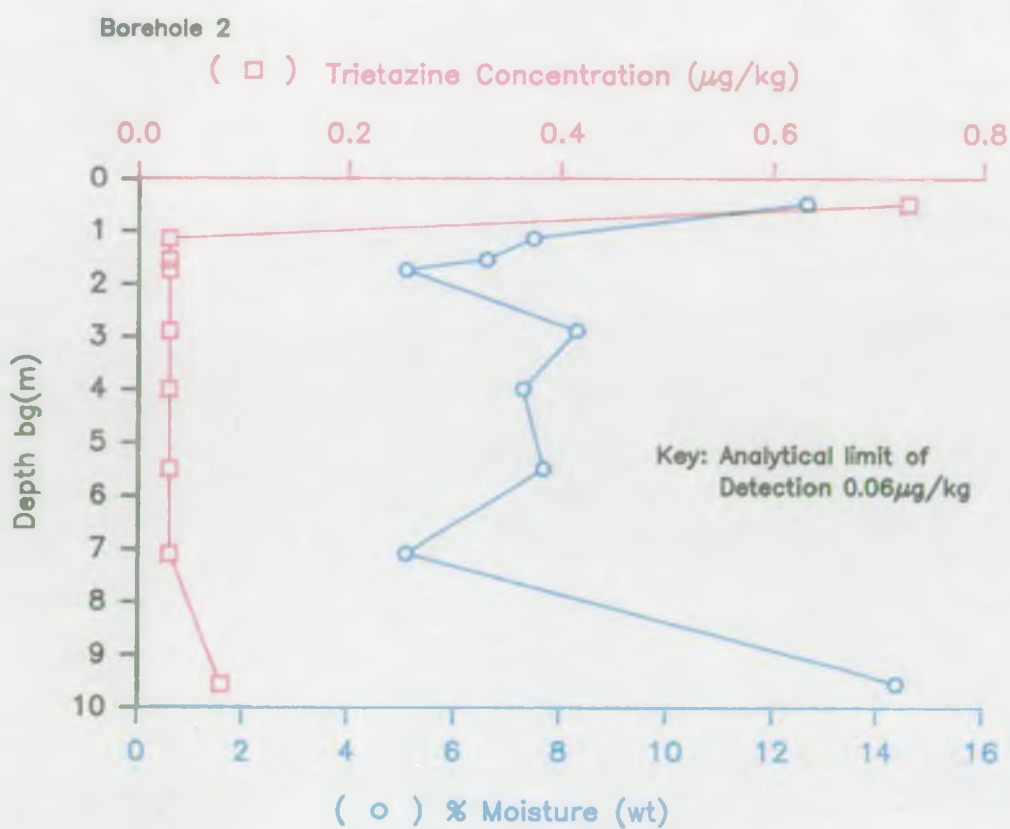
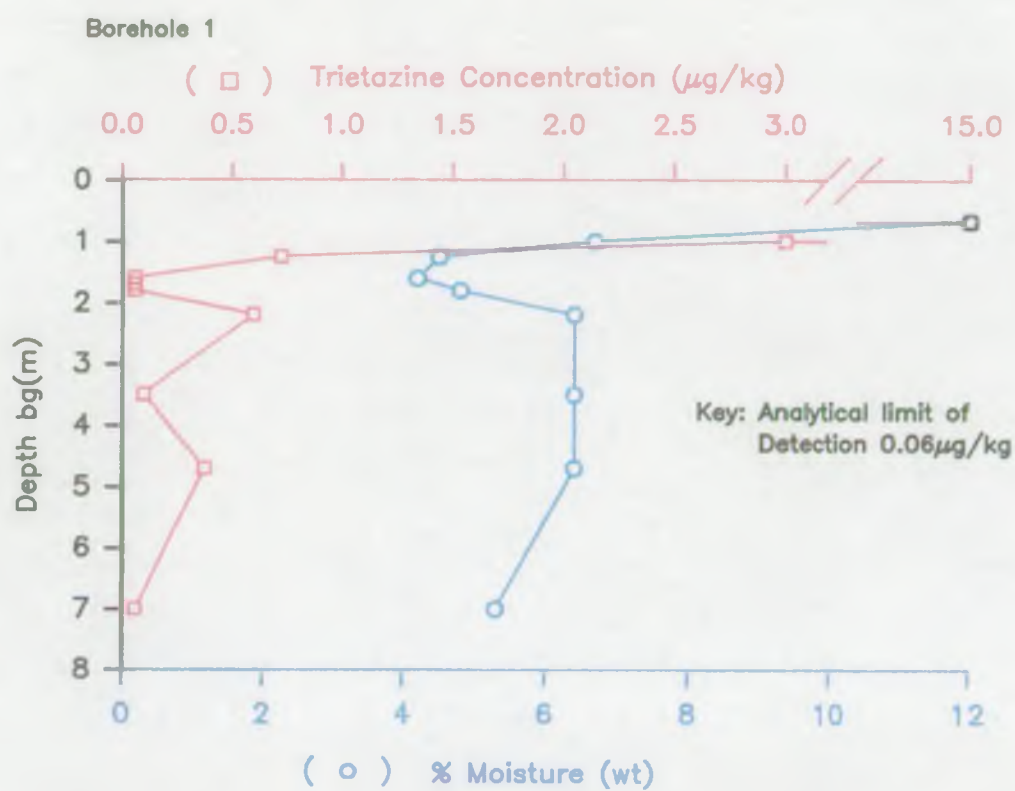


Figure: 3.10 Concentration of atrazine detected by GC-MS in the chalk at Compton, Berkshire.

Figure: 3.11 Concentration of triazine herbicides detected by GC-MS in the sandstone at Bishopfield Farm, Doncaster.



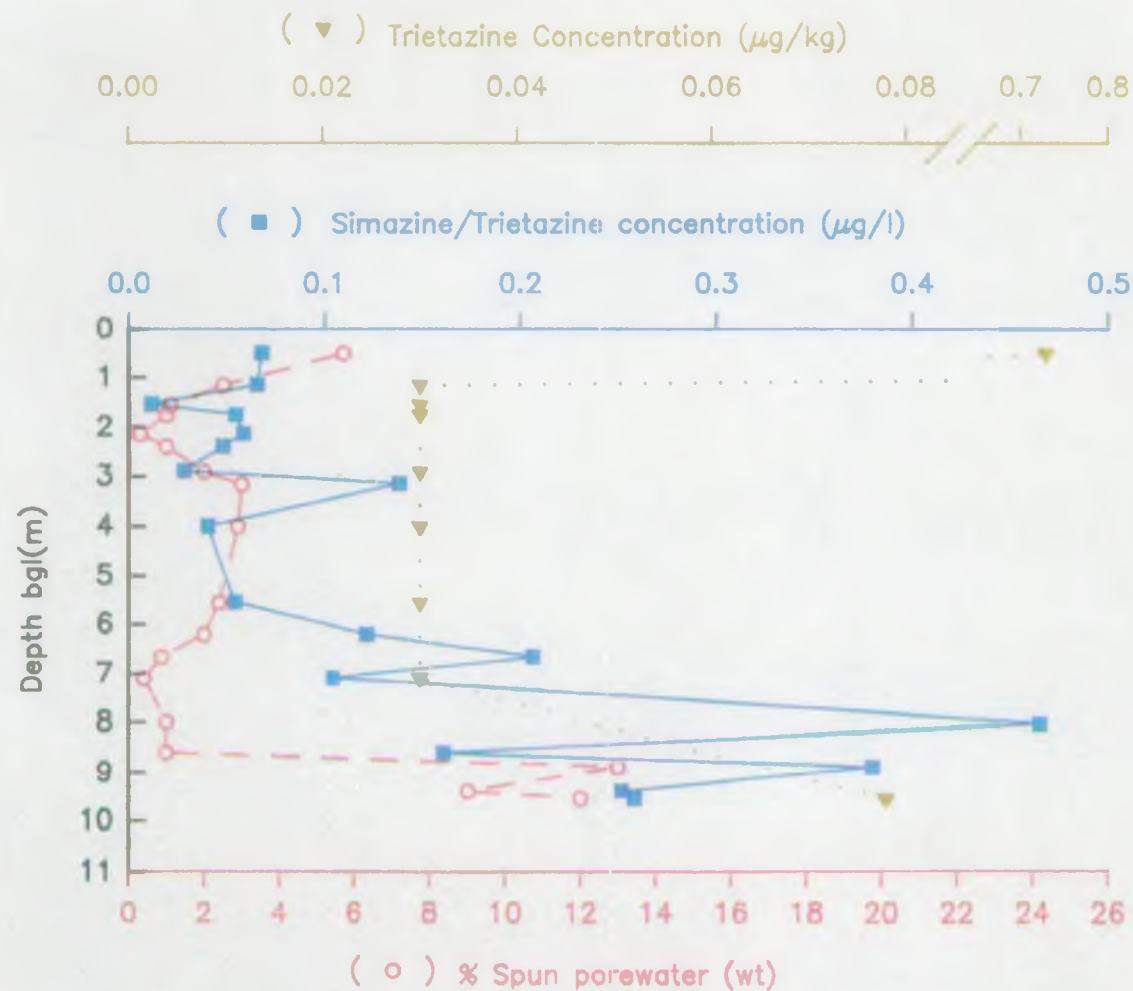


Figure: 3.12 Concentrations of simazine/trietazine detected by immunoassay ($\mu\text{g}/\text{l}$) and trietazine detected by GC-MS ($\mu\text{g}/\text{kg}$) in sandstone at Bishopfield Farm, Borehole 2.

Critical examination of the GCMS scans confirms that the large peak detected at the surface of the two sandstone samples is trietazine (the retention time for the peak in the core sample is identical to that of the standard) as opposed to cyanazine. The results therefore either reflect trietazine impurities in the cyanazine preparation applied in 1993 or show trietazine is persisting (associated with clays and organic matter) in the soil horizon from the application five years previously.

Triazine herbicides are increasingly detected in groundwaters around the UK. The results from the profiling work for both sandstone and chalk aquifers corroborate the theory that triazine herbicides are sufficiently persistent to migrate through a considerable thickness of unsaturated zone through the intergranular pore spaces to the water table and enter the groundwater. Degradation is sufficiently slow that applications can be mapped as distinct pulses of product moving down the profile. As reported previously (Gomme 1991) it is suggested that the discrete peaks are a result of concentration of these herbicides through adsorption onto organic matter in the microfissures.

3.6.2 Acid herbicides

The results of the profiling undertaken by GCMS are detailed in Appendix C in Tables C8 to C11. Moisture determinations on the selected samples are reported Tables C12 to C17. For easy comparison with borehole depth GCMS and immunoassay results have been appended to the borehole logs where appropriate (see Appendix A).

Each core was analysed for the following acid herbicides: mecoprop; MCPA; ioxynil; bromoxynil; dichlorprop; 2,4-D and 2,4-DB, of these the first four active ingredients been applied in successive cropping seasons at both the chalk and sandstone field sites.

Detection limits achieved for the analytical run were less than $0.1 \mu\text{g kg}^{-1}$ with the exception of ioxynil ($0.11 \mu\text{g kg}^{-1}$). As may be seen from Tables C8 and C9 no positive results were obtained for any of the acid herbicides in the samples taken from the Chalk Aquifer at Green Hedge Farm, Stapleford in either of the two profiles under examination. It is unlikely that the lack of detectable herbicides are a result of problems with the analytical method. Although recoveries obtained for the spiked chalk samples for ioxynil and bromoxynil were less than 50 percent, the recovery for MCPA was over 50 percent and the mecoprop recoveries were very good (95-117%). It is therefore likely that if mecoprop were present it would have been detected.

Although it is perhaps surprising that mecoprop was not detected even at the bottom of the profile, the profiling results confirm the findings of the groundwater survey undertaken by Gomme *et al.* (1992). The survey found that despite mecoprop being the second most widely used pesticide in the Granta catchment it was not detected in the groundwater at levels greater than the quantification limit of $<0.03 \mu\text{g l}^{-1}$.

The GUS index (Groundwater Ubiquity Score) as used by Gustafson (1989) is a simple method of assessing the leaching potential of a pesticide using the soil half-life and soil organic carbon partition coefficient (K_{oc}) of the pesticide. A pesticide with a short half-life is readily biodegraded in the soil horizon, whilst a low K_{oc} indicates a low affinity to adsorb onto soil particles, i.e. a high affinity for water. Table 3.6 presents $t_{1/2}$, K_{oc} and the GUS index for mecoprop, MCPA, ioxynil and bromoxynil. The GUS Index values for these particular pesticides show that with the exception of bromoxynil they would all be

expected to leach fairly readily through the soil profile. Mecoprop is on the borderline between a Transitional Leacher and Probable Leacher. The high water solubility of mecoprop (400-600 g l⁻¹), the fact that it is present in water almost entirely as the carboxylic anion, i.e it is highly hydrophilic, and low K_{oc} mean it is highly mobile in the soil horizon.

Table 3.6 Selected physico-chemical properties of mecoprop, MCPA, ioxynil and bromoxynil

Pesticides	t _{1/2} (days)	K _{oc} (ml g ⁻¹)	GUS Index	GUS Classification
mecoprop	28	127	2.74	TL
MCPA	15	58	2.63	TL
ioxynil	10	200.6	1.70	TL
bromoxynil	0.6	170	-0.79	IL

Key:

GUS Index	GUS classification
<1.8	Improbable leacher (IL)
1.8-2.8	Transition leacher (TL)
>2.8	Probable leacher (PL)

(After Fielding *et al.* 1992)

The results obtained in the profiling work have important implications for the persistence of these herbicides within the soil and unsaturated zone. Despite six years repetitive application of mecoprop and five years of ioxynil and bromoxynil respectively, no detectable accumulation in the profile under examination has occurred. The explanation of these results is probably due to a combination of scenarios:

1. Following application in the previous spring mecoprop, MCPA, ioxynil and bromoxynil have all been completely biodegraded. This is not unrealistic since these particular acid herbicides all have relatively short half-lives (28, 15, 10 and 0.6 days respectively). Although acid herbicides do not adsorb to soil particles, the organic rich soil present at the site is likely to promote a highly active microbial population. Repeat applications of the same herbicide in successive cropping seasons will also promote rapid biological degradation.
2. The herbicides in question have been completely leached from the sample profile. Again this is not unreasonable in a well-fissured chalk aquifer but does contrast with the gradual movement shown by atrazine (Figure 3.9).

These results for acid herbicides in Chalk are in contrast to those for triazines. The persistent triazines clearly contaminate groundwater but the degradable acid herbicides, under normal usage, appear to degrade in the first few metres of percolation and present little or no threat to groundwater.

The GCMS results for the sandstone profiles (Tables C10 and C11, Figure 3.13) achieved comparable limits of detection to those obtained for the chalk samples. The analyses of the nine samples from each borehole have detected no MCPA, ioxynil and bromoxynil after four years of repetitive use, these results are comparable to the picture from the chalk profiling work. The exception is mecoprop which appears to be persisting and migrating into the unsaturated zone through the shallow sandy soil horizon (approximately 60 cm). Mecoprop was detected at levels of 1 - 2.5 $\mu\text{g kg}^{-1}$ in the top 2 metres of both profiles, the levels show a reduction between 2 - 4 metres depth. No mecoprop was detected below 4 metres, and an examination of the borehole logs shows this coincides with the change in the profile from soft to hard, compact sandstone. From these results it would appear mecoprop is not penetrating the intergranular matrix, and it may be that the hard sandstone effectively acts as a barrier to leaching and provides further scope for degradation processes to be completed. This is to some extent supported by the sandstone profiles which show a significant reduction in mecoprop concentration between 1 - 4 metres. It is known that the rate of mecoprop biodegradation in soil is similar to the rate in water.

The sandstone profile shows that mecoprop is persistent and, although restricted to the upper 4 m in this profile, has a potential to pollute groundwater.

The differences between the chalk and sandstone systems are difficult to explain bearing in mind the frequency, and loading rates of active ingredient for the two aquifers are very similar. The heavier dark-coloured soil associated with chalk in this field study are likely to be richer in organic matter than a light sandy soil. It is known that organic matter and oxygen promote a richer bacterial population, increased rates of degradation and promote a higher active microbial population. It is likely that the absence of mecoprop detected in the chalk is due to a combination of significant degradation in the soil horizon coupled with leaching from the profile. If acid herbicides are applied to a chalk aquifer during periods when fissure flow is active, the hydrophilic properties of these herbicides would make it likely that they are leached through the profile very quickly, before significant penetration of the intergranular matrix occurs. It is perhaps important that if additional profiling is undertaken in the future it is timed to coincide more closely with application and the first significant rainfall event, so that these mechanisms can be further quantified.

Soil studies at Assarts Farm have shown low organic carbon content (0.39-1.01%, average 0.53%) and acid to neutral pH (4.8-7.0). The persistence of mecoprop in the sandstone may be due to the change from loose to compact sandstone acting as an effective retainer for biological degradation, since in a light sandy soil acid herbicides would be expected to be quickly leached from the soil horizon through the unsaturated zone, where degradation proceeds at a slower rate. The persistence of mecoprop in the sandstone profiles may be due to a reduced rate of biological degradation in the light organic free soils.

3.6.3 Herbicide transport

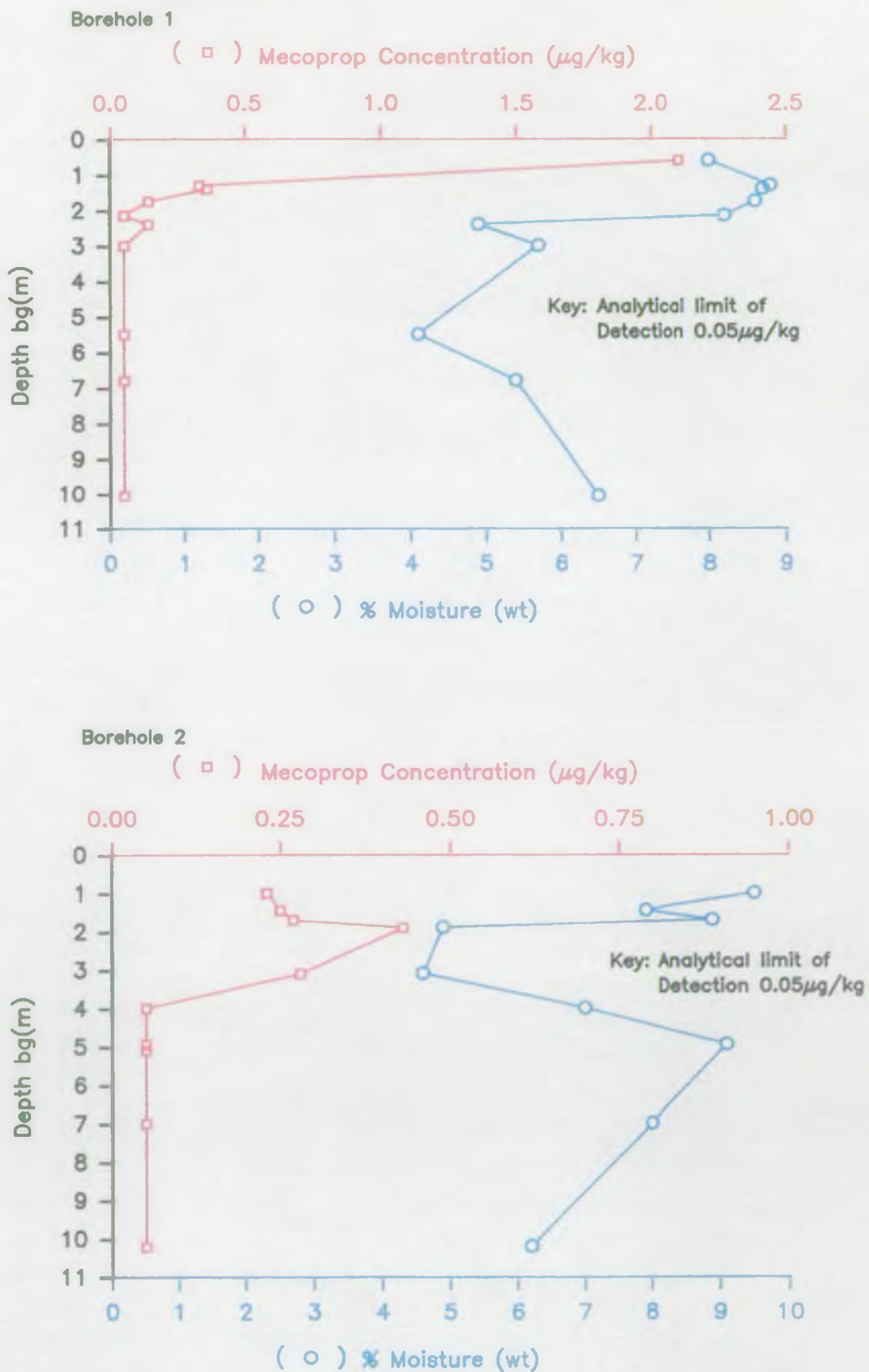
The profiling results combined with the results from earlier monitoring studies have given valuable indications of the herbicide transport mechanisms in the soil and unsaturated zone of aquifers:

- The urons, carbamates and acid herbicides tend to be degraded within a few metres of the surface and present little threat to groundwater under ordinary agricultural practice.
- The profiles of triazines show that these pesticides are persistent and present a threat to groundwater quality. A similarity in form with profiles of nitrate in the unsaturated zone suggests that the transport of pesticides may be similar to that of nitrate, i.e. by slow intergranular movement through the matrix except for that proportion carried by fast by-pass routes via fissures. This slow transport gives time for the total degradation of the more unstable pesticides but the by-pass systems allows contamination of groundwater to take place by almost any pesticide.
- The by-pass systems of fissure or karstic flow have been demonstrated in the Granta by borehole logging (Clark *et al.* 1992, p13). The variability of the fissure development in the Chalk and the rainfall intensity needed to activate the fissure systems means that the vulnerability of the aquifer is variable on a regional and local scale. The pollution potential at any site will depend on:

The pesticide loading rate;
The length of pesticide loading (multiple applications);
Time of pesticide application;
The rainfall intensity and pattern;
The fissure development in the aquifer;
Surface hydraulic features (drainage features).

All those factors tending to increase the loading at a point, or those factors tending to activate fast drainage through fissures will increase the potential for pesticide pollution.

Figure: 3.13 Concentration of phenoxyacid herbicides detected in the core profiles by GC-MS in the sandstone at Assarts Farm, Nottingham.



4. MODELLING

A model of pesticide transport through the groundwater system of the Granta catchment was constructed in Phase 1 of the project (Clark *et al.* 1992). This model was reasonably successful in simulating the pesticide concentrations observed in the groundwater but it was recognised that, to make a more robust catchment model, more data on the application of pesticides and their behaviour in the subsurface would be required.

The opportunity has been taken in Phase 2 of the project to review the whole field of pesticide transport modelling. Existing models were reviewed and the views of officers of the NRA were solicited on the need for modelling and the types of models required to fulfil the NRA's statutory duties. The modelling review is described in an R&D Note. The conclusions of the review are the following:

1. Two types of groundwater pesticide model have been identified, a screening model for the general assessment of new (or existing) chemicals in relation to risk to groundwater, and a detailed catchment based model for predicting likely time trends and the effects of aquifer management policies. Both models would require soil and aquifer components as well as appropriate meteorological data and physico chemical properties of the pesticides.
2. Hydrogeologists and water quality officers in the NRA Regional Offices see a need for such models, with an immediate requirement for an effective screening tool for groundwater. The main reason for this is that while pesticide detections in groundwater are commonly infrequent, usage patterns are changing and new products are coming onto the market. Usage of some potentially problematical compounds, such as Bentazone and Fluroxypyr, appears to be increasing. In addition, determinations are usually restricted to a selected suite of pesticides so that exceedances by other compounds may go undetected. A versatile, well tested screening model would allow the NRA to assess rapidly the likely impact of existing or new chemicals. As well as assisting in risk assessments, such models would also help to guide monitoring and analytical programmes.

The view was also expressed by some NRA staff that pesticides in surface waters were of equal concern, and an appropriate screening tool would be valuable for these conditions.

Detailed catchment simulation was considered to be a longer term requirement, and could logically follow on from the development of a screening model. The catchment model will be needed to test control policies, such as protection zones. A very large database will be required for catchment scale simulation, and staff in the NRA saw this as likely to restrict rapid development of catchment models.

3. Numerous models which simulate pesticide leaching to groundwater already exist. The models generally comprise four components: a water flow model, a soil model, an unsaturated zone model and a saturated zone model. Many of the existing models derive from the US-EPA and are not well suited to the hydrogeological conditions found in the UK. In particular, the treatment of fissure flow is considered to be of

fundamental importance in UK aquifer contaminant studies, but not in the US. Some of the existing models are essentially screening tools, for example the Jury Focht and Farmer model, and are quick and easy to run. The catchment scale models are sophisticated and require considerable user expertise. With a relatively modest amount of development suitable screening and catchment models could be developed from what already exists.

4. An extensive database is required for the routine operation of pesticide models. Some of the data already exists though in a limited form. Data sets for the physico chemical properties of pesticides, generally comprising soil organic carbon partition coefficients and biochemical decay rates, are available from a number of sources. However, there is often a significant spread in the values reported for a single pesticide, with consequent uncertainty in model predictions. For example, soil half lives for Isoproturon reported in the literature vary from 20 days to 130 days. Application to a screening model for a Chalk aquifer gave a corresponding variation from 18% to 99% as the predicted percentage of time groundwater concentrations exceeded $0.1 \mu\text{g l}^{-1}$. Data on aquifer properties is expected to be less problematical, with the exception of biochemical decay rates which are almost completely lacking. Equivalent data for the overlying soils are available in various publications. The production in 1994 by the Soil Survey and Land Research Centre of the SEISMIC database, containing soils and meteorological data for England and Wales, will greatly facilitate the provision of information for catchment modelling.
5. Geographic Information System (GIS) technology provides a convenient way of assembling land use, meteorological and soils data for use in groundwater pesticide models. SEISMIC is a relational database having much of the functionality of a GIS and fulfils the need for soil and meteorological data. Up to date information on cropping and pesticide use could also be assembled in a GIS to provide necessary data for modelling. This route has already been followed for nitrate modelling in connection with predicting the impact of the Nitrate Sensitive Areas pilot scheme. The inclusion of non-agricultural usage of pesticides within a GIS database is more problematical. Total amounts used can be estimated by a survey of major users, and broad details of geographical applications and timing may be inferred for each user, though it is difficult to do this with any great certainty.

The overall objective is to produce a pesticide information and risk assessment tool expert system (PIRATE System) for use by NRA Head Office and Regional Headquarters staff, providing outputs for monitoring and analysis guidance and strategy support. The system would facilitate inter-catchment analyses and delineation of high risk areas, identification of changes in pesticide usage through time, presentation and interpretation of measured concentrations in water, predictions of expected concentrations and associated variability and targeting of particularly problematical chemicals.

5. CONCLUSIONS

The conclusions related to Phase 2 of the 'Pesticides in Major Aquifers' project are:

1. **ANALYTICAL DEVELOPMENT;** Analytical methods for acid herbicides in sandstone and chalk have been developed successfully. The development of a similar method for triazines in chalk has been less successful. The NRA now have R&D Notes to SCA format for the following methods:

Triazines in sandstone

Acid herbicides in sandstone and chalk

Urons and carbamates in sandstone and chalk

Immunoassay analysis of triazines in chalk and sandstone has proved very successful.

2. **PROFILING:** Profiles of the triazines, urons, carbamates and acid herbicides have been completed in Chalk and Sandstone Aquifers. From the rather limited information available the profiles suggest that, under normal agricultural conditions, the urons and carbamates do not penetrate more than a few metres from the surface in either sandstone or chalk and therefore, present little risk to the groundwater quality.

The profiles of triazines show that these pesticides are a potential threat to groundwater in those areas where they are repeatedly applied over a period of several years. This is because of their persistence. The atrazine profile (Figure 3.9) has a peaky shape similar to nitrate profiles. This suggests that each peak corresponds to a pesticide application and the peak distribution shows downward migration of the atrazine. The peak also suggest that, in this case, there has been little adsorption or degradation of the pesticide. The danger of groundwater pollution from the atrazine increases in drainage areas where the hydraulic loading is high and pesticide leaching and movement are increased.

The profiling and other studies of the occurrence of acid herbicides suggest that these herbicides, specifically mecoprop, are persistent in sandstone but not in chalk. There is little direct evidence that these pesticides, despite their persistence, penetrate more than a few metres into the unsaturated zone of either sandstone or chalk. The reason for the lack of acid herbicides below 4 m could be due to rapid, total degradation or, less likely, due to flushing of the pesticides from the unsaturated zone. Given the difficulty of flushing impurities from an aquifer matrix and the demonstrated occurrence of triazines in similar circumstances, the flushing of acid herbicides is considered unlikely.

The acid herbicides, therefore, are believed to be degraded and represent little threat to the groundwater quality under normal agricultural usages.

Profiling to date is minimal and more profiles are needed to clarify these questions on pesticide transport.

3. **MODELLING:** Two types of model were identified, a screening and a detailed catchment model. A screening model is urgently needed by the NRA to assess the likely risks from existing and new pesticides. Such a model could be developed from existing software. A similar modelling approach is needed for surface waters. Catchment models were seen as longer term requirements. Extensive databases on soils, aquifers and pesticide properties will be required, but the use of GIS technology and available databases such as the SSIRC SEISMIC base mean that models could be produced with a modest development. The overall aim should be to produce a pesticide information and risk assessment tool expert system (PIRATE System) for use by NRA Head Office and Regional Headquarters staff, providing outputs for monitoring and analysis guidance and strategy support.

6. RECOMMENDATIONS

The present phase of the work has completed the 'Pesticides in Major Aquifers' project. The recommendations arising from the whole project are given in the NRA R&D Report accompanying this report. The following recommendations arise solely from Phase 2 of the project.

1. **ANALYTICAL DEVELOPMENT;** The HPLC-MS analytical method for the triazine herbicides in chalk should be progressed to prove whether or not it can be used to achieve the desired low detection limits.

Immunoassay methods for the analysis of pesticides in aquifer materials should be developed for pesticides other than the triazines. Priority should be given to isoproturon, mecoprop and bentazone.

2. **PROFILING;** Although the few profiles completed present a consistent picture of pesticide transport in the subsurface, more profiles are needed to increase knowledge of pesticide movement in the unsaturated zone and ensure that the database is consolidated and is statistically valid for application to models.

The fate of pesticides in the subsurface is very uncertain. Studies of the attenuation of pesticides in the subsurface **under field conditions** should be undertaken to provide realistic half lives of pesticides for use in models.

3. **MODELLING;** It is recommended that screening models for groundwater and for surface water be developed as a matter of urgency using, where appropriate, existing software and databases. The screening models should be based on suitable existing models. For groundwaters, particular attention will need to be given to the representation of fissure flows in the conceptual model. Land use and pesticide application data will be needed for modelling, and the use of GIS for this purpose should be investigated. The SEISMIC relational database could be incorporated to provide soils information for the model, and this possibility should be explored. The aim of the modelling should be to produce a PIRATE system for monitoring and analysis guidance and strategy support for NRA Head Office and Regional staff. A comprehensive database of pesticide physico chemical properties should be assembled; this will be needed for any risk assessment study whether or not detailed models are developed. This will provide the main method of validating and refining the databases used for model operation. For this purpose data on pesticides in groundwater should be carefully collected and collated. The occurrence in groundwater of new chemicals and banned products, such as atrazine and simazine, will be particularly useful in this regard. A catchment scale model should be developed in the longer term, building on the validated screening model and associated databases. Previous work on nitrate modelling at the catchment scale would form a useful basis.

REFERENCES

- Cable, C.J., Fielding, M., Gibby, S., Hegarty, B.F., Moore, K.M., Oakes, D.B. and Watts, C.D. (1993) Pesticides in Drinking Water Sources and Supplies (DWE 9004). WRc. August 1993. Final Report to the Department of the Environment. DoE. 3376/1.
- Chilton, P.J., Stuart, M.E., Gardner, S.J., Hughes, C.D., Jones, H.K., West, J.M., Nicholson, R.A., Barker, J.A., Bridge, L.R. and Goody, D.C. (1993) Diffuse Pollution from Land-use Practices. British Geological Survey. Hydrogeology Group. May 1993. Draft Final Report. R&D 113/9/ST to National Rivers Authority.
- Clark, L., Gomme, J., Oakes, D.B., Slade, S., Fielding, M., Moore, K., Taylor, L. and Shurvell, S. (1992) Pesticides in Major Aquifers. WRc plc. R&D Note 72 to National Rivers Authority.
- Fielding, M., Barcelo, D., Helweg, A., Galassi, S., Torstenffon, L., Van Zoonen, P., Wolter, R. and Angeletti, G. (1992) Pesticides in Ground and Drinking Water. Commission of the European Community. Water Pollution Research Report 27. Published E Guyot Brussels.
- Forbes, K., Moore, K. and Norris, M.W. (1993) Analytical Method for the Determination of Uron and Carbamate Pesticides in Sandstone and Chalk Aquifer Materials. WRc plc. R&D Note 223 to National Rivers Authority.
- Forbes, K., Moore, K. and Norris, M.W. (1993a) Analytical Method for the Determination of Triazine Pesticides in Sandstone Aquifer Materials. WRc plc. R&D Note 222 to National Rivers Authority.
- Forbes, K., Hegarty, B., Norris, M., Pattison, S. and Wilson, I. (1994) Determination of Triazine Herbicides in Chalk Aquifer Materials. WRc plc. R&D Note 439/8/A to National Rivers Authority.
- Forbes, K., Hegarty, B., Shurvell, S. and Norris, M. (1994A) Analytical Method for the Determination of Acid Herbicides in Sandstone and Chalk Aquifer Materials. WRc plc. R&D Note 439/9/A to National Rivers Authority.
- Gustafson, D.I. (1989) Groundwater Ubiquity Scale: A Simple Method for Assessing Pesticide Leachability. *Environmental Toxicology and Chemistry*, 8, 339-357, 1989.
- Shurvell, S., Kanda, R. and Hennings, S. (1993) Multi-residue Method for the Analysis of Twenty Pesticides in Rainwater, Groundwater and River Water. WRc plc. R&D Note 231 to National Rivers Authority.

Core No.	Depth/m	Description of Sample	Sub-sample taken for analysis	percentage spun porewater (by weight)	Concentration of atrazine detected by immunoassay	GC-MS (mg/kg ⁻¹) Atrazine
1	0.00-0.66	Grey/brown clay & flints to 1m	I, GC-MS	3	>2.0	25
2	0.66-1.32	Flints with chalk from 1m	I	4	.51, .51	
3	1.32-1.98	Flints with chalk	I	1, 1	.57, .62	
4	1.98-2.64	Chalk (soft with occ. flints)	I	8	.44, .45	
5	2.64-3.30	Chalk (soft with occ. flints)	I	12	.43, .43	
6	3.30-3.96	Chalk - specs of yellow	I	11	.54	
7	3.96-4.62	Chalk (soft with occ. flints)	I	11	.26	
8	4.62-5.28	Chalk (soft with occ. flints)	I	12	.4	
9	5.28-5.94	Chalk - getting wet	I	18	.47	
10	5.94-6.60	Chalk (flints) - grey, bit wet	I, GC-MS	15	.20	0.06
11	6.60-7.26	Chalk - grey and moist	I	15	.46	
12	7.26-7.92	Chalk - grey and moist	I	15	.50	
13	7.92-8.58	Chalk (soft with occ. flints)	I, GC-MS	18	.99	0.46, 0.58
14	8.58-9.24	Chalk (soft with occ. flints) WET	I	15	.72	
15	9.24-9.90	Chalk (soft with occ. flints) RWL	I, GC-MS	17, 15	.59	0.10
16	9.90-10.56	Chalk (soft with occ. flints)	I, GC-MS	15	.78	0.75
		BOREHOLE COMPLETE				

Note: Rest water level dipped at 8.70m on 7/9/93

Key:

I = Immunoassay - results reported in $\mu\text{g/l}^{-1}$ chalk porewater

Bolded immunoassay results represent replicate analyses

Table A1: Borehole logs at AFRC, Compton, Berkshire, Borehole 1.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis	GC-MS (mgkg ⁻¹) Simazine	GC-MS (mgkg ⁻¹) Trietazine
1	0.00-0.50	Sand, top soil/boulder clay	GC-MS	<0.04	15
2	0.50-1.00	Loose sand	GC-MS	<0.04	3
3	1.00-1.25	Loose sand	GC-MS	<0.04	0.73
4	1.25-1.60	Loose sand	GC-MS	<0.04, <0.04	<0.06
5	1.60-1.80	Loose sand	GC-MS	<0.04	<0.06
6	1.80-2.20	Loose sand & thin gravel bands	GC-MS	<0.04	0.60
7	2.20-2.50	Loose sand & thin gravel bands			
8	2.50-2.80	Loose sand			
9	2.80-3.00	Loose sand			
10	3.00-3.50	Compact sand SF plastic liner	GC-MS	<0.04	0.10
11	3.50-4.50	Compact sand			
12	4.50-4.70	Compact sand	GC-MS	<0.04	0.38
13	4.70-5.00	No recovery			
14	5.00-6.00	Compact sand			
15	6.00-6.75	No recovery			
		ABANDONED AT 6.0m			
B1A	0.00-5.75	No samples taken - sand & gravel			
1	5.75-6.25	Compact sand			
2	6.25-7.00	Compact sand	GC-MS	<0.04	<0.06
		ABANDONED at 7.0m			

Table A2: Borehole logs at Bishops Field Farm, Serlby, Doncaster, Boreholes 1 & 1A.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis	percentage spun porewater (by weight)	Concentration simazine/trietazine detected by Immunoassay ($\mu\text{g l}^{-1}$)	GC-MS (mg kg^{-1}) Simazine	GC-MS (mg kg^{-1}) Trietazine
1	0.00-0.50	Top soil, loose sand & clay	GC-MS, I	5.7, 6.0	.067	<0.02	0.73
2	0.50-1.15	Loose sand	GC-MS, I	2.5	.07	<0.02	<0.03
3	1.15-1.55	Loose sand	GC-MS, I	1.1	.01	<0.02	<0.03
4	1.55-1.75	Loose sand	GC-MS, I	1.0	.05	<0.02	<0.03
5	1.75-2.15	Compact sand	I	0.3, 0.2	.06		
6	2.15-2.40	Compact sand with gravel	I	1.0	.05		
7	2.40-2.90	Compact sand with gravel	GC-MS, I	2.0	.03	<0.02	<0.03
8	2.90-3.15	Compact sand	I	3.0	.14		
9	3.15-4.00	Sand	GC-MS, I	2.9, 2.8	.04	<0.02	<0.03
10	4.00-5.00	V soft sand - no recovery	I	no sample	no sample		
11	5.00-5.50	Sandstone	GC-MS, I	2.4, 2.7	.05	<0.02	<0.03
12	5.50-6.20	Sandstone	I	2.0, 2.0	.12		
13	6.20-6.65	Compact sand	I	0.8, 1.8	.20		
14	6.65-7.10	Compact sand	GC-MS, I	0.4, 0.6	.10	<0.02	<0.03
15	7.10-7.50	V soft sand - no recovery	I	no sample	no sample		
16	7.50-8.00	Gravel	I	1.0, 1.0	.47		
17	8.00-8.60	Compact sand	I	1.0	.16		
18	8.60-8.90	Compact sand, WET sample	I	13	.38		
19	8.90-9.40	Soft sand, WET sample	I	9	.25		
20	9.40-9.55	Sand, WET sample	GC-MS, I	12	.26	<0.02	0.078
21	9.55-10.0	Soft sand, Wet, No sample	I	no sample	no sample		
		BOREHOLE COMPLETE					

Key :

I = Immunoassay results reported in $\mu\text{g l}^{-1}$ in spun porewater

Table A3: Borehole logs at Bishops Field Farm, Serlby, Doncaster, Borehole 2.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis
1	0.00-0.66	Grey clay & stones, chalk at 0.6m	GC-MS
2	0.66-1.32	Chalk - firm & light grey	GC-MS
3	1.32-1.98	Chalk - firm & light grey	GC-MS
4	1.98-2.64	Chalk - firm & light grey	GC-MS
5	2.64-3.30	Chalk - firm & light grey	GC-MS
6	3.30-3.96	Chalk - firm & light grey	GC-MS
7	3.96-4.62	Chalk - firm & light grey	
8	4.62-5.28	Chalk - firm & light grey	GC-MS
9	5.28-5.94	Chalk - firm & light grey	
10	5.94-6.60	Chalk - firm & light grey	GC-MS
11	6.60-7.26	Chalk - firm & light grey	
12	7.26-7.92	Chalk - firm & light grey	GC-MS
13	7.92-8.58	Chalk - firm & light grey	
14	8.58-9.24	Chalk - firm & light grey, moist	
15	9.24-9.90	Chalk - firm & light grey, WET	GC-MS
16	9.90-10.56	Chalk - firm & light grey, WET	

Note:

Mecoprop, MCPA, Bromoxynil, and Ioxynil concentrations all less than limit of detection of GC-MS method

Table A4: Borehole logs at Green Hedge Farm, Stapleford, Borehole 1.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis
1	0.00-0.66	Grey clay & stones, chalk at 0.6m	GC-MS
2	0.66-1.32	Chalk - firm & light grey	GC-MS
3	1.32-1.98	Chalk - firm & light grey	GC-MS
4	1.98-2.64	Chalk - firm & light grey	GC-MS
5	2.64-3.30	Chalk - firm & light grey	GC-MS
6	3.30-3.96	Chalk - firm & light grey	GC-MS
7	3.96-4.62	Chalk - firm & light grey	
8	4.62-5.28	Chalk - firm & light grey	GC-MS
9	5.28-5.94	Chalk - firm & light grey	
10	5.94-6.60	Chalk - firm & light grey	
11	6.60-7.26	Chalk - firm & light grey	
12	7.26-7.92	Chalk - firm & light grey	GC-MS
13	7.92-8.58	Chalk - firm & light grey	
14	8.58-9.24	Chalk - firm & light grey, moist	
15	9.24-9.90	Chalk - firm & light grey, WET	GC-MS
16	9.90-10.56	Chalk - firm & light grey, RWL	

Note:

Mecoprop, MCPA, Bromoxynil, and Ioxynil concentrations all less than limit of detection of GC-MS method

Rest water level dipped at 9.1m on 9/9/93

Table A5: Borehole logs at Green Hedge Farm, Stapleford, Borehole 2.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis	GC-MS (mgkg ⁻¹) Mecoprop
1	0.00-0.60	Top soil and loose sand	GC-MS	2.11
2	0.60-1.30	Compact sand	GC-MS	0.33, 0.36
3	1.30-1.75	Compact sand	GC-MS	0.14
4	1.75-2.15	Compact sand	GC-MS	<0.05
5	2.15-2.40	Compact sand	GC-MS	0.14
6	2.40-2.70	Sand and gravel		
7	2.70-3.00	Compact sand	GC-MS	<0.05
8	3.00-3.50	Sand and gravel		
9	3.50-4.00	Compact sand		
10	4.00-4.25	Compact sand		
11	4.25-5.50	Sand	GC-MS	<0.05
12	5.50-6.15	Sand		
13	6.15-6.40	Compact sand		
14	6.40-6.80	Compact sand	GC-MS	<0.05
15	6.80-7.20	Compact sand		
16	7.20-7.55	Compact sand		
17	7.55-7.85	Compact sand		
18	7.85-8.00	Compact sand and gravel		
19	8.00-8.25	Compact sand		
20	8.25-8.50	Compact sand		
21	8.50-8.70	Compact sand		
22	8.70-8.85	Compact sand		
23	8.85-9.10	Compact sand		
24	9.10-9.30	Compact sand		
25	9.30-9.65	Compact sand		
26	9.65-9.90	Compact sand		
27	9.9-10.05	Compact sand	GC-MS	<0.05

Key:

MCPA, Bromoxynil, Dichlorprop, 2,4-D, 2,4-DB, Ioxynil less than limit of detection of GC-MS method

Table A6: Borehole logs at Assarts Farm, Warsop, Nottingham, Borehole 1.

Core No.	Depth/m	Description of Sample	Sub-sample for analysis	GC-MS (mgkg ⁻¹) Mecoprop
1	0.00-1.00	Top soil and sand at base	GC-MS	0.23
2	1.00-1.45	Sand	GC-MS	0.25
3	1.45-1.75	Sand	GC-MS	0.27
4	1.75-1.90	Sand	GC-MS	0.43
5	1.90-2.20	Sand		
6	2.20-2.40	Sand		
7	2.40-2.70	Sand		
8	2.70-2.85	Sand		
9	2.85-3.10	Sand	GC-MS	0.28
10	3.10-3.50	Sand and gravel		
11	3.50-3.80	Compact sand		
12	3.80-4.00	Compact sand	GC-MS	
13	4.00-4.20	Compact sand		
14	4.20-4.40	Compact sand		
15	4.40-4.60	Compact sand		
16	4.60-4.75	Compact sand		
17	4.75-4.95	Compact sand	GC-MS	<0.05, <0.05
18	4.95-5.15	Compact sand		
19	5.15-5.35	Compact sand		
20	5.35-5.65	Compact sand		
21	5.65-5.85	Compact sand		
22	5.85-6.10	Compact sand		
23	6.10-6.40	Compact sand		
24	6.40-6.70	Compact sand		
25	6.70-7.00	Compact sand	GC-MS	<0.05
26	7.00-7.25	Compact sand		
27	7.25-7.60	Compact sand		
28	7.60-7.95	Compact sand and gravel		
29	7.95-8.40	Compact sand		
30	8.40-8.65	Compact sand		
31	8.65-9.00	Compact sand		
32	9.00-9.30	Compact sand		
33	9.30-9.60	Compact sand		
34	9.60-9.90	Compact sand		
35	9.90-10.2	Compact sand	GC-MS	<0.05

Key:

MCPA, Bromoxynil, Dichlorprop, 2,4-D, 2,4-DB, Ioxynil less than limit of detection of GC-MS method

Table A7: Borehole logs at Assarts Farm, Warsop, Nottingham, Borehole 2.

LABORATORY PROTOCOL REF. NO. WMEC L19
Title: Extraction of porewater from core material using centrifugation
Issued by:

Apparatus:

Decon® and methanol for equipment cleaning
 RO water for cleaning and rinsing pots between samples
 250 ml Teflon® pots, lids, stainless steel liners, and Teflon® filter discs
 Glass microfibre filters (5 or 8cms diameter)
 Metal spatula
 Analytical balance (2 decimal place)
 8ml amber glass vials, with black screw caps and Teflon® faced silicone septa (available from Phase Separations Ltd.)

Method:

1. Cores should all be stored at -10°C in the freezer double wrapped in plastic layflat tubing and the ends tied with bags ties to effectively seal the sample. Select the appropriate number of core samples from the freezer and defrost for 12hrs at room temperature, prior to spinning. The maximum number of spins which can be completed in an average working day is 5, therefore 30 cores is the maximum which should be defrosted for any one working day. Once removed from the freezer the samples must be spun on the next day and the extracts stored in a refrigerator.

2. All centrifuge equipment should be soaked in 10% Decon® solution for 24 hours prior to use. When soaking is complete rinse three times in Reverse Osmosis (RO) water. Then rinse once in methanol or acetone, and dry in the warm air cabinet.

Note: When rinsing and drying pots always place on clean tissue or benchcote. Plastic gloves should be worn at all times when handling the samples and equipment.

3. Make-up a table in the laboratory notebook (across a clean double page) with the following headings:
 - o Sample reference;
 - o Pot number (make sure pots are clearly numbered with an indelible marker pen);
 - o Weight of pot (g) = A;
 - o Weight of pot + liner + lid + filter paper (g) = B;
 - o Weight of sample (g) = C - B = D;
 - o Weight of pot + porewater (g) = E;
 - o Weight porewater (g) = E - A = F; note $F \div D \times 100$ = approximate % moisture content (by weight);
 - o Comments.
4. Weigh the pot (A) and record the weight, then weigh the pot + liner + lid + filter paper (B) and record the weight.
5. Select a core for spinning and record the core reference number against the pot weight in the laboratory note book.

The core sample should be labelled 'top and bottom',. When taking a sample for spinning always take the sample from the bottom of the core (the drilling process means the depth of removal can be estimated more accurately for the bottom of the core than the top). Open up the core and using a metal spatula (plastic if sampling for trace metals) sample approximately 200g of material. Discard the material which has been in contact with the wrapping material and take the sample from the centre. If the

aquifer material is very dry first try doing multiple spins to obtain sufficient porewater. If this is unsuccessful add 5mls of RO water prior to spinning. This must be noted down in the 'Comments' column in the laboratory notebook.

Record the total weight of pot + lid + liner + filter paper + sample (C)

6. Place the sample in the stainless steel inserts and then into the Teflon shells. The maximum number of pots per run is six although four or two can be run if there is less than a full batch. However the pots (with liner, sample and lid) must all be balanced to within $\pm 0.1\text{g}$.
7. Spin the pots at a maximum speed of 6000 rev/minute for 30 minutes at a temperature of 4°C .
8. The porewater will drain through the porous insert and collect in the Teflon® /PTFE® shell. Remove inner liner and re-weigh pot and porewater (E). Pour a small amount of the spun porewater into a clean labelled amber glass vial (pre-rinsed in RO water), screw on cap and septa and shake and discard this aliquot. Pour the remaining spun sample into the vial replace lid and septa and at 4°C .
9. After each spin, the set of shells and inserts must be cleaned as in (2) before re-use.

Additional Notes

1. The septa in the amber vials are designed to go with the thin Teflon® (shiny plastic) side towards the sample.
2. Each vial should be labelled using adhesive labels with the following information
 - o sample reference number;
 - o site location;
 - o date of spinning;
 - o name of spinner;
 - o contract number;

APPENDIX C

ANALYTICAL RESULTS

Table C1: Concentration of triazine herbicides detected by GC-MS in the core profiles at AFRC, Compton, Berkshire (Borehole 1)

Project No: 7077
Form No: 1171 **Date Received:** 28/10/93
Analyst: SS **Date Analysed:** 10/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in chalk
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Approx. concentration ug/Kg		
	Simazine	Atrazine	Trietazine
Blank		<0.06	
Spike 0.1ug/kg		<0.06	
Spike 0.1ug/kg		<0.06	
Core 1		25	
Core 10		0.06	
Core 13		0.46	
Core 13 dup		0.58	
Core 15		0.10	
Core 16		0.75	

% Recovery	Simazine	Atrazine	Trietazine
Spike 1		32%	
Spike 2		55%	

NOTES:

**Table: C2 Concentration of triazine herbicides detected by GC-MS
in the core profiles at Bishopfield Farm, Doncaster
(borehole 1 & 1A)**

Project No: 7077
Form No: 1171 **Date Received:** 28/10/93
Analyst: SS **Date Analysed:** 16/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Sandstone - Borehole 1
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg		
	Simazine	Atrazine	Trietazine
Blank	<0.04	<0.03	<0.06
Spike 0.1ug/kg	0.025	0.037	0.033
Spike 0.1ug/kg	0.085	0.066	0.03
Core 1	<0.04	<0.03	15
Core 2	<0.04	<0.03	3.0
Core 2B1A	<0.04	<0.03	<0.06
Core 3	<0.04	<0.03	0.73
Core 4	<0.04	<0.03	<0.06
Core 4 dup	<0.04	<0.03	<0.06
Core 5	<0.04	<0.03	<0.06
Core 6	<0.04	<0.03	0.60
Core 10	<0.04	<0.03	0.10
Core 12	<0.04	<0.03	0.38

% Recovery	Simazine	Atrazine	Trietazine
Spike 1	25%	37%	33%
Spike 2	85%	66%	30%

**Table: C3 Concentration of triazine herbicides detected by GC-MS
in the core profile at Bishopfield Farm, Doncaster
(borehole 2)**

Project No: 7077
Form No: 1171 **Date Received:** 29/10/93
Analyst: SS **Date Analysed:** 09/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Sandstone - Borehole 2
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg		
	Simazine	Atrazine	Trietazine
Blank	<0.02	<0.02	<0.03
Spike 0.1ug/kg	0.096	0.081	0.077
Spike 0.1ug/kg	0.085	0.075	0.066
Core 1	<0.02	<0.02	0.73
Core 2	<0.02	<0.02	<0.03
Core 3	<0.02	<0.02	<0.03
Core 4	<0.02	<0.02	<0.03
Core 7	<0.02	<0.02	<0.03
Core 9	<0.02	<0.02	<0.03
Core 11	<0.02	<0.02	<0.03
Core 14	<0.02	<0.02	<0.03
Core 19	<0.02	<0.02	0.078

% Recovery	Simazine	Atrazine	Trietazine
Spike 1	96%	81%	77%
Spike 2	85%	75%	66%

**Table C4: Percentage moisture content determined in Borehole 1
AFRC Compton, Berkshire**

Project No: 7077
Form No: 1171
Analyst: SS

Date Received: 28/10/93
Date Analysed: 10/12/93

Instrument: Trlo 1
Instrument Mode: (+EI)
Sample Type: Triazines in Chalk
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	60.94	108.17	97.97	21.6
Core 1	83.26	130.25	123.36	14.7
Core 10	90.37	140.99	129.41	22.9
Core 13	85.53	135.74	123.93	23.5
Core 15	41.56	64.03	60.45	15.9
Core 16	83.25	130.25	123.36	14.7

**Table: C5 Percentage moisture content determined in borehole 1
AFRC Compton, Berkshire, after freeze drying.**

Project No: 7077
Form No: 1171
Analyst: SS

Date Received: 02/12/93
Date Analysed: 02/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Chalk
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	62.29	112.36	112.25	0.22
Core 1	54.40	104.65	104.43	0.44
Core 10	67.69	117.37	117.28	0.18
Core 13	68.16	118.36	118.24	0.24
Core 15	97.62	147.81	147.64	0.34
Core 16	67.75	117.74	117.68	0.12

% Recovery **Simazine Atrazine Trietazine**

Spike 1 32%
 Spike 2 55%

NOTES:

* =semi-quantitative only as no internal std was detected

Results for Simazine and Trietazine are not reported due to large interference peaks

**Table: C6 Percentage moisture content determined in boreholes
1 & 1A Bishopfield Farm, Doncaster**

Project No: 7077
Form No: 1171 **Date Received:** 28/10.93
Analyst: SS **Date Analysed:** 16/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Sandstone - Borehole 1
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	60.95	111.06	109.91	2.3
Core 1	83.24	134.28	128.14	12.0
Core 2	48.42	97.35	94.07	6.7
Core 2B1A	28.00	77.49	74.87	5.3
Core 3	83.24	134.02	131.71	4.5
Core 4	90.38	139.60	137.53	4.2
Core 5	85.53	134.02	131.71	4.8
Core 6	97.27	146.48	143.34	6.4
Core 10	62.08	111.91	108.71	6.4
Core 12	72.53	122.29	119.11	6.4

**Table: C7 Percentage moisture content determined in borehole
Bishopfield Farm, Doncaster**

Project No: 7077
Form No: 1171
Analyst: SS

Date Received: 29/10/93
Date Analysed: 09/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Sandstone - Borehole 2
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	62.27	111.97	109.36	5.3
Core 1	83.24	133.31	127.02	12.6
Core 2	97.26	147.15	143.41	7.5
Core 3	72.52	120.08	116.96	6.6
Core 4	48.41	101.01	98.31	5.1
Core 7	28.00	81.54	77.11	8.3
Core 9	90.36	141.03	137.33	7.3
Core 11	62.07	110.00	106.32	7.7
Core 14	67.97	116.42	113.96	5.1
Core 19	85.52	137.10	129.65	14.4

**Table: C8 Concentration of chlorophenoxyacid herbicides detected by GC-MS in the core profiles,
at Green Hedge Farm, Cambridge**

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 02/12/93
Date Analysed: 02/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH1/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg						
	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Laboratory Spike 1 (1 ug/Kg)	0.95	0.43	0.49	0.83	0.30	1.24	0.24
Laboratory Spike 2 (1 ug/Kg)	1.01	0.61	0.37	0.61	0.46	0.56	0.23
Laboratory Blank	<0.05	<0.05	<0.06	<0.07	<0.12	<0.09	<0.10
Core 1	<0.05	<0.05	<0.06	<0.07	<0.14	<0.10	<0.11
Core 1 repeat	<0.05	<0.05	<0.06	<0.07	<0.14	<0.10	<0.11
Core 2	<0.05	<0.05	<0.05	<0.07	<0.12	<0.09	<0.10
Core 3	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 4	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 5	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 6	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.11
Core 8	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 12	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.11
Core 15	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10

% Recovery	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Spike 1	95%	43%	49%	83%	30%	124%	24%
Spike 2	101%	61%	37%	61%	46%	56%	23%

Table: C9 Concentration of chlorophenoxyacid herbicides in borehole 2, Green Hedge Farm, Cambridge

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 06/12/93
Date Analysed: 09/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH2/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/kg						
	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Laboratory Spike 1 (1 ug/Kg)	1.15	0.63	0.41	0.87	0.70	0.81	0.11
Laboratory Spike 2 (1 ug/Kg)	1.17	0.63	0.43	0.83	0.57	1.24	0.14
Laboratory Blank	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 1	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 2	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 3	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 4	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 5	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 6	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 8	0.06	0.03	0.03	0.06	0.06	0.10	0.03
Core 12	0.06	0.03	0.03	0.11	0.06	0.10	0.03
Core 15	0.06	0.03	0.03	0.06	0.06	0.10	0.03

% Recovery	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Spike 1	115%	63%	41%	87%	70%	81%	11%
Spike 2	117%	63%	43%	83%	57%	124%	14%

**Table: C10 Concentration of chlorophenoxyacid herbicides detected in borehole 1,
Assarts Farm, Nottingham**

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 24/11/93
Date Analysed: 24/11/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Sandstone : Batch BH/A1
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg						
	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Laboratory Spike 1 (1 ug/Kg)	1.15	0.72	0.48	0.62	0.70	0.67	0.29
Laboratory Spike 2 (1 ug/Kg)	1.09	0.65	0.52	0.67	0.61	0.78	0.24
Laboratory Blank	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 1	2.11	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 2	0.33	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 2 repeat	0.36	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 3	0.14	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 4	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 5	0.14	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 7	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 11	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 14	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11
Core 27	<0.05	<0.04	<0.06	<0.09	<0.09	<0.08	<0.11

% Recovery	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Spike 1	115%	72%	48%	62%	70%	67%	29%
Spike 2	109%	65%	52%	67%	61%	78%	24%

**Table: C7 Percentage moisture content determined in borehole
Bishopfield Farm, Doncaster**

Project No: 7077
Form No: 1171
Analyst: SS

Date Received: 29/10/93
Date Analysed: 09/12/93

Instrument: Trio 1
Instrument Mode: (+EI)
Sample Type: Triazines in Sandstone - Borehole 2
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	62.27	111.97	109.36	5.3
Core 1	83.24	133.31	127.02	12.6
Core 2	97.26	147.15	143.41	7.5
Core 3	72.52	120.08	116.96	6.6
Core 4	48.41	101.01	98.31	5.1
Core 7	28.00	81.54	77.11	8.3
Core 9	90.36	141.03	137.33	7.3
Core 11	62.07	110.00	106.32	7.7
Core 14	67.97	116.42	113.96	5.1
Core 19	85.52	137.10	129.65	14.4

**Table: C8 Concentration of chlorophenoxyacid herbicides detected by GC-MS in the core profiles,
at Green Hedge Farm, Cambridge**

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 02/12/93
Date Analysed: 02/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH1/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg						
	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Laboratory Spike 1 (1 ug/Kg)	0.95	0.43	0.49	0.83	0.30	1.24	0.24
Laboratory Spike 2 (1 ug/Kg)	1.01	0.61	0.37	0.61	0.46	0.56	0.23
Laboratory Blank	<0.05	<0.05	<0.06	<0.07	<0.12	<0.09	<0.10
Core 1	<0.05	<0.05	<0.06	<0.07	<0.14	<0.10	<0.11
Core 1 repeat	<0.05	<0.05	<0.06	<0.07	<0.14	<0.10	<0.11
Core 2	<0.05	<0.05	<0.05	<0.07	<0.12	<0.09	<0.10
Core 3	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 4	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 5	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 6	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.11
Core 8	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10
Core 12	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.11
Core 15	<0.05	<0.05	<0.06	<0.07	<0.13	<0.09	<0.10

% Recovery	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	loxynil
Spike 1	95%	43%	49%	83%	30%	124%	24%
Spike 2	101%	61%	37%	61%	46%	56%	23%

**Table: C17 Percentage moisture content determined in borehole 2,
Assarts Farm, Nottingham**

Project No: 7077
Form No: 1186
Analyst: DW
Date Received: 29/11/93
Date Analysed: 06/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Sandstone : Batch BH/A2
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	61.00	111.37	109.20	4.3
Core 1	44.42	95.01	90.22	9.5
Core 2	45.33	95.34	91.37	7.9
Core 3	48.41	98.40	93.93	8.9
Core 4	62.09	112.09	109.64	4.9
Core 9	27.99	77.83	75.52	4.6
Core 12	47.65	97.90	94.36	7.0
Core 17	67.76	117.85	113.29	9.1
Core 25	44.70	95.14	91.09	8.0
Core 35	54.87	105.43	102.28	6.2

**Table: C12 Percentage moisture content determined in borehole 1,
Green Hedge Farm, Cambridge**

Project No: 7077 **Date Sampled:**
Form No: 1186 **Date Received:** 02/12/93
Analyst: DW **Date Analysed:** 02/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH1/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	72.53	123.84	112.99	21.1
Core 1	67.76	145.22	135.00	13.2
Core 2	45.35	99.61	88.09	21.2
Core 3	62.09	116.69	105.87	19.8
Core 4	28.01	89.04	77.78	18.4
Core 5	48.42	96.65	86.93	20.2
Core 6	44.72	92.12	83.61	18.0
Core 8	47.63	100.38	90.42	18.9
Core 12	61.02	120.72	111.97	14.7
Core 15	59.39	106.04	96.47	20.5

Table: C11 Concentration of chlorophenoxyacid herbicides in borehole 2, Assarts Farm, Nottingham

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 29/11/93
Date Analysed: 06/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Sandstone : Batch BH/A2
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Concentration ug/Kg						
	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	Ioxynil
Laboratory Spike 1 (1 ug/Kg)	1.16	0.65	0.50	1.11	0.68	0.72	0.33
Laboratory Spike 2 (1 ug/Kg)	1.01	0.63	0.42	0.58	0.52	0.66	0.25
Laboratory Blank	<0.05	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 1	0.23*	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 2	0.25	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 3	0.27	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 4	0.43	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 9	0.28*	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 17	<0.05	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 17 repeat	<0.05	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 25	<0.05	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10
Core 35	<0.05	<0.05	<0.07	<0.07	<0.10	<0.09	<0.10

* = Interferent present on quantitation ion (169)

% Recovery	Mecoprop	MCPA	Bromoxynil	Dichlorprop	2,4-D	2,4-DB	Ioxynil
Spike 1	116%	65%	50%	111%	68%	72%	33%
Spike 2	101%	63%	42%	58%	52%	66%	25%

**Table: C13 Percentage moisture content determined in borehole 1,
Green Hedge Farm, Cambridge, after freeze drying**

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 02/12/93
Date Analysed: 02/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH1/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	72.53	99.91	99.86	0.18
Core 1	67.82	141.40	141.19	0.29
Core 2	90.37	148.93	148.79	0.24
Core 3	35.49	68.76	68.72	0.12
Core 4	28.00	82.85	82.77	0.15
Core 5	83.25	136.60	136.54	0.11
Core 6	44.81	88.41	88.35	0.14
Core 8	47.68	101.66	101.57	0.17
Core 12	61.08	114.61	114.53	0.15
Core 15	97.29	151.79	151.70	0.17

Table: C14 Percentage moisture content of borehole 2, Green Hedge Farm, Cambridge

Project No: 7077
Form No: 1186 **Date Received:** 06/12/93
Analyst: DW **Date Analysed:** 09/12/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Chalk : Batch BH2/S
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	72.53	123.84	112.99	21.1
Core 1	54.88	106.95	99.63	14.1
Core 2	90.36	140.10	129.27	21.8
Core 3	45.33	104.47	92.23	20.7
Core 4	83.24	136.23	125.19	20.8
Core 5	83.23	130.92	120.84	21.1
Core 6	44.45	93.14	82.89	21.1
Core 8	85.51	135.75	125.20	21.0
Core 12	67.97	116.96	108.86	16.5
Core 15	97.27	149.51	139.28	19.6

Table: C15 Percentage moisture content of borehole 2, Green Hedge Farm, Cambridge, after freeze drying

Project No: 7077
 Form No: 1186
 Analyst: DW

Date Received: 06/12/93
 Date Analysed: 09/12/93

Instrument: Finnigan ITD
 Instrument Mode: (+EI)
 Sample Type: Phenoxyacid herbicides in Chalk : Batch BH2/S
 Sample extracted: 250g
 Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	72.53	99.91	99.86	0.18
Core 1	54.90	115.36	115.31	0.08
Core 2	45.34	108.73	108.67	0.09
Core 3	62.09	122.64	122.61	0.05
Core 4	83.25	130.40	130.39	0.02
Core 5	48.42	98.32	98.30	0.04
Core 6	44.46	90.85	90.83	0.04
Core 8	85.53	142.80	142.74	0.10
Core 12	67.98	140.45	140.42	0.04
Core 15	59.42	114.82	114.76	0.11

**Table: C16 Percentage moisture content determined in borehole 1,
Assarts Farm, Nottingham**

Project No: 7077
Form No: 1186
Analyst: DW

Date Received: 24/11/93
Date Analysed: 24/11/93

Instrument: Finnigan ITD
Instrument Mode: (+EI)
Sample Type: Phenoxyacid herbicides in Sandstone : Batch BH/A1
Sample extracted: 250g
Final Extract Vol: 100 ul

Sample	Weights/g			Moisture %
	Glass	Wet solid	Dry solid	
Laboratory Blank	62.07	114.46	111.66	5.3
Core 1	67.99	116.51	112.64	8.0
Core 2	72.53	121.22	116.92	8.8
Core 2 repeat	97.33	160.11	154.66	8.7
Core 3	90.40	140.84	136.52	8.6
Core 4	83.24	130.71	126.84	8.2
Core 5	83.29	139.29	136.53	4.9
Core 7	58.75	110.35	107.42	5.7
Core 11	59.37	114.47	112.23	4.1
Core 14	85.60	133.09	130.53	5.4
Core 27	62.27	112.29	109.02	6.5