Project 439

Pesticides in Major Aquifers

NRA

National Rivers Authority

Guardians of
the Water Environment

WRc plc

R&D Report 17

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Pesticides in Major Aquifers

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Statement of use

Reliable data on pesticide occurrence in aquifers have been obtained following the development of analytical methods for this purpose. The report gives an insight into the likely fate of pesticides in aquifers and it will be of interest to Government departments, water utilities, farmers and other interested parties.

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GLOSSARY

BGS	British Geological Survey
CEC	Council of the European Communities
DoE	Department of the Environment
EC	European Community
FARMSTAT	Farm statistics
GCMS	Gas chromatography-mass spectrometry
GIS	Geographical information system
IA	Immunoassay
LCC	Land Capability Consultants
LCMS	Liquid chromatography-mass spectrometry
MAC	Maximum admissible concentration
MAFF	Ministry of Agriculture, Fisheries and Food
MCPA	4-chloro-2-methylphenoxyacetic acid
NRA	National Rivers Authority
PAR	PAR Consultants
PCV	Prescribed concentration value
POPPIE	Prediction Of Pesticide Pollution In the Environment
SEISMIC	Spatial environmental information system to model the impact of chemicals
SSLRC	Soil Survey and Land Research Centre
TP	Transformation product
UK	United Kingdom

NOTATION

m	metres
mm	millimetres
$\mu g\ l^{-1}$	micrograms per litre
$\mu g\ kg^{-1}$	micrograms per kilogram

EXECUTIVE SUMMARY

The National Rivers Authority (NRA) recognises the threat pesticides pose to aquifers across England and Wales. As a result, the NRA has continued to investigate the problems in the Granta Catchment.

The objectives of this work were:

- to determine the fate and transport of selected priority 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.

National, regional and catchment scale pesticide-usage surveys have been completed. Monitoring of the concentrations of pesticides in groundwater, surface water and rain over extended periods of time has provided reliable data on pesticide occurrence in environmental waters, and has enabled these concentrations to be related to the original pesticide usage.

A multi-residue method for the analysis of up to twenty common pesticides in water samples has been developed for the project. Analytical methods for major groups of pesticides in aquifer materials from the Chalk and Sherwood Sandstone aquifers also have been completed. The NRA now has validated methods of analysis for the urons, carbamates and acid herbicides in chalk and sandstone. A method for triazines in sandstone has also been developed, but a similar method for triazines in chalk could not be fully validated.

Immunoassay techniques of analysis have been used successfully for the triazines, specifically atrazine, simazine and trietazine, in chalk and sandstone. The technique has been extremely valuable in the profiling of the unsaturated zone of the aquifers for these pesticides.

The first profiles of the three main pesticide groups in both the Chalk and Sherwood Sandstone aquifers have been completed. Under normal agricultural usage, most acid herbicides, urons and carbamates appear to be attenuated in the soil and unsaturated aquifer. They are rarely detected below 3 m from the surface and are believed to present little threat to groundwater quality. Triazines are more persistent beneath crops and do present a distinct threat to groundwater quality. Mecoprop, an acid herbicide, appears to be persistent in sandstone, but there is no evidence of deep penetration.

Any pesticide may contaminate groundwater in situations where the attenuation properties of the soil may be by-passed or overcome. Such situations include karstic conditions, fissured aquifers, repetitive pesticide loading over years or where the hydraulic loading is particularly high. The latter may include drains or soakaways. Pesticide contamination of the Chalk aquifer is believed to depend largely on by-passing the zone of attenuation through fissures within this aquifer.

Profiling of our aquifers is very new and many more detailed pesticide concentration profiles are needed to evaluate transport and attenuation through the soil and unsaturated zone with more certainty.

A preliminary model of pesticides in groundwater was developed for the Granta catchment and gave reasonable simulations of observed concentrations. The future modelling needs of the NRA are seen to rest on two types of model; a screening model and a catchment scale model. It is suggested that either model will depend heavily on geographical information system (GIS) technology and that an improved or enlarged pesticide database, particularly on pesticide behaviour in the sub-surface, is essential for the development of accurate models.

The most important fields of future research with pesticides in groundwater/aquifers will be concerned with:

- non-agricultural pesticides;
- pesticide transformation products;
- pesticide degradation in aquifers;
- pesticide transport modelling - screening and catchment models.

KEY WORDS

Pesticides, analysis, profiling, groundwater, hydrogeology, 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 to 1994 with funding by the National Rivers Authority (NRA).

The key objectives of the work have been:

- 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 work began in the catchment of the River Granta near Cambridge which lies on the Chalk aquifer, a major source of potable water in the region. In 1989, the scope of the study was extended to include work on the Sherwood Sandstone, the second most important aquifer in the UK. The area chosen for the Sherwood Sandstone studies was Assarts Farm near Warsop, Nottinghamshire.

The research programme covering some ten years of work was designed to study and quantify the various aspects of pesticide occurrence and transport in the hydrological cycle. The pattern of pesticide transport expected within a normal river catchment is summarized in Figure 1.1, and the main elements of the pesticide continuum shown on this Figure are:

- pesticide application;
- infiltration and attenuation through the soil profile;
- percolation and attenuation through the unsaturated aquifer or transport to rivers by run-off or drainage;
- transport and attenuation through saturated aquifer to rivers or boreholes.

The Project programme linking these main elements of pesticide transport together is given, in outline, in Table 1.1. Two other important aspects of the programme that had to be developed to support the field work and monitoring studies were those of analytical method development and mathematical modelling of pesticide transport.

In 1984, when this project began, the analysis of water samples for pesticides was in its infancy and the analysis of solid aquifer samples had not begun. Suitable methods of analysis had to be developed before the monitoring of pesticides in river water, rain water or groundwater could begin. The analysis of aquifer material had to be developed before measurement of pesticides and therefore studies of their transport, in the unsaturated zones of aquifers could be undertaken. The analytical method development has been successful in this project and the NRA now have:

- a multi-residue method for environmental waters;
- a method for triazines in sandstone;
- a method for acid herbicides in sandstone and chalk;
- a method for urons and carbamates in sandstone and chalk;
- an immunoassay method for triazines in sandstone and chalk.

Mathematical models are now widely used to predict pollution transport and for catchment protection. The development of a predictive model of pesticide transport and fate was therefore identified as one of the primary aims of this project. The development had to wait for the assembly of data on pesticide concentrations in the various elements of the pesticide continuum identified above. A preliminary model, based on the WRc Nitrate Model, was given in Clark *et al.* (1992).

In a parallel related programme of work funded by the NRA, the British Geological Survey (BGS) also studied the movement of pesticides through aquifer materials (Chilton *et al.* 1993).

The present report seeks to highlight the important features of the project without undue duplication of material available in previous reports and publications.

Table 1.1 Outline Project Programme

Fields of work	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
Pesticide Usage Surveys	Regional and National usage surveys[1]	Detailed usage surveys of Granta catchment.[2,3,4,5,6,7,8]			Usage surveys of Assarts Farm[9,10]			FARMSTAT usage survey[11]		
Analytical Method Development		Multi residue method of analysis in environmental waters[3,12]				Development of analytical methods for three groups of pesticides into chalk and sandstone aquifer materials Method for urons and carbamates[13] Method for triazines in sandstone[14]			Method for acid herbicides[15] Immunoassay method for triazines[3]	
Monitoring of pesticides in surface water	Development of sampling protocols		Monitoring of pesticides in Granta River[16]	Study of input from rainfall[16,17]						
Monitoring of pesticides in groundwater	Development of sampling protocols			Sampling of water from production and observation boreholes[18,19]		Study of surface/ groundwater interaction[16]				
Movement of pesticides in soils						Development of inert sampler suction[20,21,22] Studies of pesticides in soils at Assarts Farm and the Granta catchment[9,10]				
Profiling of pesticides in unsaturated aquifers								Profiling of urons in sandstone and chalk[3]	Profiling of acid herbicides and triazines in sandstone and chalk[23]	
Modelling of pesticide transport							Development of preliminary pesticide transport model on catchment scale[3]			Modelling Review[24]

Notes:

1 Baxter (1986)
2 Fischer *et al.* (1991)
3 Clark *et al.* (1992)
4 Cartwright *et al.* (1991)
5 LCC (1986)
6 LCC (1987)
7 LCC *et al.* (1989)
8 PAR (1985)
9 Carter *et al.* (1990)
10 Carter and Beard (1991)
11 FARMSTAT Ltd. (1991)
12 Shurvell *et al.* (1993)
13 Forbes *et al.* (1993a)
14 Forbes *et al.* (1993b)
15 Forbes *et al.* (1994a)
16 Gomme *et al.* (1991a)
17 Hennings and Morgan (1987)
18 Clark *et al.* (1991)
19 Gomme *et al.* (1992)
20 Clark *et al.* (1990)
21 Clark and Gomme (1992)
22 Fogg and Carter (1992)
23 Turrell *et al.* (1994)
24 Oakes (1994)

2. ANALYTICAL METHOD DEVELOPMENT

2.1 Background

The methods available for analysis of pesticides in environmental samples in 1985 were inadequate to achieve the objectives of the planned work programme.

Surveys of pesticide usage had identified a large number of pesticides in common use in the Granta catchment. No method was available to analyse water for such a wide range of chemicals with detection limits less than 0.1 $\mu g\ l^{-1}$. This concentration is the Maximum Admissible Concentration (MAC) for pesticides in the European Community (EC) Directive on Water Intended for Human Consumption (CEC 1980), later incorporated in the UK Water Supply (Water Quality) Regulations 1989 (SI 1147) as the prescribed concentration value (PCV) for pesticides. Similarly, no analytical methods were available for the analysis of samples of solid aquifer materials such as chalk or sandstone at relevant detection limits.

2.2 Achievements

An important part of the research work has been the development of new analytical methods. These were not only essential for the analysis of pesticides during the project but are also of wider use to the NRA.

A multi-residue method for the analysis of 20 pesticides in rainwater, groundwater and river water has been developed. The selection of the suite of pesticides was based on the usage of pesticides in the Granta catchment, the known occurrence of pesticides in groundwater and the feasibility of their analyses. The method development was successful, and the method was used in the routine environmental monitoring of groundwater in the project.

The progression of the field studies in the project, particularly the study of the movement of pesticides through the groundwater system, showed the total absence of data on the occurrence of pesticides in the unsaturated zone of the aquifers. The difficulty with monitoring pesticides in the unsaturated zone is that only small amounts of water can be obtained. This pin-pointed the lack of, and need for, analytical methods for pesticides in solid samples. Three major groups of pesticides of potential concern were selected for method development:

- triazines;
- urons and carbamates;
- acid herbicides.

Methods were successfully developed and validated for the two aquifer matrices of particular relevance to the study: sandstone and chalk. The methods were used to support the field studies (see Section 3.4) to obtain profiles of the pesticides in the unsaturated zone.

The multi-residue methods are based on extraction of pesticides from the matrix, clean-up of the extract followed by gas or liquid chromatographic analysis (GC or LC) and mass-spectrometry detection. The use of mass spectrometry yields the important benefit of selectivity to the methods.

The development of a sensitive method - gas chromatography or high performance liquid chromatography - for triazines in chalk presented problems due to interferences from co-extracted impurities present in the matrix. No method was found capable of selectively removing the interferences while adequately analysing the triazines. It appears that chalk may contain significant amounts of interfering substances, probably organic in nature, which (at present) are uncharacterized in terms of type and origin. The record of the method development and its present status has been described (Forbes *et al.* 1994b).

As a substitute for chemical analysis for triazines in chalk, the use of immunoassay analysis of water samples for triazines to the analysis of triazines in aquifer materials (Clark *et al.* 1992) was extended. The main benefit of immunoassay methods is that they can be used on the small volumes of pore-water obtained from aquifer materials by centrifugation. Detailed profiles of triazine concentrations can be obtained at relatively low cost by this method. The method was successfully used for the profiling of the Chalk aquifer for atrazine and the Sherwood Sandstone aquifer for trietazine and simazine (Turrell *et al.* 1994). However the techniques do not discriminate between triazines.

The new analytical methods developed and used in the project are summarized in Table 2.1, which includes references to the relevant reports where details of the methods can be found.

2.3 Future Needs

The present study has seen the development of several multi-residue pesticide methods applied to a range of aqueous and solid environmental samples (Table 2.1). These methods may be used by the NRA in future monitoring for the majority of pesticides of potential concern used in the UK.

Table 2.1 Analytical methods developed for the NRA

Determinand	Technique	Sample matrix	Reference
Twenty pesticides	GCMS [1]	Rain, groundwater and river water	Shurvell *et al.* 1993
Urons/carbamates	LCMS [2]	Chalk and sandstone	Forbes *et al.* 1993a
Triazines	GCMS [1]	Sandstone	Forbes *et al.* 1993b
Acid herbicides	GCMS [1]	Chalk and sandstone	Forbes *et al.* 1994a
Triazines	IA [3]	Pore-water	Clark *et al.* 1992

Notes: [1] GCMS Gas chromatography-mass spectrometry
[2] LCMS Liquid chromatography-mass spectrometry
[3] IA Immunoassay

It is possible to identify deficiencies in current analytical methods for satisfying the future requirements for environmental monitoring. These deficiencies mainly centre on:

- methods for transformation products in aquifer materials;
- methods for other pesticides in aquifer materials;
- selective methods for triazines in chalk.

Little is known about the mobility and fate of the transformation products (TPs) of pesticides in groundwater or in surface waters, or the effects such TPs have on the environment. Few analytical methods for TPs are available, even for water samples; none are available for TPs in aquifer materials. This area represents the greatest unknown in protection of natural waters. New analytical methods for TPs are required for studying the degradation of pesticides and movement of TPs in groundwater, aquifer material and surface waters.

The usage of pesticides is subject to many influences and is constantly changing. For example, the withdrawal of atrazine and simazine from non-agricultural application has forced users to choose alternatives such as diuron and imazapyr for these applications. New analytical methods are therefore constantly required for other pesticides in drinking water, to monitor compliance with the PCV. There is a corresponding need to develop methods for such pesticides in aquifer materials. Both chromatographic and immunoassay methods for pesticides of concern should be applied to aquifer material and pore-water respectively, as they become available, to obtain knowledge of the distribution of pesticides between aquifer material and pore water. The pesticides of concern can be identified by simple screening models (Section 4.3).

Preliminary experiments on the use of High Performance Liquid Chromatography - Mass Spectrometry for the analysis of triazines in chalk were encouraging but indicated that further development of extraction, clean-up and separation steps is required before the method can be used routinely for triazines in chalk.

3. FIELD STUDIES

3.1 Pesticide Usage Surveys

3.1.1 Agricultural usage

Although general characteristics of pesticide usage in the UK were known in 1985, detailed data on the distribution and intensity of pesticide loadings were not readily available. Such data were vital if a relationship between the application and the occurrence of pesticides in environmental waters was to be established.

The first studies (Baxter 1986) reviewed pesticide usage data available from the Ministry of Agriculture, Fisheries and Food (MAFF) and the Department of the Environment (DoE) to provide a national and regional picture. The data from MAFF and DoE were supplemented by a national survey (1985) commissioned from PAR (Agricultural Research) Consultants (PAR). The data review demonstrated the preponderance of herbicides used in cereal cultivation with respect to total agricultural pesticide usage. The pesticide loading data therefore reflect the extent of cereal cultivation and are highest in East Anglia. This conclusion helped in the choice of the Granta catchment for the original catchment study.

The regional database of PAR was inadequate for the assessment of the pesticide usage in the Granta catchment. A detailed pesticide-usage survey of the Granta catchment was commissioned from Land Capability Consultants Ltd (LCC). This survey covered the years 1985 to 1988. The results were reported annually and are summarized in Fisher *et al.* (1991) and Clarke *et al.* (1992). This pesticide use survey was one of the most intensive surveys at that time in the UK and provided information on the range of pesticides in use in the catchment and their relative rankings in terms of total loading on the catchment. These ranked results were used to select the list of priority pesticides to be monitored in the environmental waters.

The results of the LCC pesticide usage surveys of the Granta catchment were supplemented by a pesticide-usage analysis for East Anglia (FARMSTAT Ltd (1991)). The FARMSTAT data are based on a nation-wide network of some 2000 farms which gives them a sound statistical basis. The pesticide loadings derived from the LCC and the FARMSTAT surveys were quite similar, emphasizing the usefulness of FARMSTAT on a national scale in the UK.

The increased scope of the project to include a typical sandstone aquifer at Assarts Farm in Nottingham required a similar detailed pesticide usage survey of the study area. The work was commissioned from the Soil Survey and Land Research Centre (SSLRC) which studied the farm records for each field for the period 1985 to 1989. The results were reported in 1990 (Carter *et al.* 1990) and showed that a quite different suite of pesticides were in use on the light sandy soils of the Midlands. The detailed data available from the farmer's records allowed field trials based on dedicated trial plots to be planned (Section 3.3).

3.1.2 Non-agricultural usage

Monitoring of the River Granta for pesticides began in 1987 and continued into 1989. These results, together with results from groundwater analyses from public supply and observation boreholes, suggested that the major agricultural herbicides were under-represented in environmental waters compared with two triazine herbicides, atrazine and simazine. The triazines are used in comparatively small quantities in agriculture though they are now recognized as the most widespread pesticide contaminants of groundwater in the UK.

The relative lack of agricultural pesticides in groundwater raised the question of the origin of the triazines. In view of the common use of triazines for total weed control on roads, railways and by domestic consumers, it was suggested that the triazines may be derived from such non-agricultural sources. A survey of the use of non-agricultural pesticides in the Granta catchment was undertaken in 1989/1990 (Hennings *et al.* 1990). The institutions responsible for the maintenance of railways, roads, car parks and playing fields were approached for pesticide use data. Local works, village councils, schools and garden centres also were visited. The survey highlighted a basic lack of record keeping within these establishments and, as a consequence, little data were available for historical loadings of non-agricultural pesticides in the catchment. For example, British Rail had no data on applications to the former railway passing through the catchment to Haverhill and the Department of Transport had no information on herbicide usage on the main roads (A604 & A505) in the catchment. This lack of data on a local scale makes it very difficult to relate the occurrence of pesticides in water to their loading rates .

The lack of meaningful data on non-agricultural use of pesticides on a catchment scale is regarded as a serious drawback in advancing pesticide research.

3.2 Monitoring Water Quality

3.2.1 Surface waters

The monitoring for pesticides in surface waters in this project has been restricted to the Granta catchment. This catchment was chosen for the study, in part, because of excellent monitoring facilities in place. Surface water monitoring was based on monthly samples taken from three gauging weirs in the catchment over a full year.

The results from all three stations are similar with the most obvious feature of these data being that there are more pesticides, at higher concentrations, in the winter season when the river flows are highest. This could be related to the higher usage of pesticides in autumn or to the higher proportion of surface run-off in the river flow in winter. Simazine occurs quite commonly but the most common pesticide in surface water in the Granta is isoproturon. In the winter months, isoproturon consistently exceeds the EC MAC or the PCV in England and Wales for drinking water.

The relationship between the river stage and concentration of pesticides was studied by monitoring in detail a flood event at Babraham on the Granta. The results showed a clear positive relationship between the river flow, particulates, isoproturon, simazine, propyzamide and chlortoluron. There is a similar relationship between the period of actual rainfall and peaks of simazine, atrazine, mecoprop and propyzamide. The first correlation is the result of run-off from agricultural land via the surface and field drains carrying pesticides to the river. The second relationship is believed to reflect very rapid run-off of contaminated water into the river from hard surfaces such as roads.

A common question regarding pesticide transport in surface waters is: what proportion of the pesticide load is carried adsorbed on the particulate load compared to that dissolved in water? The monitoring exercise at Babraham was used to test this question by analysing the total pesticide load (unfiltered) for the first part of the flood and just the dissolved pesticides in the second part. There is no observable change in the data between filtered and unfiltered samples suggesting that most of the pesticide load, for the pesticides examined, is in the dissolved phase.

The influence of rainwater on the inputs of pesticides to a catchment was unknown in 1985. It could be supposed that rain would contain some pesticide through aerosol effects, adsorption on to airborne dust or through volatilisation. Three large inert rain-catchers were built (Hennings and Morgan 1987, Gomme *et al.* 1991a) capable of collecting 5-litre samples for analysis. These samplers were installed in the Granta catchment in 1987.

Major logistical problems were met with the sampling of the rain. The most important of these involved the ability to predict accurately the beginning and the intensity of any rain event that may affect the sampling site. Before any rainfall event, each sampler had to be opened and scrupulously cleaned ready for sampling and then closed as soon as the rain had passed. Forecasting of rainstorms on a local scale proved very inexact but, despite the problems, several rainstorms were sampled. The results show that rainfall does contain significant concentrations of pesticides, particularly lindane and triallate. The interpretation of the results, however, is difficult as the provenance of the pesticides cannot be proven; i.e. are they from within or from outside the catchment? The phenomenon of atmospheric transport of pesticides could have significant environmental impact and has been reported in Cousins and Watts (1995).

3.2.2 Groundwaters

The start of groundwater quality monitoring in the Granta catchment had to await the development of the multi-residue method of analysis (Watts *et al.* 1989, Shurvell *et al.* 1993). The groundwater sampling technology used at the beginning of the Granta Catchment Study was that described in Clark and Baxter (1989). Throughout the period of the entire project of Pesticides in Major Aquifers, the techniques have been refined to ensure the integrity of every sample as far as possible. The present groundwater quality monitoring and sampling philosophy and technology are discussed in detail in Clark (1992). With respect to sampling groundwater for pesticides, the most important technical refinements have been:

- introduction of quality assurance and quality control procedures while sampling;
- improvements in site hygiene to avoid contamination during sampling;
- improvements in sampling equipment.

The first groundwater samples were taken from four public supply boreholes in October 1987. Later, their sampling was repeated and extended to include ten observation boreholes and wells to show the variation in pesticide concentrations over the catchment. The pesticides in groundwater were believed to enter the sub-surface mainly in the autumnal recharge and their concentrations, therefore, possibly could show variations

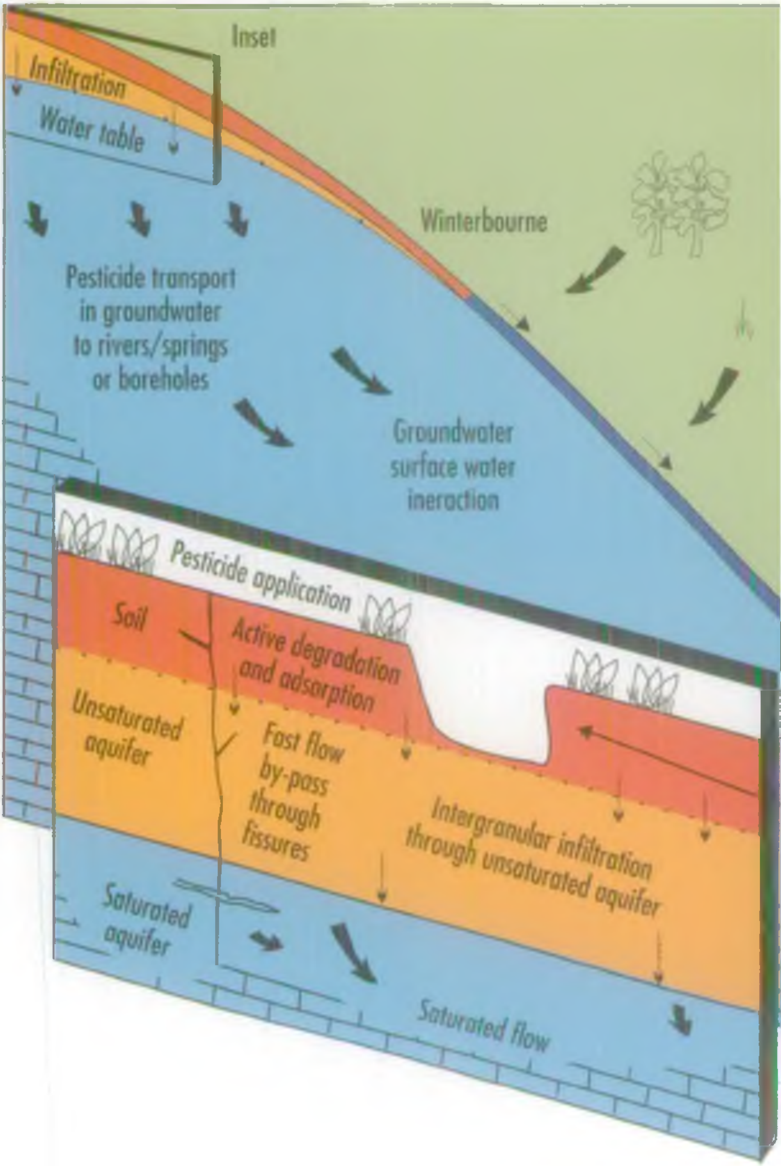
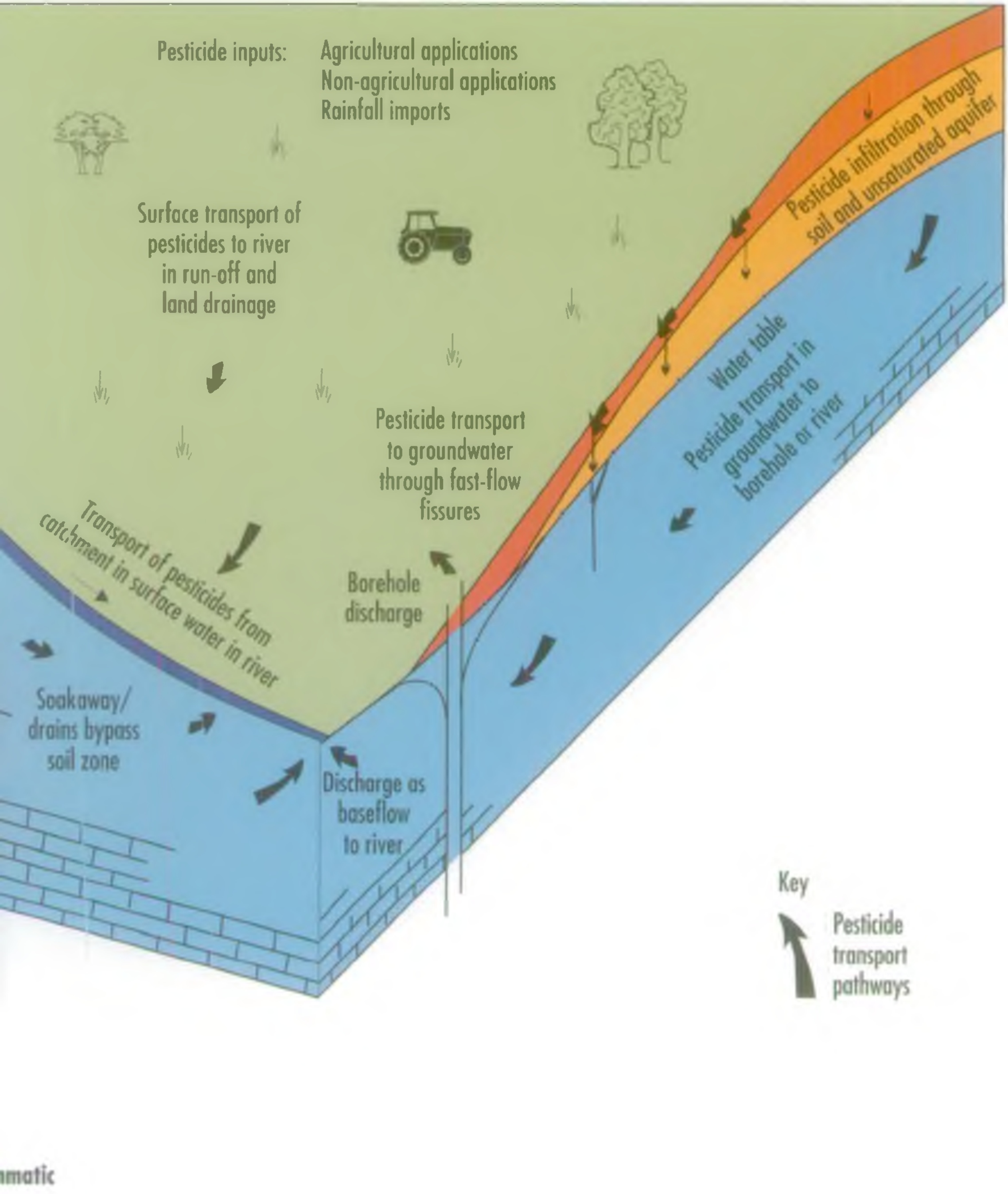


Figure 1.1 Pesticide transport pathways in the hydrological cycle: diagram


Pesticide inputs:
Agricultural applications
Non-agricultural applications
Rainfall imports
Surface transport of pesticides to river in run-off and land drainage
Pesticide infiltration through soil and unsaturated aquifer
Water table
Pesticide transport in groundwater to borehole or river
Pesticide transport to groundwater through fast-flow fissures
Transport of pesticides from catchment in surface water in river
Borehole discharge
Soakaway/ drains bypass soil zone
Discharge as baseflow to river
Key
Pesticide transport pathways

matic

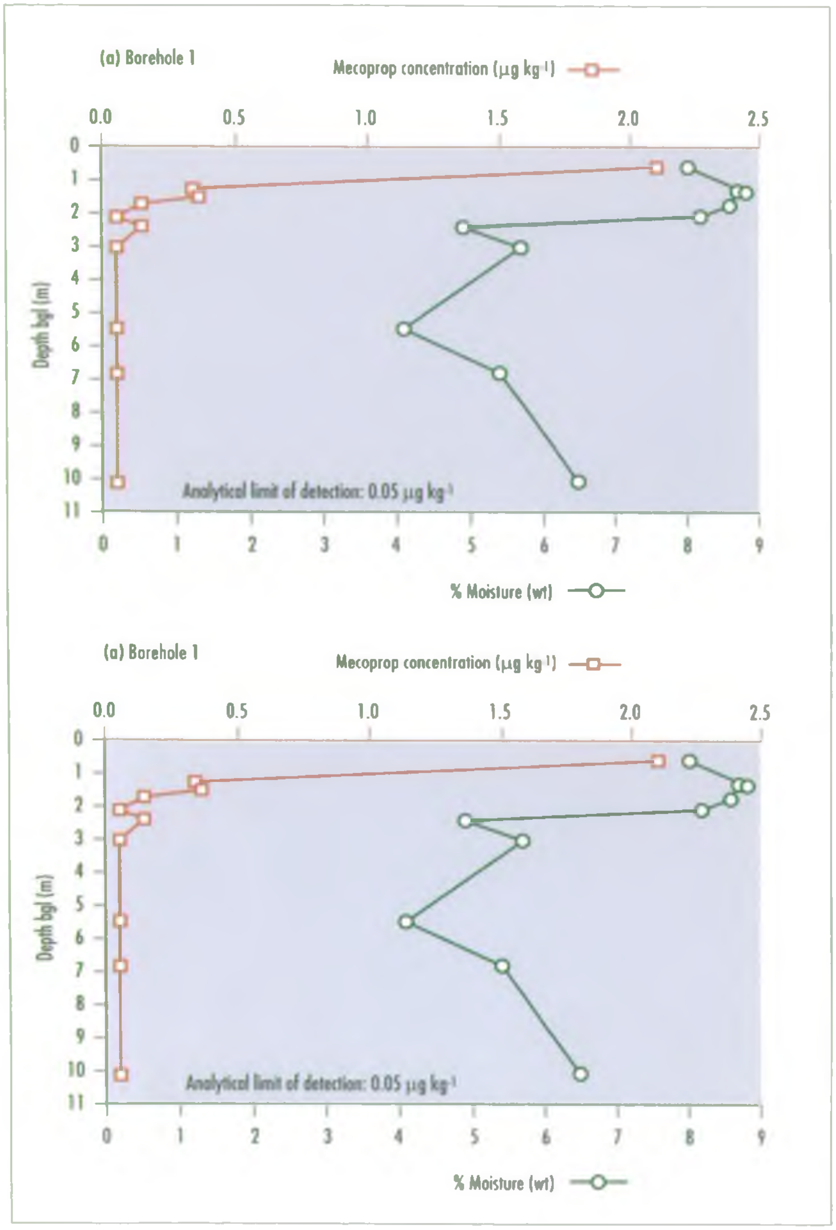


Figure 3.1 Concentration of phenoxyacid herbicides detected in the core profiles by GC-MS in the sandstone at Assarts Farm, Nottingham

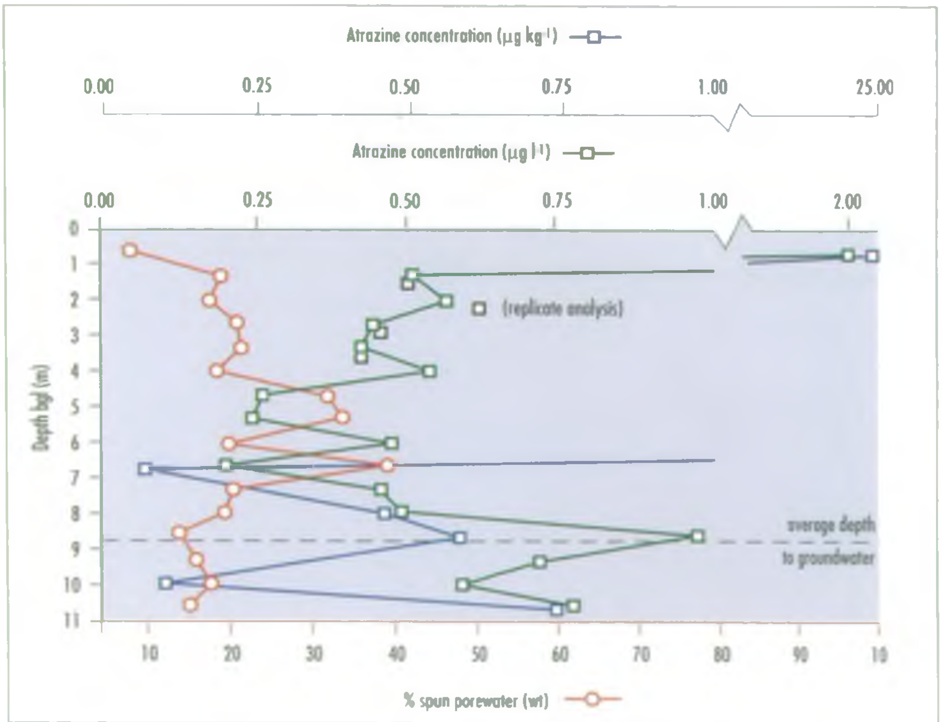


Figure 3.2 Concentration of atrazine detected by immunoassay (μg l⁻¹) and GC-MS (pg kg⁻¹) in the Chalk at Compton, Berkshire

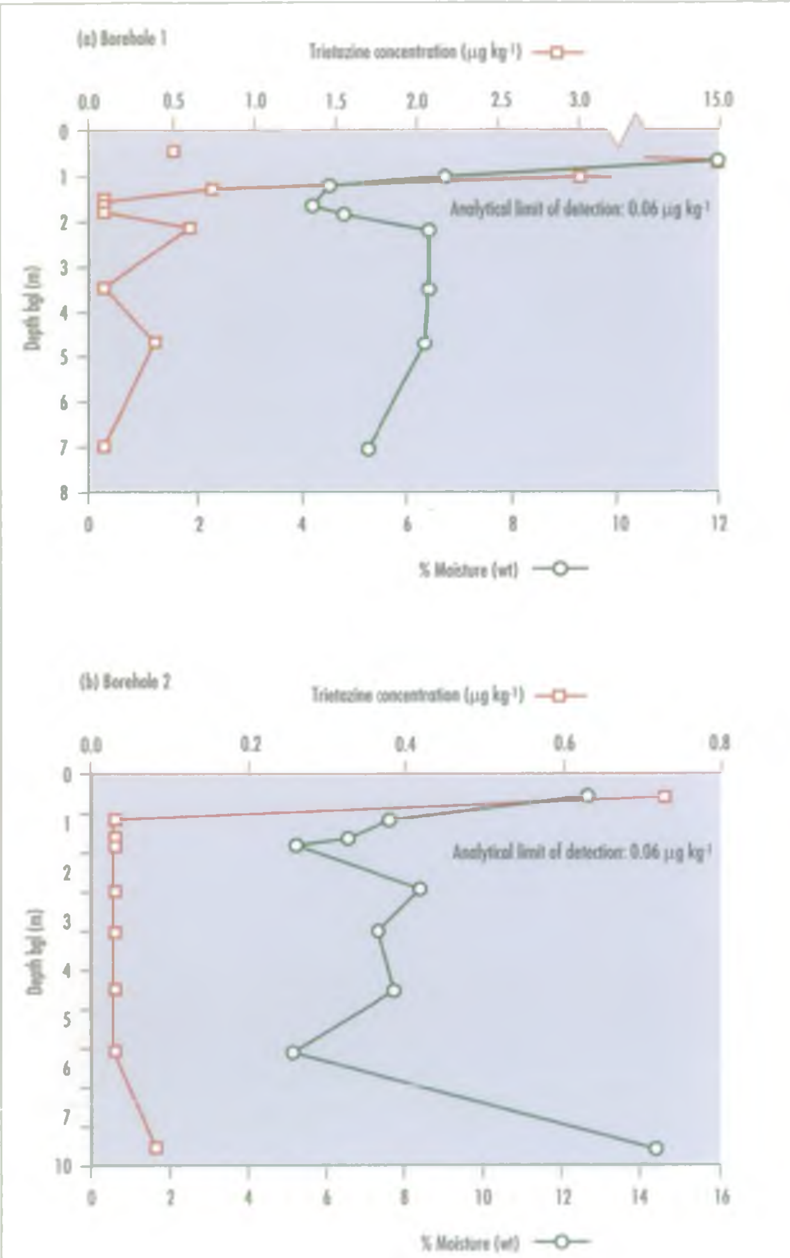


Figure 3.3 Concentration of triazine herbicides detected by GC-MS in the sandstone at Bishopfield Farm, Doncaster

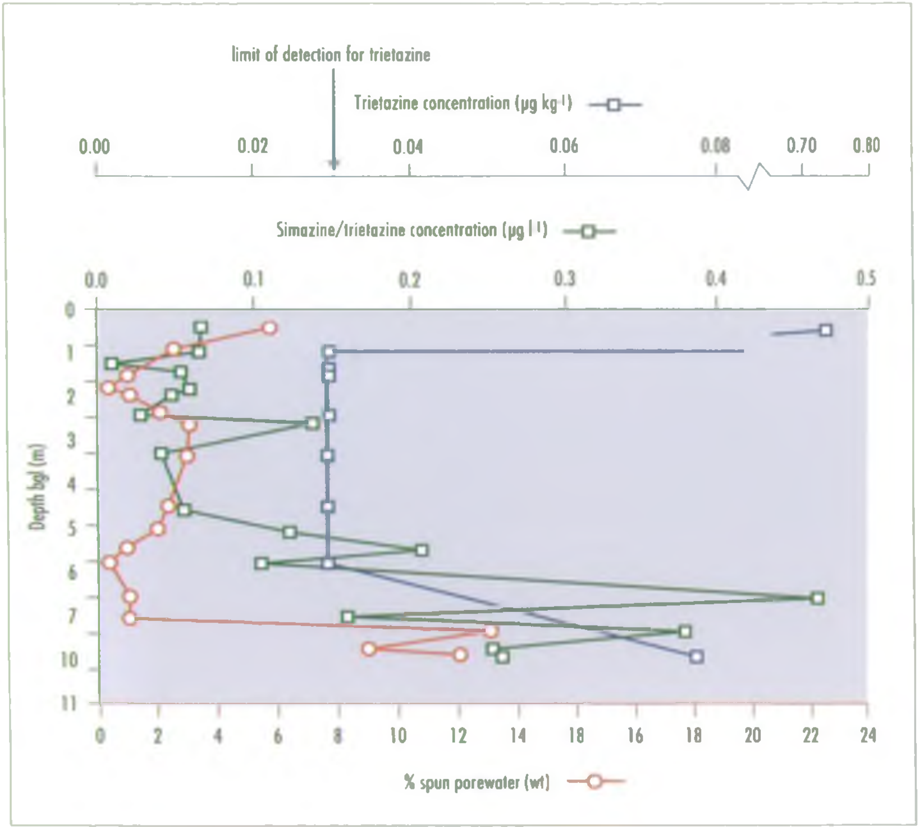


Figure 3.4 Concentrations of simazine and trietazine detected by immunoassay (µg l^{-1}) and trietazine detected by GC-MS (µg kg^{-1}) in the sandstone at Bishopfield Farm borehole 2

Installing soil suction samplers in Granta catchment through the year reflecting this origin. Two boreholes were sampled at monthly intervals through a complete year to measure any such temporal variations.

The groundwater monitoring confirmed that relatively few pesticides at low concentrations occur in the groundwater. There is no clear spatial pattern of occurrence and no variation through time. The most commonly occurring pesticides are atrazine, simazine and isoproturon. Two boreholes (Gomme *et al.* 1992) have shown high concentrations of uron pesticides up to 1.2 $\mu g\ l^{-1}$, but this occurrence is believed to be caused by local karstic recharge of surface run-off to deep groundwater. This illustrates the importance of fissures in by-passing the attenuation zone of the Chalk aquifer.

The variation in pesticide concentrations in surface waters (Section 3.2.1) suggested that low concentrations in summer may reflect the importance of baseflow in the river flow at that time of the year, and demonstrated the low concentrations of pesticides to be expected in groundwater. A series of shallow piezometers were installed close to the River Granta at Bartlow (Gomme *et al.* 1991b) to study the groundwater/surface water interactions. The site was chosen because it could be demonstrated that, at Bartlow, groundwater does contribute to the baseflow of the River Granta. The results of this monitoring confirmed that the pesticide concentrations in the groundwater are similar to those in the river in summer. The shallow groundwater quality may vary considerably over short distances but is relatively constant at any one site. The most common pesticides in the shallow groundwater are simazine, isoproturon and atrazine.

3.3 Soil Studies

The pesticide usage surveys had provided information on the surface loadings of pesticides from agricultural practices. The groundwater and surface water monitoring had shown the impact of the pesticides usage on the water resources of the Granta catchment. Little was known, however, about the transport of the pesticides from the surface through the soil profile and the underlying unsaturated zone of the Chalk aquifer to the groundwater. Quantitative information on this part of the pesticide transport through the groundwater system would be needed to enable mathematical models of the transport to be completed and calibrated.

The measurement of the movement of pesticides through the unsaturated zone of the Chalk and Sherwood Sandstone aquifers had to wait for the development of sufficiently sensitive analytical methods (Chapter 2) to allow profiling of these aquifers (Section 3.4). In the interim period, detailed studies of the movement through the soil were undertaken at Assarts Farm near Warsop (overlying the Sherwood Sandstone) and at Abington Park Farm in the Granta catchment (overlying the Chalk). These studies were designed to measure the concentrations of pesticides in the percolating rainwater as it passed from the base of the soil profile into the top of the unsaturated zone of the underlying aquifer. These measurements would enable one to demonstrate the attenuation effects of the soil profiles and confirm the attenuation predictions of established pesticide leaching models.

3.3.1 Assarts Farm

The studies at Assarts Farm began with a detailed assessment by SSLRC (Carter *et al.* 1990, Carter and Beard 1991) of the land-use, pesticide-use and soil characteristics of the farm. These surveys led to the choice of a site in one field where the pesticide application history was known and the soil water could be sampled under normal agricultural usage.

The need for analysing solid samples was avoided by sampling pore-water directly from the soil using suction samplers. An inert suction sampler was constructed by SSLRC (Clark *et al.* 1990). This sampler is suitable for pesticide work, is capable of taking samples up to one litre, and is now widely used in the UK.

Twelve suction samplers were installed in four groups of three (for triplicate samples) in the trial plot at Assarts Farm with their suction cups set at 1.5-m depth. Sampling started in December 1989 and samples were analysed for mecoprop, MCPA, isoproturon and linuron, the main pesticides applied to the field, using methods suitable for the relatively small sample volumes (Hennings *et al.* 1990).

The following year, 1990, mecoprop was applied to the plot on 24 April and the pore-water monitored up to 7 June when the suction samplers ceased to yield water (Gomme *et al.* 1991b) because of the summer soil moisture deficit. On 27 October isoproturon and pendimethalin were applied to the trial plot and the soil water monitored to 19 February 1991.

The suction samplers were moved to a new plot in 1991 (Clark *et al.* 1992) because of a change in land use on the farm. In the spring (24 April), mecoprop, MCPA, bromoxynil and ioxynil were applied, whilst in the autumn (20 November), isoproturon and pendimethalin were applied. The pore-waters were monitored for mecoprop following the spring application and for isoproturon following the autumn application.

The results of the soil water monitoring at Assarts Farm show that there is no consistent infiltration of pesticides through the soil profile following their surface application under normal agricultural practice. The concentrations of pesticides in the pore-waters at the base of the soil, when they are detected, are low. This supports the conclusions from pesticide leaching models and the data from aquifer profiling (Section 3.4).

A dye tracing exercise using methylene blue was undertaken at Assarts Farm (Gomme *et al.* 1991b, Clark *et al.* 1992). This exercise showed that the dye was adsorbed within a few centimetres of the surface and that there were no preferred flow paths. The infiltration appears to be dominated by intergranular flow. This suggests that sandy soils and subsoils are not prone to pesticide percolation, or are less so than clayey soils which have low primary permeability but are vulnerable to rapid flow via cracks or soil structures.

3.3.2 Granta catchment

Six suction samplers were installed in 1990 at Abington Park Farm in the Granta catchment; three were set to 0.5 m and three to 1.0 m depth. The period of their installation and the subsequent monitoring coincided with a period of intense drought in the area and no samples could be obtained.

The failure of these samplers in the top of the Chalk aquifer illustrates a weakness of such samplers; they can only obtain samples when the soil has no moisture deficit. Additional drawbacks are that the exact provenance of the water is not certain and which fraction of the soil water is drawn into the sampler is not known. The samplers, however, remain a valuable tool in the study of the movement of pesticides in the sub-surface.

3.4 Profiling in Aquifers

The profiling of the unsaturated zone of an aquifer is based on the analysis of cores of about 100-mm diameter. In this project, the Chalk aquifer coring was by the percussion method to obtain U100 cores. In the Sherwood Sandstone, drilling was by the air-flush rotary method. Great care was taken to ensure site hygiene to minimize the risk of cross-contamination. Steam cleaning of core barrels between sampling runs was standard. The Sherwood Sandstone in Nottinghamshire is unconsolidated at shallow depths and core recovery is difficult; adapted coring equipment is needed to retain the core in the core barrel.

A fully quantified analytical method for urons and carbamates in chalk and sandstone was completed in 1991 (Forbes *et al.* 1993a); this allowed the first profiling to begin. Two boreholes were drilled in May 1991 in the Granta catchment in a field used for wheat cultivation. The analytical results showed that the urons had not penetrated deeper than 2 m from the surface in detectable concentrations, despite applications of isoproturon in 1986, 1987 and 1990 (Clark *et al.* 1992).

Later that year, when an analytical method for the triazines in chalk was considered usable though not complete, a third borehole was drilled at the same farm in the Granta catchment. This borehole was drilled in a blind ditch into which the wheat field drained where the first two boreholes were sited. In this case the pesticides penetrated the unsaturated zone to at least 10 m from the surface. Both isoproturon and simazine were present at significant concentrations in the unsaturated zone. It is suggested that the latter borehole demonstrates the importance of both hydraulic and pesticide loading in the ability of pesticides to percolate into aquifers. The field drains receiving run-off from fields may be more important sources of contamination than the fields themselves. It is important also to recognize that profiling may not reveal transport routes through the unsaturated zone via cracks and fissures as shown in the Granta Chalk at two observation boreholes (Section 3.2.2).

In September 1991 four boreholes were drilled at Assarts Farm and the cores analysed for urons and carbamates, and for triazines. The results for urons and carbamates confirm the results from the Granta; no pesticides were detected below a depth of 2 m. Analysis of samples for triazines showed no triazines in these profiles as expected, as none had been applied to the field in question.

The completion of the analytical method for acid herbicides in aquifer materials in 1993 (Forbes *et al.* 1994a) permitted profiling of these pesticides in the autumn of 1993 (Turrell *et al.* 1994). A site on the Chalk aquifer in the Granta catchment was selected on the basis of pesticide usage (mecoprop, MCPA, bromoxynil and ioxynil). Two boreholes were drilled. A return visit to drill two new boreholes was arranged at Assarts Farm (on the Sherwood Sandstone aquifer) where similar pesticide usage had been reported. The details of the sites, borehole drilling and analysis of these four boreholes are given in Turrell *et al.* (1994). With detection limits of less than 0.1 $\mu g\ kg^{-1}$ for mecoprop, MCPA, bromoxynil, and 0.11 for ioxynil, one could have expected evidence of some accumulation in the top few metres of the profiles. No acid pesticides, however, were detected in the chalk profiles from the Granta and, in the sandstone profiles, the only acid herbicide detected was mecoprop, and that was not detected below 4 m from the surface (Figure 3.1). This behaviour is similar to that observed previously with the urons and carbamates and supports the results of the soil studies which indicated that pesticide penetration under normal agricultural usage is quite restricted.

Attempts to develop a reproducible, quantifiable analytical method for triazines in chalk to a low detection limit failed (although the method was successful in sandstone - Chapter 2). A limited method is available for chalk but each sample must be treated on an individual basis, with relatively poor detection limits due to inadequate chromatographic separation. WRc has developed an application of a commercial immunoassay kit for triazines to pore-water analysis for both chalk and sandstone. This provides an invaluable back-up to the GCMS-based method (Clark *et al.* 1992). A borehole drilled in 1993 in the Chalk aquifer at Compton in Berkshire at a site close to one previously drilled by BGS, has been profiled using the immunoassay analyses (Figure 3.2).

The pore-water for the immunoassay analysis is extracted from the aquifer material by centrifugation; the kit therefore measures the pesticide in the most mobile water in the aquifer, compared with the GCMS-based method which measures the total extractable pesticide in the rock plus pore-water. The results obtained from Compton suggest that the concentrations measured by both methods are broadly similar.

A GCMS-based method of analysis for triazines in sandstone had been developed successfully. Two boreholes were drilled in 1993 near Doncaster, in a legume field with a history of triazine applications. The profiles by GCMS detected only trietazine and showed that it penetrated to the bottom of the borehole at 10 m (Figure 3.3). The immunoassay cannot differentiate the triazines, but the profile (Figure 3.4), compared to the GCMS-based profile, suggests that both methods give broadly comparable results.

4. MODELLING

4.1 Background

The transport and fate of pesticides in aquifers are complex processes, as results from the field studies have shown. In order to be able to extrapolate the findings from this project to other areas and other aquifers, it is necessary to fit the findings into a scientific framework. The best way to do this is to build a computer model which includes the main controlling processes. This was recognized in the initial specification for the project by the inclusion of two modelling components:

- development of a model of the Granta Chalk aquifer with the initial aim of demonstrating the feasibility of simulating pesticide fate in groundwater;

- assessment of the needs of the NRA for pesticide prediction tools.

4.2 Achievements - the Granta Catchment Model

The modelling development undertaken in the project benefited significantly from the previous work on nitrate in aquifers. The nitrate models incorporated the processes of leaching from the soil, migration through the unsaturated and saturated zones, interaction between solutes in the fissure water and pore water, and discharge of water and nitrate to wells and rivers, and could be widely applied because of the ready availability of time series data on nitrate concentrations.

A similar model was developed for pesticides in the Chalk of the Granta catchment with special attention being paid to movement through the soils and the processes of retardation and biochemical decay. SSLRC provided soil data for the area, principally the soil thickness and organic carbon content. These were combined with hydrological information, pesticide application rates and pesticide physico-chemical data to determine the quantities which would leach from the soils into the underlying aquifer. Results from the previous nitrate studies had indicated that transport through the unsaturated zone of the Chalk would be either in relatively small quantities through the fissures or in larger amounts through the porous matrix. The pesticide profiling studies showed that degradation continues during transit through the top few metres of the unsaturated zone and it was demonstrated that pesticides could not reach a deep water via this route. Transport through the fissure system is rapid, however, and it was inferred that this is the only viable route for pesticide transport to the water table.

Predictions of pesticide concentrations in groundwater were subsequently undertaken utilising a mixing cell calculation with solute diffusion between the mobile matrix water and immobile pore water. Isoproturon and chlortoluron were simulated with reasonable accuracy, given the limited amount of data available for comparison with the model results. Predictions for simazine and atrazine were generally within a factor of five of measured values. This difference was thought to result from the difficulties in quantifying the spatial distributions of application of these two predominantly non-agricultural herbicides.

The study demonstrated that although the processes of pesticide transport and fate are very complex, appropriate models can be developed and applied with success. Such models could be used for predicting future trends, or for assessing the likely impact of various land use control options. At present, however, the model used here must be considered as a research tool. Its application to other catchments would require a significant input of expertise and associated field studies. In order to produce a widely applicable model, particular attention must be given to the problems of integrating land use (i.e. cropping), pesticide application and soils data. The importance of this component will be apparent from the fact that, in general, over 99 per cent of a pesticide application is degraded during leaching through the soil. It is also very important to correctly simulate the passage of the remaining 1 per cent through the aquifer because a 1 per cent leaching loss would imply significant exceedances of 0.1 $\mu g l^{-1}$ in groundwater in most cases.

4.3 Future Needs - Modelling Strategy for the NRA

Discussions were held with appropriate staff in the Regional offices on the need for models for pesticide simulations. Both a screening tool and a detailed catchment model were seen as future requirements for the NRA, with a validated screening model high on the list of priorities. Such a model is needed to assess the overall risks to water resources of existing and future pesticide usage; this is particularly important in view of the difficulties of monitoring for all pesticides used. Similar requirements exist for groundwater and surface water. It is therefore suggested that appropriate models are developed over the next two or three years to meet these needs, building on software which is already available. Lessons learnt from the considerable programme of research on nitrate in groundwater should be utilized in developing suitable conceptual models for contamination by agrochemicals. The main requirement should be to undertake development and testing in tandem so that new findings and data sets can be quickly included in the model formulation, and data gaps rapidly identified.

Screening models should include the capability to undertake a statistical assessment of pesticide concentrations in water. The same capability could be included in detailed catchment models, but computer run-times may preclude this option. The objective of any modelling approach should be to use the simplest model that will satisfactorily meet the requirements. A versatile screening tool would be easier to develop than a detailed catchment model, and it is suggested that initial efforts are directed to this end. As far as a detailed catchment model is concerned, components of the screening tool should be adopted and used with a groundwater flow and transport simulator to provide an initial version. The use of a GIS-based soil component is also recommended.

Major programmes of research are not required for model development, but rather a gradual progression of software and testing. Testing in a variety of situations is seen as the key to the successful production of a useful product.

The concerns expressed by some NRA staff on the availability of data for use in models are undoubtedly justified. However, models are good for testing hypotheses and for cross checking data; the systematic collection and storage of data on pesticide properties and occurrences should go some way to meeting these concerns in the medium term. Pesticide physico-chemical data are almost completely lacking in the saturated zone; the few values which are available have come from laboratory measurements on aquifer samples. Procedures to measure pesticide properties *in situ* should be investigated, starting with those chemicals which are currently causing most concern.

The main objective of model development will be to produce a pesticide information and risk assessment system for guidance and strategy support to the NRA. This system would facilitate inter-catchment analysis, delineation of high risk areas and the evaluation of those parameters needed for a pesticide risk analysis. In order to take this area forward, the NRA is developing the Prediction Of Pesticides Pollution In the Environment (POPPIE) system.

5. CONCLUSIONS

5.1 Pesticide and Land-use Surveys

The pesticide usage surveys undertaken for the Pesticides in Major Aquifers project gave a synthesis of the national and regional loadings derived from various sources. The detailed land-use and pesticide-use surveys of the Granta catchment were some of the first and most detailed surveys on a catchment scale in the UK, and provided the NRA with an insight into the great number of pesticides in use, the relation between pesticide use and cropping patterns, and the inadequacy of the available analytical methods for the environmental monitoring of pesticides. The analytical methods developed in this project have remedied to a large extent, the latter deficiency.

Pesticide loading data on a catchment scale can now be provided adequately by services such as the FARMSTAT service, so long as the data collection on which such services are based continues. Detailed land-use surveys will continue to be required for specific research projects or small catchment studies.

A major need identified by this project is for non-agricultural pesticide use and impact surveys. The land-use with least known about it but with the most observed impact on groundwater is the non-agricultural pesticide use for weed control on our road and rail systems. It is known that some Water Utilities are undertaking work on this problem.

5.2 Analytical Method Development

Validated methods of analysis of core materials from Chalk and Sandstone aquifers have been developed for the uron, carbamate and acid herbicide groups of pesticides. A method has also been validated for triazines in sandstone, but not in chalk. Further development of the method for triazines in chalk should be considered. This would then provide the NRA with methods for the major groups of pesticides present in the most important UK aquifer materials.

The development of immunoassay techniques for the analysis of pesticides in water is progressing rapidly. The technique has been applied in this project for the first time to the analysis of atrazine, simazine and trietazine in pore-waters in aquifer materials. This work has demonstrated the value of the technique, particularly in the profiling of soils and unsaturated aquifers where the volume of recoverable water for analysis is limited. As immunoassays for other pesticides of concern become available, particularly when the methods provide low detection limits ($<1\ \mu g\ l^{-1}$), their application to the study of pore-waters should be considered.

New pesticides are coming into use and the development of methods for their analysis in water is being actively pursued. Extension of the methods to cover core materials should be considered particularly for pesticides of large usage and with a potential to contaminate water.

5.3 Transformation Products (TPs)

A group of compounds that have not been studied in the present project (and for which little research is being undertaken in the UK) is pesticide transformation products (TPs). In the environment, pesticides degrade and breakdown to their TPs and eventually disappear. At present, the data on pesticide TPs, their occurrence in the hydrological cycle, and their persistence and properties are very limited. Some TPs could have pesticidal properties and therefore be subject to the pesticide concentration limit of $0.1\ \mu g\ l^{-1}$. Other forthcoming EC legislation may highlight the potential problem of pesticide TPs. It is suggested that a programme of work is instigated to begin the study of TPs in aquifers.

The knowledge of TPs is so limited that a programme of work based on the small number of pesticides for which analytical methods are available is recommended. The programme would be aimed initially at demonstrating the occurrence of TPs and their concentrations at sites where the occurrence and behaviour of the primary pesticides are well known. The work could be based on sites studied in the present project. The programme may be extended, depending on progress in the initial phases, to other TPs, other pesticides and other aquifer materials. In addition, a preliminary review of the potential of high-use pesticides (that are not mobile/persistent themselves) to produce significant levels of TPs would be valuable.

5.4. Pesticide Concentration Surveys and Monitoring

The surface and groundwater monitoring has given the NRA detailed information on the occurrence of pesticides in these waters on a catchment scale. The study also has provided the NRA with information on the behaviour of pesticides in surface and groundwaters, and permitted the development of a catchment scale model of pesticide transport. The project has provided a basic understanding of the transport of pesticides in the main UK aquifers.

The need for specific pesticide monitoring will continue for detailed catchment studies or research projects.

Surveys of pesticide concentrations similar to those undertaken by the present project are no longer considered necessary. The monitoring of pesticides in environmental waters by the Water Utilities and the NRA is now considered adequate for the main pesticides in the UK, provided that the analytical data are made generally available. It is suggested that a mechanism is set up whereby the enormous amount of pesticide data now being generated are gathered in a centralized pesticide database.

There still may be a need for regional surveys in surface and groundwater for new pesticides that are not included in the routine monitoring by the NRA and utilities.

A preliminary survey of pesticides in rainfall has been completed. The survey has shown that rain contains significant concentrations of pesticides but the logistical difficulties of successful sampling are great. A more focused study may present the NRA with valuable data on this potential catchment input.

5.5 Aquifer Studies

Following the successful field demonstration of the analytical methodology for pesticides in solid aquifer material, the NRA now has a valuable capability for producing detailed profiles of pesticide movement in the unsaturated zones of both Chalk and Sandstone aquifers.

The profiles provide previously unavailable data of pesticide persistence and migration in the unsaturated zone and give the NRA a tool for quantifying herbicide fluxes moving towards the water table. The profiles obtained in the 1993 field season are given in Figures 3.1 to 3.4.

The few profiles available should be interpreted with caution. The urons, carbamates and acid herbicides do not appear to penetrate deep into the unsaturated zone. Under normal agriculture they are believed to degrade and present little threat of groundwater pollution. The more persistent herbicides like the triazines penetrate deep into the unsaturated zone, particularly after repeated applications, and do present a pollution threat.

The profile of the atrazine (Figure 3.2) is peaked similar to profiles of nitrate percolation. This suggests that the 'normal' mode of transport of pesticides may be by intergranular movement as for the inorganic contaminants. Each peak on the profile may represent one pesticide application. The slow movement this interpretation suggests, would allow time for degradation to remove most of the pesticides.

The pollution potential increases with persistence and with the possibility of by-passing intergranular flow through fast-flow fissures in the aquifer. Factors affecting this chance of initiating the by-pass mechanism include:

- loading rate each year;
- number of years of application;
- intensity and pattern of rainfall;
- time of application;
- soil characteristics;
- fissure development in aquifer;
- drainage features (natural or man-made).

The data have important consequences for land management and aquifer protection as the accuracy of any modelling of pesticide transport depends heavily on these measurements of pesticide behaviour in the sub-surface.

The profiling work completed to date has improved current understanding of the fate of agriculturally-applied pesticides and their possible impact on water quality. The profiles have been useful but their number is still pitifully small, and more profiling is needed to supplement the current database. The present project could be used as a basis for repeat profile studies in the future to study the rates of decay in aquifers and further improve the pesticide transport models.

5.6 Modelling

A preliminary catchment scale model of pesticide transport in the Chalk aquifer has been completed, but it is recognized that to make this an operational model a great deal more data on the behaviour and occurrence of pesticides in the environment will be required.

A review of the present status of pesticide models has shown that two types of model are required - screening models and catchment models. A priority should be given to the development of screening models to enable the NRA to assess the likely impact on the environment of new pesticides or changes in the usage of existing chemicals. Comparable screening models for surface waters were also identified as an immediate requirement.

The development of catchment models is less urgent but will be required to allow control policies of the NRA, such as pollution zones, to be evaluated. The development of such catchment models is expected to rely heavily on GIS technology but will also depend on the improvement of the pesticide database, most importantly the database on pesticide properties and their behaviour in the sub-surface. Accurate measurement of the rates of breakdown of pesticides under natural conditions will be essential in this modelling. The major aquifers in the UK are all to some extent dual porosity aquifers and part of the water transmission system is through fast-flow pathways such as fissures. Catchment models for the UK will have to incorporate this fast-flow element of pesticide transport in their simulations.

6. RECOMMENDATIONS

As a result of this work, a range of potential future options have been identified. These will be considered by the NRA and, where appropriate, taken forward through the National Centre for Toxic and Persistent Substances.

A programme of study addressing the transformation products of the pesticides in major use should be instigated. An outline of an initial project is given in Section 5.3.

An associated project should be started to quantify the rate of degradation of major pesticides in the sub-surface. Under closely controlled conditions, a well-field could be drilled to allow a target pesticide to be injected into one borehole, travel through the aquifer and be abstracted from another. Careful monitoring of the pesticide concentrations as injected and recovered would provide information on the degradation rates.

A comprehensive database of the physico-chemical properties of pesticides and their TPs should be assembled. This will be needed for any risk assessment study whether or not detailed models are developed. Particular attention will need to be given to obtaining data on degradation rates in groundwater, though as a worst case assumption zero decay could be assumed.

A review of research in the UK into the transport and fate of pesticides, particularly on a catchment scale, should be undertaken to provide a coherent database of such research.

In view of the widespread occurrence of non-agricultural pesticides (Section 3.1) in groundwaters, a detailed survey of the impact of non-agricultural use of pesticides on water resources is recommended. This survey should be based on a catchment in which the impact of both road and railway usage could be studied.

The detailed survey could be supplemented by a regional and/or national survey of non-agricultural pesticide use. The latter would incorporate or add to similar surveys funded by other agencies.

Screening models for assessing the risk of pesticides to water resources should be developed taking particular account of UK conditions, such as the importance of fissure flow in the major aquifers. Catchment models should be developed within the next 2 or 3 years building on concepts and databases used in the screening models and making full use of GIS technology. The general aim of development would be to produce a pesticide information and risk assessment system of direct use to the NRA's pesticide studies.

Particular emphasis should be given to testing models as they 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.

Various aspects of analytical method development for pesticides could be pursued:

(a) The development of the analytical method for triazines in chalk should be completed.

(b) The use of immunoassay for pesticide analysis in water should be reviewed and, where feasible, should be transferred to the analysis of aquifer materials.

(c) Analytical methodology should be developed to include major TPs believed likely to be present in environmental waters and therefore of concern.

(d) Analytical methodology should be developed to encompass new pesticides in water, and extended to the analysis of aquifer materials.

This project has seen the development and implementation of pesticide profiling in the unsaturated zone. Such profiling is vital for the calibration of mathematical models of transport through the unsaturated zone. The present profiling database is very small and further profiling of pesticide concentrations in aquifers could be undertaken in future projects.

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