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Transport and fate of pesticides in the Chalk aquifer of southern England

Groundwater Systems and Water Quality Programme

Research Report RR/02/04

BRITISH GEOLOGICAL SURVEY

RESEARCH REPORT RR/02/04

Transport and fate of pesticides in the Chalk aquifer of southern England

P J Chilton, M E Stuart, D C Gooddy, R J Williams*, A C Johnson* and A H Haria*

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Key words

Chalk; pesticides; groundwater

Front cover

Sampling an observation borehole at the margin of a maize crop

Bibliographical reference

CHILTON, P J, STUART, M E, GOODDY, D C, WILLIAMS, R J, JOHNSON, A C, AND HARIA, A H. 2002. Transport and fate of pesticides in the Chalk aquifer of southern England. *British Geological Survey Research Report*, RR/02/04. 36pp.

ISBN 085272 405 5

Keyworth, Nottingham British Geological Survey 2002

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Foreword

This report is the published product of a six-year study by the British Geological Survey (BGS) and the Centre for Ecology and Hydrology (CEH) that evaluated the transport of pesticides through soil and the unsaturated zone of the Chalk aquifer.

The project was undertaken jointly by BGS and CEH staff and staff who contributed significantly to the project are listed below together with their roles.

British Geological Survey

John Chilton – BGS team leader, hydrogeology

Daren Gooddy – development of field sampler, field programme

Marianne Stuart – data compilation, pesticide properties

Julie West – microbiology, pesticide degradation

Kerry Dodd – field sampling, chemical analysis

Steve Baker – microbiology, degradation experiments

Pat Coombs – degradation experiments

Ian Harrison – pesticide analysis

John Bloomfield – fracture surveys

Peter Williams – field sampling, pore water extraction

Centre for Ecology and Hydrology

Richard Williams – CEH team leader, modelling

Andrew Johnson – microbiology, laboratory studies of degradation, column studies

Atul Haria – soil physics

Tim Besien – development of ABPSS field sampler, column studies

Craig White – field sampling, soil physics

Lal Bardwaj – pesticide analysis

Andy Dixon – drilling and sampling

Acknowledgements

In addition to the BGS and CEH staff acknowledged in the Foreword, a number of others have contributed to the project. The authors are grateful to the following groups and individuals:

- CEH and BGS workshops and CEH Instrument Section for supply and repair of project instrumentation
- CEH analytical staff, James Dodd, Heather Wickham, Linda Hill, Margaret Neal and Christopher Smith for processing of samples and laboratory analysis
- David Kinniburgh and other staff of the BGS 'denitrification' project for provision of core material from Bridgets Farm
- ADAS staff at Bridgets Farm, Hampshire for the supply of climatic data.

Most importantly thanks are due to the farmers in whose fields the fieldwork sites were located for their help in allowing access to their land, accommodating field requirements and providing comprehensive information on cropping and pesticide use.

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Summary

Increasing numbers of pesticides have been detected in groundwater as pesticide-monitoring programmes have been developed in recent years. These findings have stimulated interest in research into the mechanisms by which pesticide pollution might occur, the routes by which pesticide residues could move from the land surface through the soil and the unsaturated zone to the water table, and the environmental conditions which would promote such movement.

This report summarises the results of a NERC-funded, multidisciplinary project carried out jointly by the Centre for Ecology and Hydrology (CEH) and the British Geological Survey (BGS). The project commenced in April 1993, originally ran for three years and was eventually extended to March 1998. The transport of pesticides through soils and the unsaturated zone is a subject at the interface between the work of the two institutes within the continuum of the hydrological cycle. The project was able to make use of the sites and installations established by BGS in a previous project for the Environment Agency and the field instrumentation techniques developed and used by CEH.

This study was focused on the Chalk aquifer of southern England, with the overall objective of establishing the routes of transport to and within the aquifer and examining and quantifying the processes that control pesticide fate and behaviour. The project objectives were formulated into two principal scientific questions; how do pesticides move through aquifers and how active are attenuation processes beneath the soil. Within these overall objectives the specific aims of the study were to:

- observe pesticide residues in the soil and the unsaturated and saturated zones of the Chalk, including the development of appropriate sampling techniques
- study the mechanisms and establish the importance of different recharge routes in the Chalk aquifer
- assess and measure the potential for degradation and adsorption in the soil and the Chalk.

Project activities included a broad range of field and laboratory techniques, some of which were modified or developed specifically for the project:

- shallow coring and pore water sampling
- development of automated borehole sampling equipment
- study of recharge using soil moisture measurements
- tracer testing
- degradation studies in laboratory microcosms.

The results of the study provide some of the first field evidence in the UK for the fate of agricultural herbicides in the Chalk aquifer. Sampling in the unsaturated zone at five sites in southern England has observed low concentrations of atrazine (generally <3 μg/L) and almost negligible concentrations of isoproturon in both solid chalk and pore water samples. Regular sampling of groundwater from the uppermost part of the saturated zone has also produced consistently low, although not negligible, concentrations (<0.9 μg/L atrazine and <0.6 μg/L for isoproturon), indicating that relatively little pesticide is reaching the water table. It may be that some short-lived occurrences at the water table could have been missed. However, it seems unlikely that troublesome concentrations of pesticides derived from normal agricultural use will develop in Chalk groundwater if movement through the matrix is the only transport mechanism operating and a single compound is to be applied throughout the catchment.

While more rapid transport from the soil to the Chalk water table via fractures can be envisaged, evidence from the study suggests that conditions that promote such transport are likely only to occur on a few occasions in each recharge season. Attempts to sample directly recharging water by the development of novel sampling techniques have achieved more frequent positive detections of pesticides but still at modest concentrations.

Bacteria capable of degrading pesticides were found in the Chalk aquifer, albeit in smaller populations than in the soil. However, the degradation potential was not evenly distributed in the Chalk, and appeared to be a variable and even transient quality. For the pesticide isoproturon, although degradation is confirmed as being slower than in the soil it can still be effective in breaking down the parent compound and produces metabolites which can be identified. However, no potential was found for atrazine degradation in the present study and the results for mecoprop were equivocal. The observed spatial and temporal variability of pesticide persistence in the subsurface provides an indication both of the dangers of using data from a single location or time in predictions of pesticide fate and behaviour and of the difficulty and cost of obtaining more applicable data.

A number of important uncertainties remain and further work is required in the following areas:

- developing microcosm studies at observed (low) pesticide concentrations and ambient (low) temperatures
- identification and characterisation of microbial populations and their differing abilities to degrade pesticides
- characterising degradation pathways, identification of pesticide metabolites and determining their transport properties
- characterising fracture flow conditions and sampling fracture flow as it occurs.

1 Introduction

1.1 BACKGROUND

Advances in understanding of the processes responsible for the widespread increase in nitrate concentrations in groundwater led naturally to consideration of the risk to water supplies from pesticides. If nitrate could be leached from agricultural land to the underlying groundwater, then it seemed likely that, with intensification of pesticide usage, some of the more mobile pesticide compounds could also be leached. Research into pesticide fate and behaviour in the subsurface was initially hampered by the technical sophistication and high cost of achieving the detection limits required in relation to the EC Directive maximum allowable concentration in drinking water of 0.1 µg/L for any compound (Lawrence and Foster, 1987; Foster et al., 1991). Although analysis was indeed difficult and expensive, pesticides began to be detected in groundwaters (Croll, 1986; Cohen, 1990; Leistra and Boesten, 1989). As monitoring programmes have been developed, often in response to stricter environmental regulation and/or drinking water standards, more recently published results have shown increasing numbers of pesticides occurring in groundwaters in the UK (NRA, 1995; EA, 1998), Europe (Spliid and Køppen, 1998) and North America (Barbash and Resek, 1996; Kolpin et al., 1996).

These findings have stimulated interest in research into the mechanisms by which pesticide pollution might occur, the routes by which pesticide residues could move from the land surface through the soil and the unsaturated zone to the water table, and the environmental conditions which would promote such movement. In view of the relatively slow response time of groundwater systems, knowledge gained from such research is required if the current situation is to be adequately appraised, the implications for future groundwater quality are to be evaluated and any necessary controls on pesticide use are to be introduced. The results of the research are, therefore, of interest to environmentalists, regulatory agencies, water utilities and the agrochemical companies.

The principal aquifers providing public water supplies in the UK are the consolidated sedimentary formations of the Triassic Sherwood Sandstone, the Jurassic Lincolnshire Limestone and the Cretaceous Chalk. These aquifers have the potential to permit transport of pesticides through both the matrix and fractures and the latter, which is often referred to as 'preferential flow', could allow very rapid transport to the water table and in the saturated zone towards abstraction sources. In such aquifers, both of these possible routes for contaminant transport, and the perhaps very different potential for pesticide attenuation that they offer, need to be characterised.

Prior to the present joint study, both the Centre for Ecology and Hydrology (CEH) and the British Geological Survey (BGS) had been independently studying the fate and behaviour of pesticides in the aquatic environment for several years. The former concentrated largely on the transport of pesticide residues in runoff and drain flow to surface waters (Williams et al., 1995), and the latter on transport of pesticides through the unsaturated zone of the Chalk to the water table (Chilton et al., 1993). The experience gained in these studies confirmed that the study of pesticide fate and behaviour was indeed difficult and complex. It was considered appropriate, therefore, to bring together the skills of both institutes into a joint project, which was undertaken by the multidisciplinary team listed in the front of this report. The transport of pesticides through soils and the unsaturated zone is a subject that comes exactly at the interface between the work of the two institutes within the continuum of the hydrological cycle. It is, therefore, an ideal topic for joint study with NERC funding, and a three-year project commenced in April 1993, and was eventually extended to March 1998. The project was able to make use of the sites and installations established in the BGS project and the field instrumentation techniques developed and used by CEH.

1.2 OBJECTIVES OF STUDY

Information is required on the three-dimensional subsurface distribution of pesticide residues, especially where intensive agricultural land overlies the recharge areas of aquifers providing potable water supplies. The present study was focused on the Chalk aquifer of southern England, with the overall objective of establishing the routes of transport to and within the aquifer and examining and quantifying the processes that control pesticide fate and behaviour. The project objectives can be formulated into two principal scientific questions:

- How do pesticides move through aquifers?

  Matrix flow allows time for attenuation; more rapid fracture flow might not

- How active are attenuation processes beneath the soil?

  Most existing data come from studies on soils, very few from aquifers

Answers to both questions are required if soundly based predictive models are to be developed to assess the scale of present or future problems of pesticide contamination of aquifers from agricultural activities.

1.3 SCOPE OF REPORT

The present report is the final technical report of the study. It provides a summary of the work undertaken and the results achieved, briefly discusses the implications for groundwater quality and highlights some of the remaining uncertainties that require further work. Greater detail concerning methods, results and interpretations is given in the two interim technical reports produced in 1995 (British

Geological Survey and Institute of Hydrology, 1995) and 1996 (British Geological Survey and Institute of Hydrology, 1996) and the various scientific publications originating from the study. These are referred to where appropriate, and should be consulted by the interested reader. However, it is the intention that this report can be read as a self-contained document, particularly as the interim reports were produced in very limited numbers. A full list of publications originating from or containing results obtained in the joint study is given in Section 6.

2 Methods of study

2.1 CONTEXT OF STUDY

2.1.1 The Chalk aquifer

The Chalk is a soft, microporous and fractured calcium carbonate aquifer with high intergranular porosity (25–45%) but low intergranular hydraulic conductivity because of the small pore-neck sizes. The Chalk is, however, usually fractured, and the fracture component has low porosity (0.1–1%) but can increase the hydraulic conductivity by up to three orders of magnitude (Price et al., 1982). There is, therefore, scope for water to move very slowly through the matrix and much more rapidly via the fractures. A number of hydrological and tracer studies have examined water movement through the Chalk. Tracer profiles in the Chalk unsaturated zone were interpreted by Barraclough et al. (1994) and Foster (1993) as suggesting that flow was dominantly through the matrix. An extensive investigation at a nearby Chalk site, using the same range of soil instrumentation as in the present study, also suggested that unsaturated zone water movement was largely through the matrix (Wellings, 1984).

The re-appraisal of data from the large and heavily-instrumented chalk lysimeter at Fleam Dyke (Jones and Cooper, 1998), confirmed the findings of Wellings (1984) that fissure flow was only likely to occur when matric potential exceeded –50 cm H_2O. Hydraulic conditions, which would promote flow in the fractures, occurred rarely, but if this happened while there were significant amounts of pesticide in the soil soon after application, then rapid transport to the water table could be envisaged. However, Price et al. (2000) suggest that fissure flow is not necessarily generated by water moving down from the soil but may occur anywhere in the profile where matric suction has fallen sufficiently.

2.1.2 Pesticide persistence in aquifers

With respect to the second scientific question, identified in Chapter 1, much of the available information on the physicochemical properties of pesticides is derived from the trials that are undertaken by the manufacturers as part of the registration process. These are invariably performed on ‘standard, fertile, organic clay soils’ and there is a lack of information on the behaviour of pesticides in aquifers. Because little is known about subsurface microbial ecology, predictions about pesticide degradation in this environment are particularly difficult. Much of the albeit limited work on pesticide degradation in groundwater systems has focused on shallow, unconsolidated, usually sandy aquifers (Klint et al., 1993; Heron and Christensen, 1992). Far less is known about how microbial communities might behave with respect to pesticides in a consolidated and fractured rock such as the Chalk aquifer of the UK, although very recent work in Denmark has begun to address this (Albrechtsen et al., 2001).

In many incidents of point source contamination of groundwater, high concentrations of xenobiotic substrates can stimulate the indigenous microflora (Harrison et al., 1998). In contrast, pesticides applied during normal agricultural practice will arrive at the water table at much lower concentrations, as this and other studies have confirmed. Thus, knowledge is required of whether the indigenous microbial population is competent to degrade these compounds, and whether they will do so at the low ambient temperatures and at sub μg/L concentrations. Skipper et al. (1996) suggested that a pesticide concentration of 0.5 μg/L would be insufficient on its own for micro-organisms to derive growth or energy benefit. However, if the degradation were due to co-metabolism, due to a fortuitous similarity with a natural substrate, then concentrations would be less important.

2.2 SCIENTIFIC APPROACH AND SUMMARY OF PROJECT ACTIVITIES

Within the broad overall objective of understanding transport mechanisms and attenuation processes, the specific aims of the study were to:

- observe pesticide residues in the soil and the unsaturated and saturated zones of the Chalk, including the development of appropriate sampling techniques
- study the mechanisms and establish the importance of different recharge routes in the Chalk aquifer
- assess and measure the potential for degradation and adsorption in the soil and the Chalk.

Project activities included a broad range of field and laboratory techniques, some of which were modified or developed specifically for the project, as shown in Table 2.1. These are briefly summarised in the following sections, and described in more detail in the interim reports and published papers, which are referred to where appropriate.

2.3 SELECTION OF FIELD SITES

Selection criteria for field sites were developed in the earlier BGS study (Chilton et al., 1993). A very important consideration was to locate sites where the water table would be within 5–10 m of the ground surface to allow reasonably easy sampling of groundwater from the saturated zone. Such sites with shallow water tables would also be the most vulnerable to pollution and hence offer the best chance of pesticide residues reaching the underlying groundwater. Perusal of hydrogeological maps (British Geological Survey, 1979) shows that suitable areas of the Chalk outcrop in which the water table is shallow are rather

Table 2.1 Summary of scientific tasks and methods employed.

Scientific task	**Method employed**	**New development or adaptation**
Determine pesticide residues in soil and Chalk matrix	Drill and retrieve core samples for solid and liquid extractions	Use of the ELISA technique
Detect arrival of pesticides at the water table	Regular groundwater sampling from observation boreholes	Multi-level hanging sampler and automatic pumped sampler
Mechanisms of water movement in the unsaturated zone	Installation of soil moisture instrumentation to 3 m depth. Soil and chalk inspection pit	Integration of structural geology and hydrology
Confirmation of origin of pesticide in groundwater	Application of pesticide chlortoluron not used before	
Solute movement in deep unsaturated zone	Laboratory chalk columns. Shallow coring in field	New lab method developed Bromide tracer test
Pesticide degradation potential of aquifer material	Laboratory microcosms using chalk and groundwater	Method refined in project

restricted. In the river valleys, water tables are indeed shallow, but alluvial deposits overlie the Chalk and on the interfluves the unsaturated zone can be as much as 60 m thick, so the most likely sites are on the valley flanks. Thus, sites were selected which met the following criteria:

a) on the Chalk outcrop with the water table at a depth of 5–10 metres

b) regular use of the selected compounds

c) good records of cropping and fertiliser use going back at least five years

d) farmer willing to permit drilling and sampling, including the construction of permanent observation boreholes.

Site selection to meet these criteria was a three-stage process. Firstly, areas meeting condition a) were selected from hydrogeological maps and other sources of existing groundwater information, particularly the BGS national borehole archive. Secondly, the designated areas were passed on to local ADAS staff, so that potential farms meeting criteria b) to d) could be identified. Finally, BGS staff visited a number of the farmers to explain the aims and methods of the study, to confirm cropping records and pesticide usage and to agree access for fieldwork. A condition of their participation was that precise locations would not be used in reporting the results of the study.

Several sites were selected (Figure 2.1) and, following on from the work described by Chilton et al. (1993), fieldwork continued at three sites in Hampshire within the joint study. Two of the sites, AWC and ASM situated on the Upper Chalk in the upper part of the Itchen Valley, have been used only for continuing saturated zone sampling. The third site, WON, has been the main focus of activity in

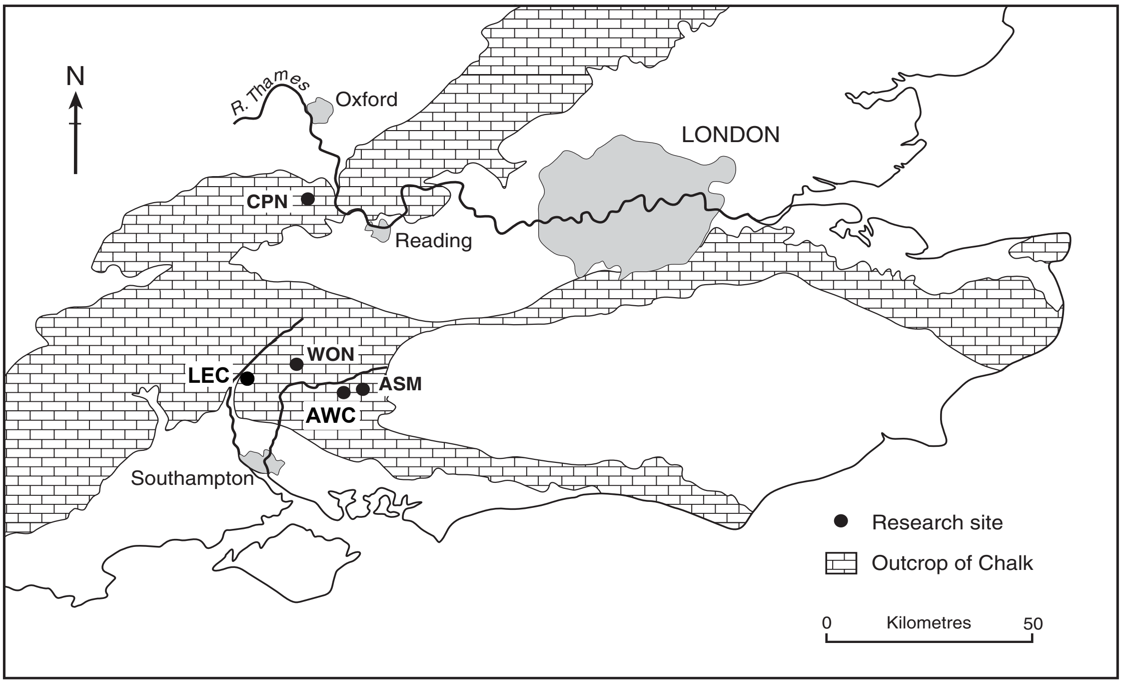

Figure 2.1 Location of field sites on the Chalk outcrop of southern England.

the joint study, and the hydrogeological setting of the site is summarised below. Earlier data from sites CPN and LEC are also discussed for completeness.

2.4 HYDROGEOLOGICAL SETTING OF SITE WON

The site is located on the flank of a shallow east–west trending valley of a tributary of the River Test, at about 70 m OD. Although some alluvial deposits are present in the valley itself, they are absent from the site, which is indicated from the hydrogeological map (British Geological Survey, 1979) to be directly on the aquifer outcrop. The site is situated on the Upper Chalk (in the traditional stratigraphy, equivalent to the White Chalk Formation in the revised stratigraphy of Bristow et al., 1997). The overlying soil is of the Andover series, which has a 0–20 cm Ap horizon of dark brown, slightly stony silty clay loam, and a 20–40 cm Cu horizon of fragmented chalk and flints in brown soil.

The strongly weathered upper zone of the Chalk is found at depths of 30–60 cm and this becomes consolidated at 1 m below ground level. Although there is no trace of the original bedding surfaces at this depth, discrete fracture surfaces can be identified. Field observations at this site suggest that fracturing in the consolidated chalk increases in intensity with depth.

The field in which the study activities have taken place has a 5^{o} slope westwards towards a small northward-trending side valley. The depth to groundwater thus varies from about 18–20 m at the top of the field to 4–5 m in the north west corner where the first boreholes were drilled (Figure 2.2). The regional direction of groundwater flow is towards the west and west-south-west and the River Test, with a hydraulic gradient of 0.002 to 0.004. More locally, the hydraulic gradient may be even less, reflecting the position on a broad Chalk interfluve, and modified by the local topography to a more northerly direction (Figure 2.3), towards the tributary stream referred to above. The locations of boreholes and the inspection pit are also shown in Figure 2.3.

2.5 CROPPING PATTERNS AND PESTICIDE USAGE

Records of cropping and pesticide usage at the three sites are summarised in Table 2.2. In practice, pesticide usage on the different crops in the rotation is highly complex, with many compounds and mixtures being employed. Table 2.2, therefore, summarises only the target compounds of interest within the present study, and full details are given in Chilton et al. (1993) and British Geological Survey and Institute of Hydrology (1995). In addition, chlortoluron was applied at site WON to part of the field at 2 kg/ha in October 1996 so that the fate and behaviour of a pesticide which had not been previously used could be examined (Table 2.1).

2.6 SOIL AND UNSATURATED ZONE SAMPLING

Several aspects of the study (Table 2.1) required sampling from the soil and from the unsaturated zone of the Chalk. Sampling for pesticides in the unsaturated zone followed two approaches: to look for residues in the soil and chalk matrix and in the contained water. The methods employed in the present study are summarised in Table 2.3, indicating where more detailed descriptions can be found. The pore water method was initially developed by BGS for the study of inorganic solutes, particularly nitrate, and comprises high-speed centrifugation of crushed core material to

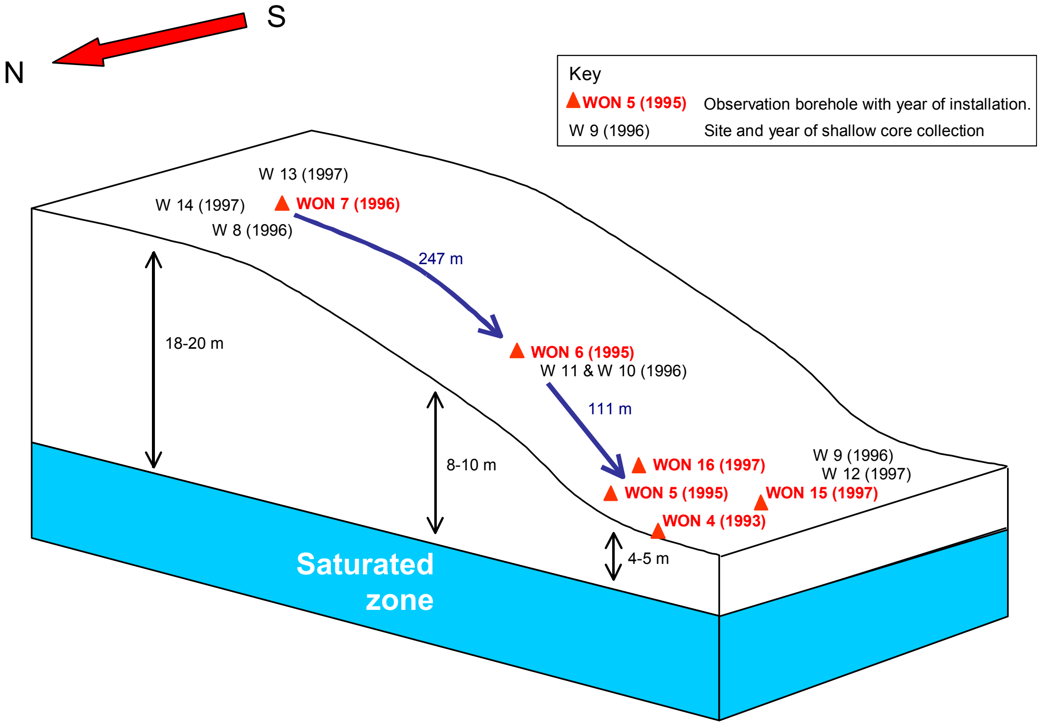

Figure 2.2 Schematic cross-section through site WON.

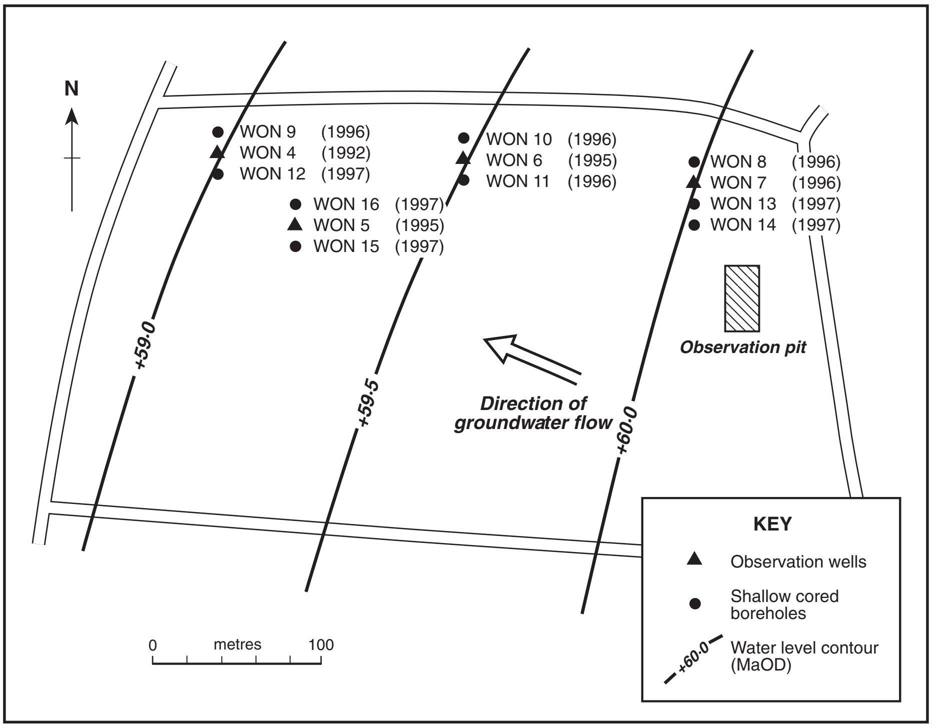

Figure 2.3 Site WON, showing boreholes, inspection pit and Chalk piezometric contours.

remove water from the aquifer matrix and collection by the centrifuge drainage method (Kinniburgh and Miles, 1983). In the initial part of the study, while analytical methods were still under development, 250-mL samples were required for pesticide analysis, the collection of which was a time-consuming task.

Use of an enzyme linked immuno-sorbent assay (ELISA) method has the great advantage of requiring much smaller volumes of water — 2 mL of 0.20 µm filtered pore water was sufficient. Additional unfiltered pore water samples of 4–10 mL were taken for dissolved organic carbon (DOC), and two 0.45 µm filtered 4–10 mL samples were taken, one unacidified for anions and the other acidified for cations. Methods for extracting pesticide residues from the solid chalk core have been developed for isoproturon, chlortoluron and atrazine as shown in Table 2.4 at the end of the Section.

As the basis for the sampling programme, continuous, undisturbed cores from the Chalk unsaturated zone were obtained using a lightweight site investigation rig of the Pilcon Wayfarer type (Plate 1). The undisturbed samples were retrieved by driving steel tubes of 100 mm diameter and 0.45 m length into the chalk. For the 1991–92 drilling at the four sites in Hampshire, 150 mm diameter tubes were used to allow for the extraction of the larger volumes of pore water referred to above (Chilton et al., 1993). The cores were retained within a PVC liner, capped and taped securely with the top and bottom depths carefully recorded. The cores were stored at –20^{o} C until extraction. Moisture contents were routinely measured by oven drying for soil

Table 2.2 Cropping patterns and pesticide usage at study sites.

Crop Year	WON		AWC		ASM	
	Crop	Isoproturon in kg/ha (Date applied)	Crop	Isoproturon in kg/ha (Date applied)	Crop	Atrazine in kg/ha (Date applied)
1987	Winter wheat	-	Oilseed rape	-	Maize	0.1(5/87)
1988	Winter wheat	2.6 (2/88)	Winter wheat	2.2 (11/87)	Maize	0.14(5/88)
1989	Winter barley	0.25 (1/89)	Winter wheat	2.0 (11/88)	Winter wheat	-
1990	Turnips & barley	-	Winter barley	2.2 (11/89)	Maize	0.14(4/90)
1991	Grass	-	Winter barley	3.0 (10/90)	Winter wheat	-
1992	Peas	-	Oilseed rape	-	Maize	0.1(6/92)
1993	Winter wheat	-	Winter wheat	2.2 (12/92)	Winter wheat	-
1994	Winter wheat	2.1 (3/94)	Winter wheat	2.2 (12/93)	Maize	0.1(6/94)
1995	Winter barley	0.45 (11/94)	Set aside	-	Set aside	-
1996	Spring barley	-	Winter wheat	-	Winter wheat	-
1997	Grass	-				

Table 2.3 Summary of unsaturated zone sampling methods.

Material sampled	Objective	Approach	Detailed method description
Soil	Determine isoproturon residues after application	Weekly from top 0.02 m and occasionally to 0.2 m. Methanol extraction for pesticide.	BGS and IH (1996)
Solid chalk	Determine vertical distribution of pesticide residues	Subsamples from cores at regular depth intervals, methanol extraction	Chilton et al. (1993)
	Determine bacterial numbers	Scraping with sterile spatula from centre of cores	Johnson et al. (1998)
Chalk pore waters	Determine vertical distribution of dissolved pesticides	Centrifuge extraction of water from crushed core for analysis by HPLC and ELISA	Chilton et al. (1993), Gooddy et al. (2001)
	Determine transport of applied bromide tracer	Centrifuge extraction of water from crushed core for chemical analysis	Haria et al. *(in preparation)*
	Examine unsaturated zone transport mechanisms	Centrifuge extraction of water from crushed core for analysis for nitrate and chloride	Gooddy et al. (2001)

and unsaturated zone samples. Material from the cores was used for the batch sorption and column leaching studies, as well as for the microcosm experiments on pesticide degradation, as summarised in Section 2.8 below.

2.7 SATURATED ZONE SAMPLING

In the initial phase of fieldwork, one permanent observation borehole was constructed at each of the Hampshire sites. The 150 mm diameter drilling was continued to approximately 3 m below the rest water level at the time of construction. Sufficient slotted 78 mm ID PVC casing was installed to accommodate the seasonal fluctuations in water level, and the annular space adjacent to the slots filled with clean gravel, then a 0.5 m bentonite seal and cement grout to the surface. These boreholes were sampled once or twice per month using a battery-operated submersible pump especially designed for groundwater sampling. This was used to purge the equivalent of 4–5 volumes of the water standing in the borehole prior to sampling. Pesticide (2.5 L) and total organic carbon (8 mL) samples were collected in suitably cleaned glass bottles capped with aluminium foil-lined tops. In addition, two 30-mL filtered (0.45 µm) samples were taken for chloride and nitrate analysis. The groundwater level was measured on each occasion with an electric dipper prior to sampling.

At site WON, groundwater samples were obtained in this way from boreholes WON 6 and WON 7 following their construction in 1995 and 1996 respectively (Figure 2.2). The overall objective of the saturated zone sampling was to determine the pesticide concentrations arriving at the water table in the infiltrating water. While the regular pumped samples were restricted to the uppermost part of the aquifer, they would nevertheless still reflect the influence of dilution of the infiltrating recharge from the aquifer immediately around the borehole in the broader lateral groundwater flow. To try to focus sampling more closely on the direct and more rapid infiltration through fractures in the Chalk, a hanging multi-level sampler and programmable automatic pumped sampler (ABPSS) were developed and installed at site WON. Further details of the construction and operation of these samplers are given by Gooddy et al. (2001).

The first, accompanied by a pressure transducer to measure groundwater levels, collected water samples during periods of rapid water table rise. It consisted of a 3.5 m long frame suspended by a chain from the borehole top, and containing nine 500-mL sampling flasks, each with a novel float-controlled sealing mechanism (Figure 2.4). As the water table rose following recharge, successive flasks filled, and the continuous record of the water level allowed the exact time of sampling to be determined. Following recharge events, the sampler was withdrawn and the collected water from each canister was decanted into pre-cleaned 500-mL amber glass bottles for analysis. Small, filtered samples were also collected for anion determination.

The ABPSS could be programmed to take pumped groundwater samples at frequent intervals immediately following pesticide application (Plate 2). Prior to sampling, the pump automatically purged the borehole by removing 4–5 volumes to waste. Sampling intervals ranged from daily to every eight hours following pesticide application. Because a large number of samples were collected in this way, rainfall and water level data were used to select samples from during possible recharge events for analysis.

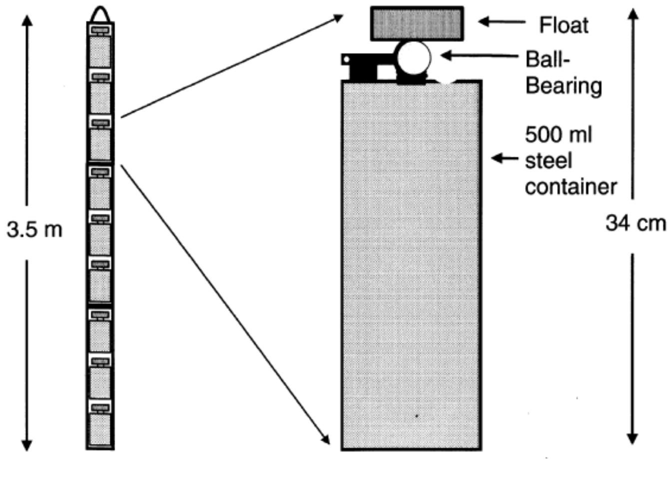

Figure 2.4 Schematic diagram of multi-level sampler system.

Plate 1 View of top of site showing drilling rig at WON 7 and the observation pit with excavated material.

Plate 2 Groundwater sampling at WON 5 using the ABPSS.

Plate 3 Installation of a pressure transducer tensiometer.

Plate 4 Taking readings from a pressure transducer tensiometer array with neutron probe access tubes behind.

2.8 SOIL AND UNSATURATED ZONE HYDROLOGICAL MEASUREMENTS

A comprehensive array of soil and unsaturated zone hydrological instrumentation was installed at site WON (Figure 2.5 and Plates 3 and 4). Rainfall was measured by a recording tipping-bucket rain gauge (0.5 mm per tip). Soil temperature was recorded by three soil thermistors at 0.015, 0.1 and 0.3 m depths. Changes in soil water content were recorded by capacitance probes set at depths of 0.1 and 0.3 m. Soil water potentials were measured by eight pressure transducer tensiometers (PTTs) at the depths shown on Figure 2.5. These were installed by augering through guide tubes to ensure accurate depth placement and tight contact with the soil. Data loggers recorded hourly for rainfall, thermistors, capacitance probes and PTTs throughout the field season. Weekly measurements of soil water content were obtained by neutron probes installed to 3 m depth. Limited samples of surface runoff were collected by run-off traps (Johnson et al., 1994) and suction samplers. A similar array of soil instruments was installed in the upper part of the field close to borehole WON 7 (Figure 2.3) from September 1996 to June 1997.

2.9 LABORATORY STUDIES

Laboratory studies have been a major component of the overall research programme (Table 2.1), using the core samples of Chalk obtained at various times during the project.

2.9.1 Enumeration of bacteria

Assessments of the number of viable aerobic, heterotrophic bacteria were carried out on samples of core material. These were obtained by scraping from the centre of the core with a spatula sterilised in methanol. Bacterial enumeration was carried out using the method described by Johnson et al. (1998). This technique had previously been employed successfully for subsurface samples (Johnson and Wood, 1992).

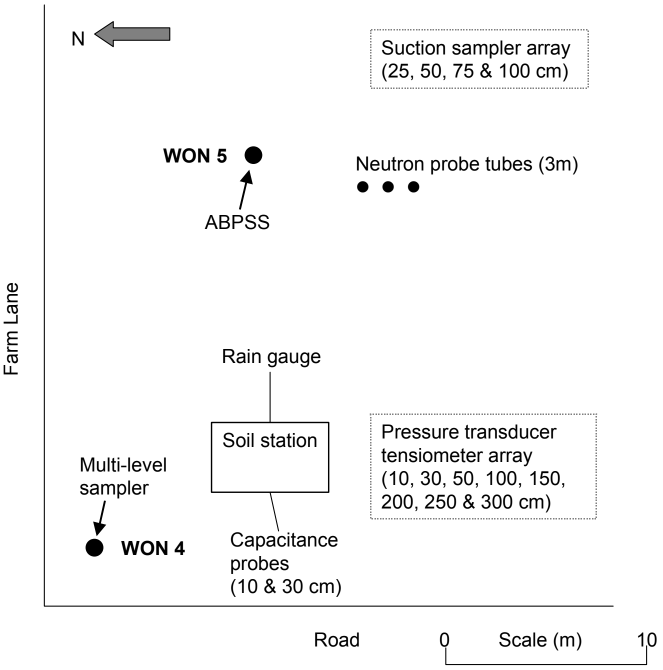

Figure 2.5 Schematic layout of soil and unsaturated zone instrumentation at Site WON.

2.9.2 Degradation of pesticides in microcosms

For the microcosms, fresh chalk from the unsaturated and saturated zones was obtained from new cores drilled in the upper part of the field. Samples were aseptically removed from the centre of the cores. The sampling technique is described more fully in Johnson et al. (1998). Some of the unsaturated zone chalk was autoclaved for use as a sterile control. Groundwater for the microcosms was obtained as described in section 2.6 above. The microcosms used in the screening experiments contained 30–50 mL of groundwater, together with 5–10 g of chalk, maintained within disposable sterile 120-mL polypropylene containers. An isoproturon spike was added to give an initial concentration of 100 µg/L. Treatments were in triplicate and incubated at 20^0C in the dark, without shaking for up to 300 d. Samples were pre-filtered prior to analysis by high performance liquid chromatography (HPLC, Table 2.4).

2.9.3 Chalk metabolic potential

Microcosm experiments were also set up with radiolabelled acetate to assess the metabolic potential of chalk samples. Acetate is a simple organic molecule that can be metabolised by aerobic or anaerobic bacteria and, because of its presence in many natural environments, is a reasonable choice as substrate to ascertain the level of indigenous microbial activity in oligotrophic environments (Johnson and Wood, 1992). The microcosms were set up as described in British Geological Survey and Institute of Hydrology (1995), and the $^{14}CO_2$ produced measured by liquid scintillation.

2.9.4 Column experiments

Bearing in mind the expected very slow travel times for solutes in the Chalk matrix, further efforts were made to examine the potential for isoproturon degradation in the unsaturated zone. In the experiments described above, the microcosms had been fully saturated with groundwater, which might not properly reflect unsaturated moisture conditions. Column experiments were developed, in which undisturbed chalk columns were irrigated under tension and isoproturon and bromide tracer spikes applied. For the column experiments, 0.2 m long sections of chalk core obtained at site WON in May 1995 and November 1996 and sealed in PVC liners were mounted above 2 L Buchner flasks (Besien et al., 2000). Unsaturated conditions were simulated by applying a suction of 1 kPa to the base of the columns, and tensiometers installed horizontally into the chalk were used to monitor and maintain unsaturated conditions. The columns were eluted with groundwater drawn from one of the observation boreholes at site WON and, once the columns had reached steady state, solutions of isoproturon and bromide were applied to the tops of the columns. The leachate was collected and measured and analysed for isoproturon and bromide at intervals of a few days, and after the experiment had been completed the cores were sectioned and sampled to assess the progress of solutes and the efficiency of recovery. The method is described in detail by Besien et al. (2000).

2.9.5 Batch sorption

Batch sorption experiments were undertaken on chalk from the same cores as the column experiments. The first set was carried out in triplicate at three different concentrations, but sorption to the chalk was too low to be measured. A second set of experiments using dried chalk and an isoproturon solution of 1000 µg/L was set up to investigate the very low sorption potential of the chalk.

2.10 ANALYSIS FOR PESTICIDES

The methods employed for analysis for the pesticides studied are summarised in Table 2.4, making reference to project reports and published papers for further details. Methods developed or adapted and employed in the earlier BGS study are described in Chilton et al. (1993).

Table 2.4 Summary of pesticide analytical methods used in present study.

Sample type	Compound	Method	Detection limits	Detailed description
Soil	Isoproturon	Methanol extraction and HPLC	0.09 – 0.23 (µg/kg)	BGS and IH (1996)
Solid chalk	Isoproturon Chlortoluron	Methanol extraction and HPLC	0.09 – 0.23 (µg/kg)	BGS and IH (1996)
Pore water	Isoproturon	ELISA Methanol extraction and HPLC	0.01(µg/L)	Gooddy et al. (2001)
Pumped groundwater	Isoproturon	Solid phase extraction and HPLC	0.1 (µg/L)	Gooddy et al. (2001)
	Chlortoluron		0.04 (µg/L)	
	Atrazine		0.1 (µg/L)	Chilton et al. (1993)
Batch sorption	Isoproturon	Filtration (0.45µm) and HPLC	0.01 (µg/L)	Besien et al. (2000)
Chalk columns	Isoproturon	Methanol extraction and HPLC	0.01 (µg/L)	Johnson et al. (2000)
Microcosms	Isoproturon	Filtration (0.2µm) and HPLC	10 (µg/L)	Johnson et al. (1998)

3 Results and discussion

3.1 PESTICIDE OCCURRENCE AND MOVEMENT IN THE UNSATURATED ZONE

The results of the earliest coring undertaken in 1991 and 1992 are included for the sake of completeness in Table 3.1. At the sites where isoproturon had been used in the cultivation of winter cereals, hardly any positives above the detection limits of 0.5 µg/L for pore waters and 0.5 µg/kg for solid chalk respectively were recorded to 5 m depths at LEC and WON and to 10 m at AWC. In contrast, beneath maize cultivation, positive atrazine detections were generally observed down to 5 m at all three sites (Table 3.1).

At site CPNb, where atrazine had been used in maize cultivation in the previous four years, atrazine was detected at most depth intervals in both the solid chalk extractions and the pore water in two cores some 100 m apart in the same field, but concentrations decreased with depth. Lower concentrations were observed in the cores beneath the second field, probably reflecting the shorter period of pesticide usage, and again concentrations decreased with depth. Pore waters from the CPN cores in particular were characterised by high nitrate concentrations (20-50 mg NO_3-N/L), reflecting the high nitrogen applications to maize, and consequent significant leaching losses. This also confirms that the sampled pore waters are representative of slowly infiltrating recharge that has passed through the soil zone, and would, therefore, have picked up pesticide residues if they had existed in substantial quantities.

Comparison of the pesticide concentrations derived by the two methods of extraction provides an indication of the degree to which downward transport of pesticide residues is retarded by adsorption. Concentrations obtained by extraction from the chalk matrix reflect a combination of any immobile pesticide sorbed onto the solid chalk and the dissolved residues. This can be converted to an approximate equivalent pore water concentration by division by the fraction moisture content of the wet rock, here 0.2–0.3. The measured pore water concentrations represent strictly the dissolved phase in all but the most difficult to extract water. Thus, if concentrations estimated from extracted rock were many times greater than those measured in pore waters, this would imply that significant pesticide residues were bound permanently or temporarily onto the chalk matrix. From the results presented in Table 3.1, solid and pore water concentrations were reasonably equivalent, bearing in mind that, for practical reasons, the solid and pore water samples were not from precisely the same points in the profile. This suggests that sorption is likely to be a much less important attenuation mechanism in the Chalk aquifer than in the soil, and was confirmed by the laboratory studies summarised below.

In September 1997, a number of shallow cored boreholes were drilled at site WON for the specific purpose of observing the movement of the chlortoluron applied to part of the field in October 1996 (Table 2.1). This also provided a further opportunity to compare matrix and pore water concentrations. Results for pore water samples from boreholes WON 7, WON 9 and WON 10 indicated very low isoproturon concentrations, at or close to the limit of detection of 0.01 µg/L (Figure 3.1). Concentrations were somewhat variable with depth and between boreholes, but the highest concentration observed was only 0.05 µg/L, although this was at a depth of 2.5 m and 650 days after application. The deepest positive detection was at nearly 10 m in borehole WON7, possibly a trace from slow matrix transport originating from applications in 1988 or 1989, or more rapid movement from that in 1995 (Table 2.2).

Concentrations of isoproturon were obtained by methanol extraction from chalk cores from boreholes WON8 and WON11 drilled in 1996 and for both isoproturon and chlortoluron from boreholes WON12 to WON16 drilled in 1997. The locations of these boreholes

Table 3.1 Summary of unsaturated zone pesticide observation from 1991–1992 work.

Site	Crop	Pesticide	Appl. rate (g/ha)	Months since appl.	Solid chalk			Pore water		
					No. samples (no. positive)	Concentration (µg/kg)		No. samples (no. positive)	Concentration (µg/L)	
						Mean	Range		Mean	Range
LEC	Winter wheat	Isoproturon	1000	11	11 (1)	<0.5	<0.5 – 0.5	11 (0)	-	<0.5
WON	Winter barley	Isoproturon	250	31	10 (1)	<0.5	<0.5 – 1	10 (0)	-	<0.5
AWC	Winter barley	Isoproturon	1800	13	9 (1)	<0.5	<0.5 – 1	9 (3)	?	<0.5 – 3.8
ASM	Maize	Atrazine	1700	20	8 (8)	0.3	0.11 – 0.48	14 (14)	3.65	0.1 – 6.7
CPNa	Maize	Atrazine	?	3	15 (2)	0.1	<0.1 – 0.47	8 (7)	0.59	<0.02 – 3.38
CPNb	Maize	Atrazine	?	3	16 (10)	0.74	<0.1 – 8.6	9 (9)	0.76	0.21 – 1.86

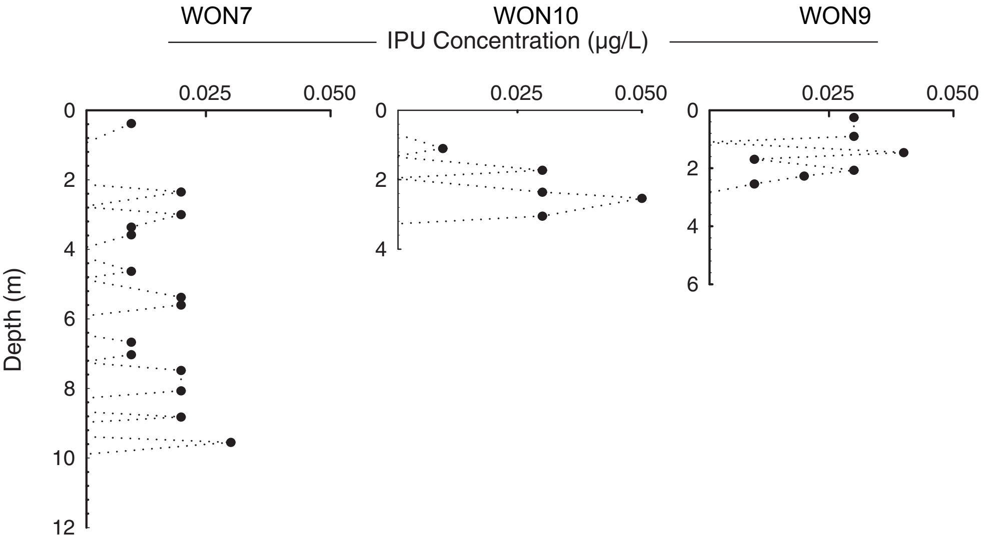

Figure 3.1 Isoproturon concentrations by ELISA in three cores taken across the field site.

Table 3.2 Pesticide concentrations in Chalk matrix by methanol extraction and HPLC, 1996 and 1997 drilling

Date	Borehole	Total depth (m)	No. of samples	Number positive		Maximum concentration (µg/kg)	
				IPU*	CTU*	IPU	CTU
1996	WON 8	2.9	5	5	-	31.3	na
	WON 11	3.2	5	5	-	94.4	na
1997	WON 12	6.3	9	1	1	0.95	0.27
	WON 13	4.9	7	2	1	0.67	0.21
	WON 14	5.1	7	1	0	2.6	-
	WON 15	8.4	12	1	1	6.37	7.08
	WON 16	7.6	11	1	1	1.47	2.77

*IPU = isoproturon *CTU = chlortoluron na = not applied

are shown in Figure 2.2, and the results are summarised in Table 3.2.

The relatively high concentrations of isoproturon in boreholes WON 8 and WON 11 come from the base of the soil, and the difference between the two may reflect the fact that WON 11 was sampled 287 days after last application, compared to 651 days for borehole WON 8. A year later, maximum concentrations were much reduced (Table 3.3), and positive detections were restricted almost entirely to the uppermost 0.6 m depth, i.e. the soil zone, probably as a result largely of degradation in the soil. The reduction in isoproturon concentrations over a year between different applications around boreholes WON 8 and WON 11 and between the 1996 and 1997 drilling are roughly consistent. Concentrations of chlortoluron are equally low, considering the latter pesticide was applied only 330 days prior to the 1997 sampling, and this may reflect its documented more rapid soil degradation (DT_{50} 30–40 days). The highest concentrations were observed in borehole WON 15, which was adjacent to WON 5 in which the automatic borehole sampler detected both isoproturon and chlortoluron.

While the differences between boreholes are likely to reflect local heterogeneity in infiltration, attenuation and transport properties of the chalk and soil across the field, there remains an overall discrepancy in concentrations between the ELISA-analysed pore waters and the methanol-extracted chalk rock. These differences are much greater than those found between rock and pore water results in the earlier sampling (Table 3.1) with the discrepancy between concentrations found by the ELISA analysed pore waters and the methanol extracted whole rock being up to three orders of magnitude. It is not clear whether this difference is between media (methanol extraction from solid chalk versus pore water) or analytical method (ELISA versus HPLC). One possibility is that methanol extraction considers herbicide concentrations in the whole rock, including any sorption onto the rock matrix (likely to be negligible) or onto colloidal particles whose downward progress has been restricted by the narrow apertures of micro fractures. The ELISA analysis of pore waters considers only the mobile water in the dissolved phase since colloids have been removed by the filtration process. It would be important to consider both of these fractions for assessing long-term groundwater pesticide concentrations.

3.2 PESTICIDE RESIDUES IN THE SATURATED ZONE

3.2.1 Results

The results of the regular sampling of the initial four observation boreholes are summarised in Table 3.3. At site

Table 3.3 Summary of saturated zone pesticide concentrations.

Site	Period of sampling	Pesticide	Range of depth to water (m)	Mean (m)	No. of samples	No. of positive detections	Positive detections (%)	Observed concentration (µg/L)	
								Median	Maximum
LEC	2/92–3/93	Isoproturon	2.90–4.38	4.04	11	1	9	<0.05	0.05
AWC	4/92–3/95	Isoproturon	6.85–9.01	7.59	24	12	50	<0.05	0.34
ASM	4/92–3/95	Atrazine	2.10–7.91	3.94	29	11	38	<0.1	0.84
WON 4	2/92–3/98	Isoproturon	0.56–6.77	5.09	44	5	11	<0.05	0.23
		Chlortoluron			21	9	43	<0.04	0.12
WON 6	10/96–3/98	Isoproturon	7.75–9.57	8.60	13	2	15	<0.05	0.13
		Chlortoluron			8	5	63	0.08	0.15
WON 7	10/96–3/98	Isoproturon	13.42–17.38	15.52	17	1	6	<0.05	0.1
		Chlortoluron			13	2	15	<0.05	0.15

LEC, practically no positive detections of isoproturon were observed, reflecting the significant lapse of time since isoproturon was used (Table 2.2), and sampling was therefore curtailed. At sites AWC and ASM, isoproturon and atrazine respectively were consistently detected, but at very low concentrations. Groundwater levels and nitrate concentrations at both sites responded to winter recharge (Figures 3.2 and 3.3), but pesticide concentrations remained very low throughout.

3.2.2 Impact of lateral groundwater flow

The establishment of several boreholes on the sloping field at site WON (Figure 2.2) enabled groundwater samples to be taken at a range of water table depths (Table 3.3). In the early years of sampling from borehole WON 4, most observed isoproturon concentrations were below the 0.05 µg/L detection limit, reflecting the long period since the last applications (Table 2.2). Chlortoluron, which had not previously been used agriculturally at site WON, was applied over a limited part of the field around the boreholes in October 1996, and was detected throughout the 1996–97 winter season in borehole WON 6 with a median concentration of 0.08 µg/L (Table 3.3). During January and February 1998, isoproturon was detected in borehole WON 4 at 0.12 and 0.23 µg/L and WON6 at concentrations of 0.1 to 0.13 µg/L, possibly originating from the application in December 1995. No positive detections of chlortoluron were found at this time, i.e. 15 months after application, supporting the likelihood of a high degree of soil attenuation, as suggested by the unsaturated zone results referred to above. The much deeper borehole WON7 produced almost no positive detections of either isoproturon or chlortoluron in pumped groundwater (Table 3.3).

The objective of the saturated zone sampling was to observe pesticide concentrations in groundwater just below the water table, within the uppermost part of the aquifer immediately beneath the field to which pesticide had been applied. The aim was to observe pesticides in the most recent recharge. However, although the sampling schedule could be modified somewhat to take account of the timing of application and of major rainfall and recharge events, such sampling still collects a mixture of recent recharge and groundwater that is moving laterally through the Chalk aquifer, driven by the local hydraulic gradient. With a local gradient of 0.002, and assuming a typical fracture hydraulic conductivity of 10 m/d and effective porosity of 0.01, lateral groundwater flow rates in the Chalk saturated zone could be about 1–3 m/d. Comparison of the pore water nitrate concentrations below the soil zone (15–30 mgN/L)

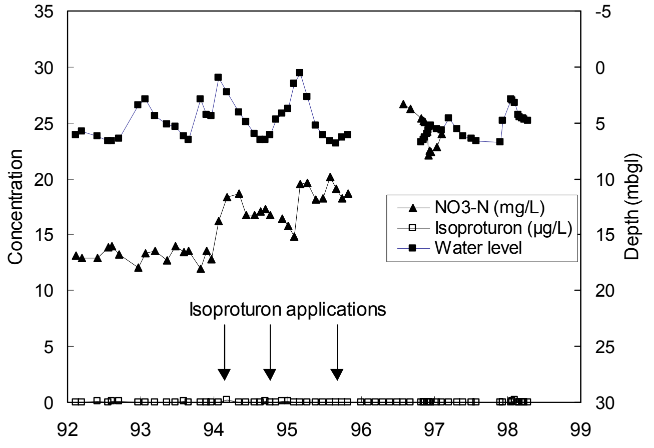

Figure 3.2 Isoproturon, nitrate and groundwater levels, Site WON (borehole WON 4).

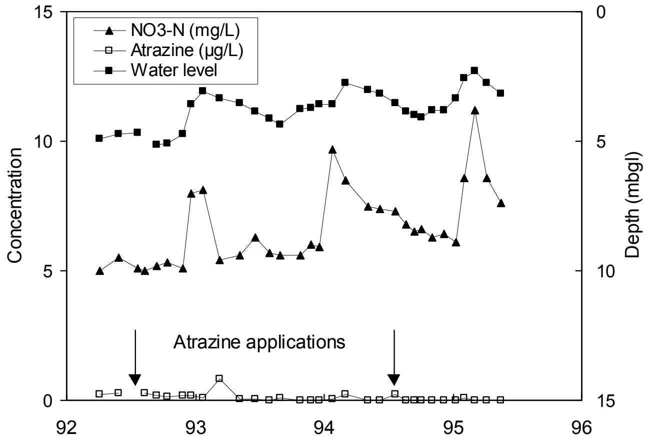

Figure 3.3 Atrazine, nitrate and groundwater levels, Site ASM.

with those measured in samples from the ABPSS (10–20 mgN/l) indicated a possible approximate dilution at the water table of about two. Thus, although possibly up to half of the water reaching the sampled boreholes would have originated relatively recently from within the field, new approaches to sampling are required to target more closely the most recent recharge.

The hanging sampler was first deployed in borehole WON 4 to observe the response to the application of isoproturon in December 1995 (Table 2.2). Concentrations of 0.1 to 0.15 µg/L prior to application increased to 0.2 to 0.3 µg/L immediately following application, associated with a rise in groundwater level of more than 2 m in response to recharge in a six-week period (Figure 3.4). This suggests the transport of albeit small amounts of pesticide in rapidly infiltrating water in the Chalk fractures. Concentrations subsequently declined to around 0.1 µg/L. Over the next winter, following the application of chlortoluron, no significant rise in concentration was observed in the multi-level sampler compared to routine pumped samples, with concentrations averaging 0.12 µg/L.

Groundwater sampling with the automatic sampler provided useful information about the occurrence and behaviour of both isoproturon and chlortoluron. Figure 3.5 shows a definite response to the 1996 chlortoluron application, with concentrations rising from a background of 0.2 µg/L to 0.4 µg/L, with peaks of 0.8 and 0.6 µg/L. Isoproturon concentrations in excess of 0.1 µg/L also appear to be reaching the water table, with peaks largely coincident with but lower than those for chlortoluron (Figure 3.5). Concentrations in groundwater obtained by this approach were up to double those detected in samples from borehole WON 4, either by routine pumping or from the multi-level sampler.

The automatic sampler was operated in borehole WON 5 over three winter seasons. Following isoproturon application in December 1995 significant peaks in concentration were observed during each recharge season (Figure 3.6), but declining from year to year, reflecting the lesser amounts of residue available for mobilisation. It is postulated that the source is probably pesticide held up at the soil/chalk interface and being mobilised seasonally through preferential flow events.

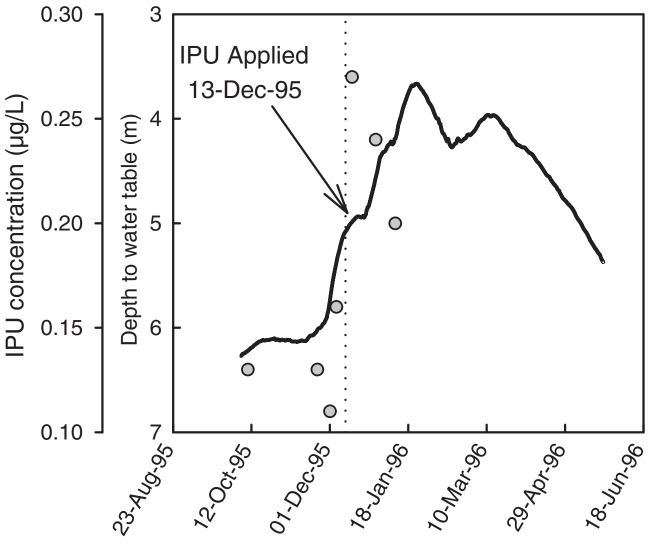

Figure 3.4 Isoproturon concentration (grey circles) from multi-level sampler and water levels in borehole WON 4, winter 1995–96.

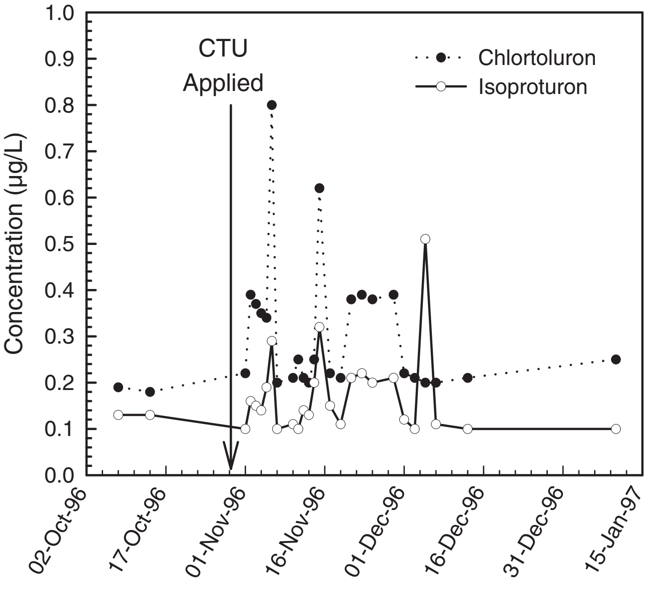

Figure 3.5 Isoproturon and chlortoluron concentrations from ABPSS in borehole WON 5, autumn 1996.

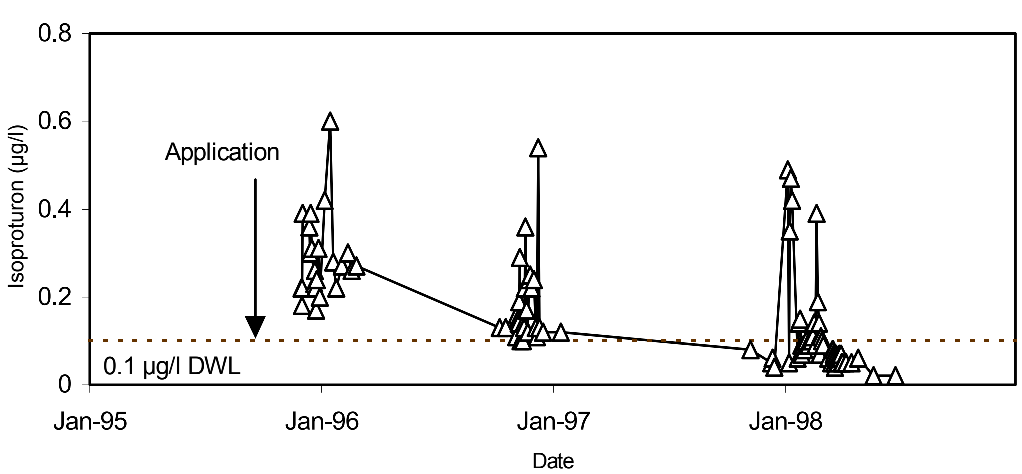

Figure 3.6 Isoproturon from ABPSS over three winter seasons in borehole WON 5.

3.3 UNSATURATED ZONE WATER MOVEMENT AND PESTICIDE TRANSPORT

3.3.1 Unsaturated zone chalk matrix

From chalk samples taken from the inspection pit, matrix porosity was measured at 43% and the median pore size at about 1µm, close to the mean pore size of 0.65 µm reported by Price et al. (1976). The pit confirmed the presence of 0.25 m of topsoil, with a thin (0.1 m) layer of reddish soil below. Below is putty chalk containing round clasts of white chalk to varying depths down to 1 m and then deeply weathered but consolidated white chalk to the base of the pit at 2.75 m (Gooddy et al., 2001). The consolidated chalk is here so strongly weathered that no trace of original bedding surfaces remains, and there is only rudimentary evidence of joint surfaces. It is, however, sufficiently consolidated for fracture surfaces to be identified and surveyed, and the field observations described by Gooddy et al. (2001) indicate that fracturing decreases in intensity with depth. Given that the unsaturated zone is almost 20 m thick under this part of the field, a high degree of fracture continuity or connectivity would be required to permit rapid movement all the way to the water table. The lack of positive pesticide detections from the sampling of nearby borehole WON 7 (Figure 2.2) is not, therefore, surprising.

3.3.2 Water movement

Water movement through the profile is determined by the intensity and duration of rainfall, antecedent conditions and the hydraulic conductivity characteristic of the profile. Measurements of chalk water potentials using pressure transducer tensiometers show the response to rainfall events for a period during February and March 1997 at WON 7 and WON 4 (Figure 3.7). The potentials at WON 4 showed the gradual wetting up of the profile at 1.5 and 2 m in response to smaller amounts of rain. On 25th February a larger rainfall event produced a rapid response at 0.5 and 1 m depths in WON 4 indicating the potential for rapid movement of water, and hence pesticide, through the top horizon of the soil profile. The response is attenuated at greater depths in WON 4 indicating water movement through this zone occurs at a reduced rate. This rate is slower than during preferential flow, which would be expected to give an instantaneous or at least very rapid response.

In contrast for the same rainfall event only matrix flow through the unsaturated zone was observed at WON 7 where the water table is deeper (18–20 mbgl). This suggested different flow pathways for this event between the higher site closest to the interfluve (WON 7) and that closest to the dry valley bottom (WON 4). In practice,

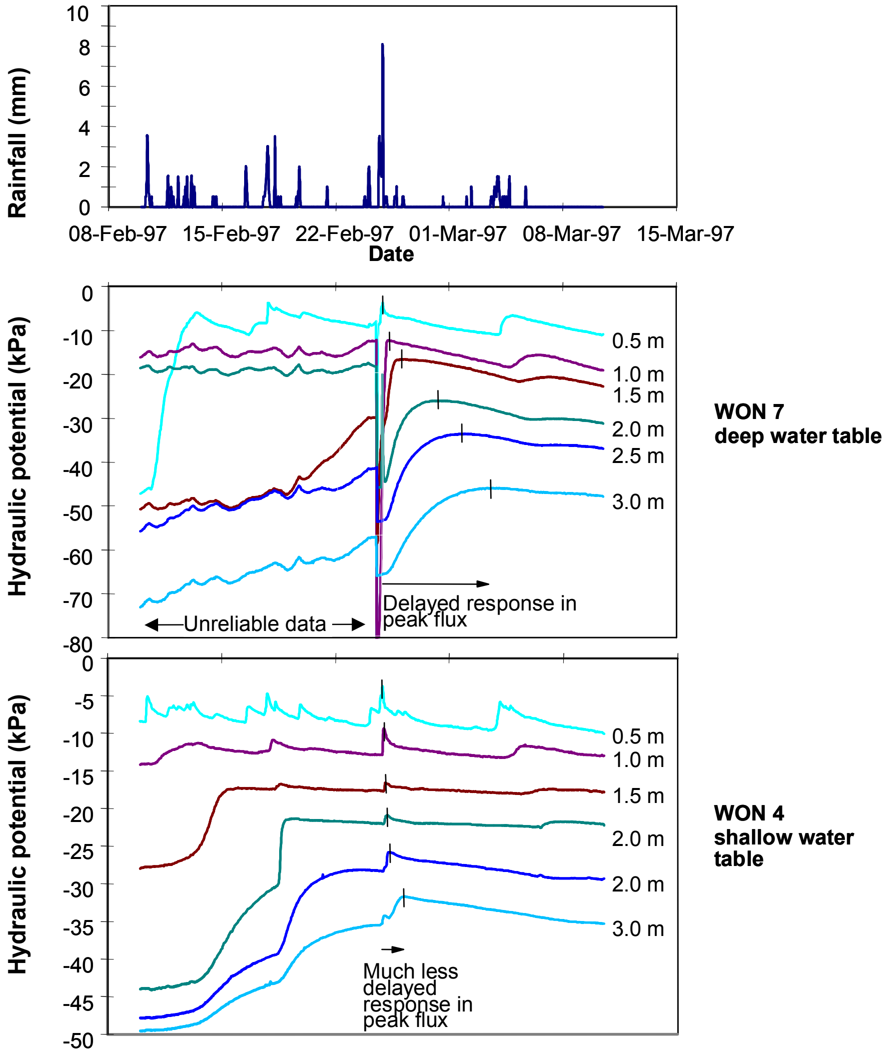

Figure 3.7 Time series data of chalk hydraulic potential response to rainfall for 0.5 to 3 m depths at WON 4 and WON 7.

there is probably a spectrum of discontinuities in the Chalk, from matrix pores through macropores and small fractures, to significant fissures, and therefore a range of possible flow and transport pathways.

While continuity and connectivity of the fractures is a prerequisite for rapid flow to reach the water table, it is the soil moisture conditions and rainfall intensity that actually determine whether and when this more rapid flow occurs. It is considered that matric potentials of more than -5 kPa indicate conditions favouring the onset of preferential flow mechanisms. Table 3.4 summarises the periods during the project where such potentials have occurred at 3 m depth in WON 4. Whilst favourable conditions occurred for several weeks in 1995–96, there were only two limited periods the following winter.

The difference in behaviour at the lower and upper parts of the field probably results simply from the greater likelihood of connected flow pathways persisting to the water table at 3–5 m depths (WON 4) than at 18–20 m (WON 7) respectively (Figure 2.2). Differences in weathering and/or slope processes may help to determine the spectrum of discontinuities in the chalk closer to the valley bottom (WON 4) and approaching the local interfluve (WON 7). It is possible that the capillary fringe may play a role (Haria et al., in prep), by keeping the shallower unsaturated zone profile at WON 4 more adequately supplied with water. This could reduce storage capacity so that less water is required to wet the profile before preferential flow occurs following infiltration after a rainfall event. Small storage sites on chalk fracture surfaces and at contact points between chalk blocks may remain empty where the groundwater level is deeper, but may be largely filled where the water table is shallow. Infiltration from the soil after heavy rain might, therefore, initiate preferential flow more easily where the water table is shallower, and the shorter fracture flow pathways through the thinner unsaturated zone may present a greater possibility of carrying this more rapid but rarely occurring flow to the water table.

3.3.3 Pesticide transport

The maximum potential mass load of pesticide that might be transported to the groundwater in the preferential flow events in 1996–7 was determined from bromide tracer studies. By looking at the bromide peak displacement, it was possible to calculate the amount of recharge through the chalk matrix (Figure 3.8). Using a water balance approach it was then possible to estimate preferential water movement and related contaminant load passing to the groundwater. Calculations under the worst case scenario showed no more than 0.13 % of the applied pesticide would be transported to the water table rapidly at the shallow groundwater site. A more realistic estimate was between 0.04 % and 0.07 % of the applied pesticide. This suggests that whilst contamination of groundwater by pesticides applied following normal agricultural practice over unconfined chalk can occur, the major pollution sites are likely to be restricted to these dry valley areas where the water table is shallowest.

Table 3.4 Periods where conditions favoured preferential flow at Site WON 4.

Season	Periods when matric potential at 3m depth was >-5kPa
1995–96	27th November 1995 – 9th December 1995
	23rd December 1995 – 5th January 1996
	9th January 1996 – 3rd February 1996
	27th February 1996 – 9th March 1996
1996–97	8th December 1996 – 10th December 1996
	25th February 1997 – 6th March 1997
1997–98	Data unreliable

3.3.4 Pesticide retardation

Samples of chalk taken for the batch sorption experiments all had total organic carbon concentrations below the detection limit of 0.1% and very low K_d values, ranging from less than 0.01 to 0.02 L/kg (Besien et al., 2000). These results support the suggestion of Foster et al. (1991) that the UK's sandstone, chalk and limestone aquifers contain little material with which to attenuate pesticides by adsorption. Pesticides would be expected to show little if any retardation by this mechanism when travelling through the chalk unsaturated zone to the water table.

Evidence for lack of retardation also comes from the behaviour of the applied pesticide relative to bromide in the column leaching experiments (Figure 3.9). Retardation (R) factors were calculated from the respective pore volumes required to leach 50% and the respective times to reach peak concentrations of bromide and pesticide (Besien et al., 2000). These ranged from 1.09 to 1.49 by the former and 1.12 to 1.43 by the latter, and can be compared with a figure of 1.08 calculated by the equation suggested by Foster et al. (1991):

$$R = 1 + \frac{K_d\,(1-n)\rho s}{\theta}$$

using a distribution coefficient (K_d) of 0.02 L/kg obtained

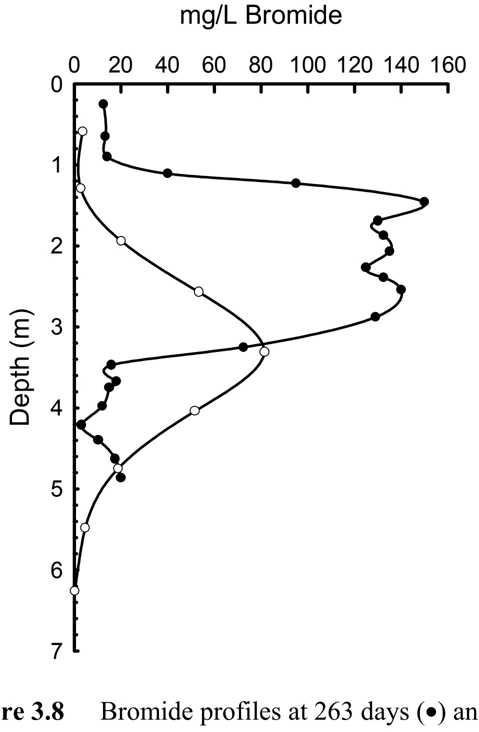

Figure 3.8 Bromide profiles at 263 days (•) and 622 days (o) after application.

from the batch sorption experiments, porosity (n) = 0.43, chalk grain density (ρs) = 2.7 g/cm^3 and volumetric water content (θ) = 0.4. This would suggest that the simple batch sorption experiments might underestimate the retardation factor, compared to the column leaching experiments.

However, the following factors should be taken into account when interpreting the results of the column studies (Besien et al., 2000):

- degradation of isoproturon within the columns will appear to change the estimated retardation factors (Figure 3.9)
- the high concentrations used may increase degradation rates and reduce adsorption onto the chalk if the sorption isotherm for isoproturon is non-linear
- the relatively high temperatures employed are likely to promote degradation
- sterile water was used to elute six of the eight columns.

Dye tracing studies undertaken on the columns indicated that most of the flow was through the chalk matrix, but with significant small-scale variations in transport. The bromide breakthrough curves could be accurately simulated using a simple convection-dispersion numerical model, although the more unusual shapes of the equivalent curves for isoproturon could not be simulated with the same model.

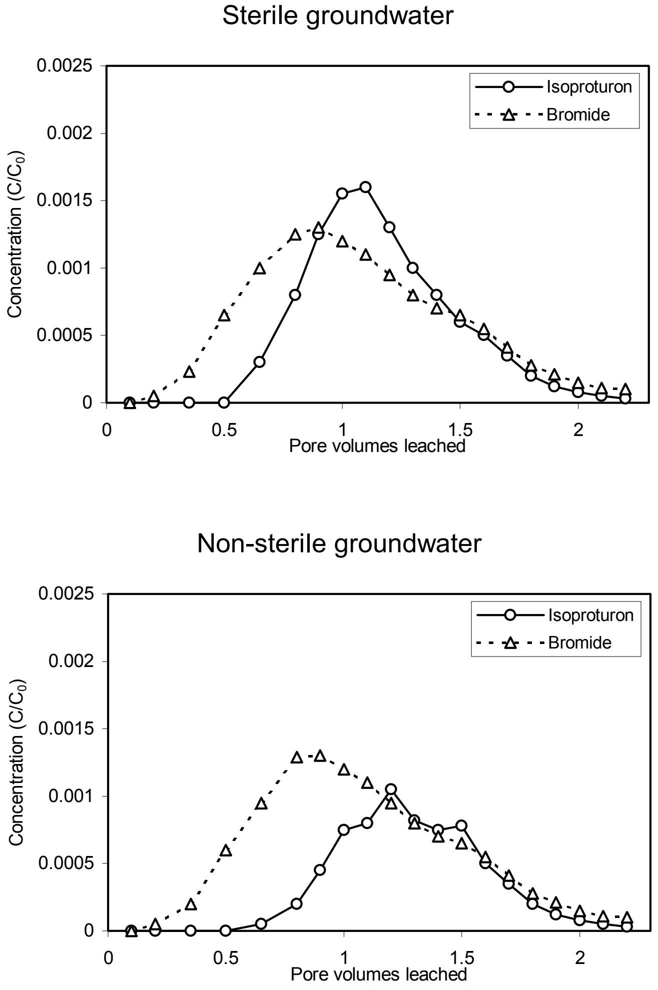

Figure 3.9 Breakthrough curves from column studies.

3.4 PESTICIDE PERSISTENCE

3.4.1 Indigenous micro-organisms

It is assumed that bacteria are not uniformly distributed throughout the chalk. The small pore size of the matrix would exclude most micro-organisms that would exist in the planar fissures present in all chalk. Such a distribution is likely to cause wide errors in sampling. Also counting colonies on complex media may greatly underestimate the number of micro-organisms present in an oligotrophic environment. Nevertheless such plate counts may assist in revealing areas within a depth profile where the greatest level of microbiological activity may be expected. Plate counts on tryptone soya agar (TSA) showed that the topsoil at site WON was 10–1000 times more active than the chalk (Table 3.5).

3.4.2 Pesticide degradation mechanisms

Both isoproturon and atrazine are commonly degraded in the subsurface by dealkylation reactions acting on groups attached to nitrogen. The first stage involving the removal of an ethyl group (CH_3CH_2) for atrazine and a methyl group (CH_3) for isoproturon is shown in Figure 3.10. Subsequent dealkylation reactions occur similarly. The metabolites of atrazine appear to be resistant to further degradation whereas isoproturon undergoes ring cleavage. Mecoprop is thought to undergo loss of the side chain to produce a phenol and subsequent ring cleavage via a hydroxylation mechanism (Figure 3.10).

3.4.3 Role of the solid phase in pesticide degradation

Early experiments in the present study confirmed that, in order for pesticide degradation to occur, subsurface microbial communities needed to have the solid matrix present as provided by a solid: liquid mix, rather than being dispersed in a groundwater-only medium. Hughes et al. (1995) demonstrated that isoproturon could be degraded in microcosms from a chalk site where isoproturon had never been used as long as chalk matrix was present. This agreed with other findings (Chilton et al., 1993; Johnson et al., 1998).

At the present study site the microbial community in groundwater from borehole WON 4, collected in May 1995 and maintained by subculturing on tryptone soya agar (Johnson et al., 1998), degraded isoproturon at similar rates for several chalk: groundwater ratios down to 1:13. However, a 1:30 ratio did not favour isoproturon

Table 3.5 Activity of indigenous micro-organisms at Site WON.

Sample depth (m)	Moisture (g/100g)	Total organic carbon (%)	Bacteria (cfu/g)
Topsoil	ND	2.77	6.1×10^6
0.5	15	0.91	6.0×10^5
3.1	23	<0.1	1.7×10^3
7.2	32	<0.1	6.1×10^4
Groundwater	ND	ND	7.2×10^3

ND = not determined

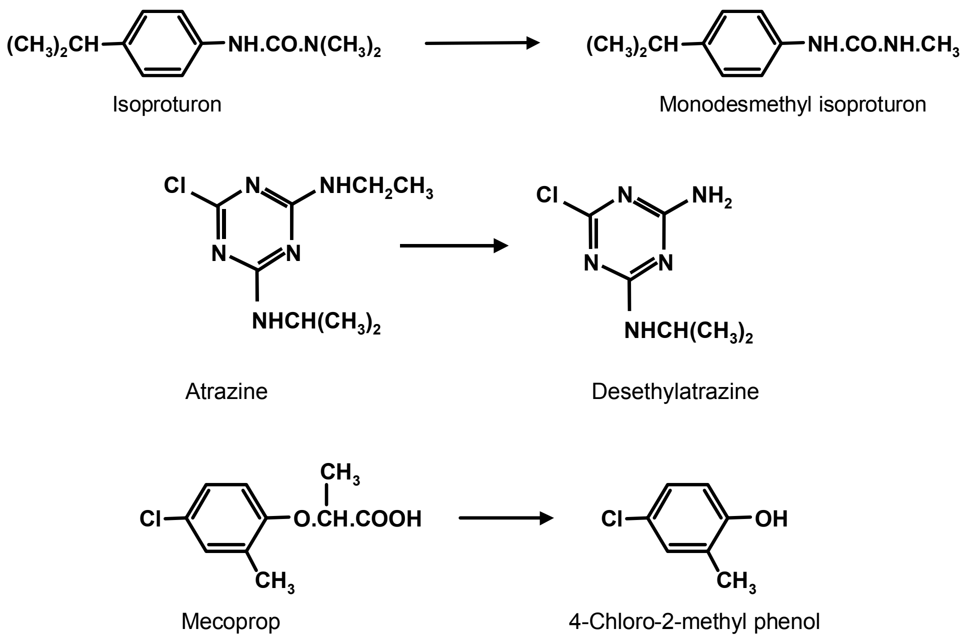

Figure 3.10 Degradation of pesticide molecules.

degradation (Johnson et al., 2000), and in succeeding groundwater experiments a ratio of not less than 1:13 was used. The requirement for the presence of a solid matrix to promote isoproturon degradation could not be attributed to isoproturon sorption on the chalk, since this could not be observed in the sterile controls. Isoproturon is not toxic to bacteria below 20 mg/L (Roberts et al., 1998), so the surface is not acting as a detoxicant. Further, the fact that degradation could be stimulated in the presence of acid washed sand implied that the presence of sterile chalk did not provide any particular nutrient benefit (Johnson et al., 1998). These findings suggest that the bacteria present in the groundwater merely require a surface for attachment, before multiplication and/or production of enzymes capable of degrading isoproturon can occur. This suggests that investigating pesticide behaviour in groundwater only (Cavalier et al., 1991) is unlikely to be a reliable guide to subsurface persistence, and this was an important finding for the subsequent design of the microcosms.

3.4.4 Microbial degradation potential

The potential of the soil at site WON to degrade isoproturon, atrazine and mecoprop was tested. Whilst isoproturon had been used previously on a number of occasions (Table 3.2), there was no record of atrazine or mecoprop use. The results show that all three compounds could be readily degraded in the soil, with half-lives of 15 to 82 days. Hughes et al. (1995) also found isoproturon degradation potential at a site where there was no recorded use, although there was a delay of some weeks before degradation began. This was attributed to ‘a period of adjustment’ by microbes that had not previously been exposed to isoproturon. A similar lag had previously been observed by Heron and Christensen (1992) and Klint et al. (1993) in sandy aquifers. This is also consistent with recently published results from Danish chalk aquifers where lag times of at least 40 days were observed before measurable degradation occurred (Kristensen et al., 2001).

3.4.5 Isoproturon degradation

The potential of the chalk from the unsaturated and saturated zones, together with groundwater, to degrade isoproturon, is shown in Fig 3.11. Over the 200 day incubation period, isoproturon degradation by the groundwater and chalk samples can be observed. The most rapid degradation (half-life of 104 days) was observed with the groundwater with sterile chalk, followed by the unsaturated zone (120–230 days) and saturated zone (250–300 days). Additional evidence for isoproturon degradation was found on analysis of the HPLC traces. Peaks were observed in all the groundwater/chalk combinations that corresponded to mono- and di-desmethyl- isoproturon (Johnson et al., 2000). These metabolites have been previously associated with soil degradation, usually accompanied by the hydroxy versions which were not determined here (Mudd et al., 1983; Lehr et al., 1996). These metabolites were not observed in any of the traces for the sterile controls.

Table 3.6 summarises the broad range of isoproturon degradation potential in groundwater samples taken from the different boreholes at site WON since May 1995. The number of viable aerobic bacteria present (measured on tryptone soya agar) varied between 1 and 7 × 10^4/mL. These results demonstrate that the potential for groundwater samples to degrade isoproturon is both spatially and temporally variable, underlining the complexity of the subsurface ecosystem. It is interesting to note in particular that WON 4 and WON 5 gave such different results, despite being only 10 m apart. The implications of these findings are discussed below.

To examine the potential for isoproturon degradation at lower concentrations, an experiment was set up using 2 litre volumes of groundwater in large flasks. This proved successful in being able to monitor low concentrations of isoproturon (0.7 µg/L over 350 days), and there was little evidence of degradation over this period. This cannot, however, be accepted as a definitive answer to whether

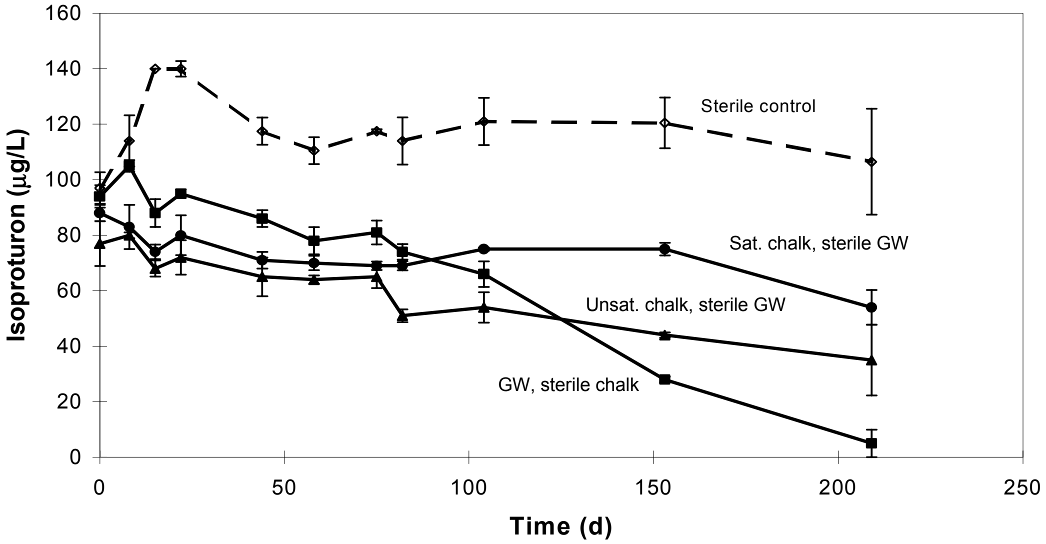

Figure 3.11 Degradation of isoproturon with subsurface chalk samples extracted from borehole WON 7. Unsaturated zone chalk (unsat. chalk) from 10.7 mbgl and saturated zone chalk (sat. chalk) from 19 mbgl. Mean of 3 observations with SD.

pesticides can be degraded at the concentrations actually observed in the field, because of the noted variability of different groundwater samples to degrade 100 µg/L isoproturon shown in Table 3.6. Clearly the question of subsurface persistence at low concentrations is a key one and such experiments need to be repeated.

In order to demonstrate that the degradation of isoproturon by groundwater bacteria could be carried out at the natural ambient temperature of 10°C an experiment was set up with Sherwood Sandstone groundwater samples from ADAS Gleadthorpe. These groundwater samples had been previously incubated at 20°C and demonstrated isoproturon degradation. The samples were re-spiked with isoproturon and then incubated at 10°C. Isoproturon was again degraded at this temperature, illustrating that biodegradation could equally well be performed at the natural ambient groundwater temperature found in UK aquifers.

3.4.6 Degradation of other herbicides

More limited attention has been given in the study to the degradation potential of other commonly used herbicides. No degradation potential was observed for atrazine at site WON over a 200-day period, or for mecoprop over 150 days in these subsurface samples, despite the soil above being able to degrade these compounds. In subsequent samples of chalk groundwater from other Hampshire sites it was found that 1–3% of atrazine was converted to desisopropyl- and desethyl-atrazine following a one-year incubation period.

The mecoprop results contrast with those in the earlier BGS study (Chilton et al., 1993), where potential was observed at all the study sites. With a starting concentration of 50 µg/L, chalk/groundwater microcosms from 2.88 m depth at site AWC showed ability to degrade mecoprop in non-sterile groundwater, falling to below detection limits in 40–60 days following a 10-30 day lag period. Results from a second set of microcosms from 5.07 m also indicated active degradation after a similar lag period, although the non-sterile, groundwater-only microcosm did not follow the same trend. A very simple, groundwater-only experiment comparing stored and fresh samples from site ASM and AWC indicated a much-reduced ability to degrade mecoprop in water that was not used soon after collection. The different results may be a further reflection of spatial variability in degradation potential. The study also highlighted the effects of storage of groundwater before use in microcosms where activity was lost with time and this could be a further reason for experimental inconsistencies.

3.4.7 Spatial and temporal variability

The apparent spatial variability in degradation potential found in this study has been highlighted in other studies. Isoproturon degradation potential has been shown to be spatially variable, even in agricultural soils where the

Table 3.6 Estimated isoproturon half-lives for 100 µg/L at 20°C (and range of values) for groundwater samples taken from different boreholes at different times.

Borehole	May 1995	November 1995	November 1996	January 1997	March 1998
WON 4	7d (7–20d)	97 d (92–102 d)	104 d (all 104 d)	None after 149d	None after 202 d
WON 5	ND*	362 d (52–575 d)	ND	387 d (227–641 d)	575 d (239–850 d)
WON 6	ND	ND	ND	None after 149 d	280 d (239–306 d)
WON 7	ND	ND	ND	174 d (138–227 d)	228 d (212–247 d)

* ND no sample taken

potential is relatively high (Walker *et al*., 2001). This study found a five-fold variation in degradation rate over a single field with nominally uniform soil characteristics together with differences in degradation kinetics. In Denmark, Kristensen *et al*. (2001) also observed large variations in rate and extent of mineralisation of mecoprop and isoproturon in a chalk aquifer and Albrechtsen et al. (2001) reported substantial spatial variability in herbicide degradation in a range of shallow aquifers. Earlier work by Heron and Christensen (1992) had noted different patterns and rates of mecoprop degradation for groundwater collected from boreholes only 2–10 m apart. None of these studies refers to the temporal variability found here but the levels of variation described must have important implications for extrapolating data from microcosms or single boreholes to be representative of larger aquifer units or geographical areas.

4 Implications for groundwater quality

4.1 PESTICIDE TRANSPORT

The study findings have important implications with regard to the potential impact of agricultural herbicides on groundwater quality in the UK. The results of the unsaturated zone sampling indicate that, beneath normal agricultural cropping with pesticide applications at recommended rates, very small amounts of pesticide are moving through the unsaturated zone matrix of the Chalk. Observed concentrations of both isoproturon and atrazine were rarely above 1 µg/L and always less than 10 µg/L. Further, these results are in good agreement with those obtained by WRc (Clark et al., 1995), also for the Chalk aquifer in southern England. Given that, from normal application rates of 1–3 kg/ha, pesticide concentrations of several hundred to more than one thousand micrograms per litre would be present in the topsoil immediately after application, this is confirmation of the effectiveness of surface and soil processes of pesticide loss or dissipation (Figure 4.1). Very little pesticide remains and is available for transport, and the proportion leached beneath the soil zone is rarely even 1% of the amount applied. Sampling in the saturated zone in the present study has confirmed that very low concentrations of agricultural pesticides are reaching the water table.

Whilst this is largely a reassuring outcome in terms of groundwater quality, two issues related to pesticide transport in fractures remain unresolved and merit further work. Firstly, even the sampling developments outlined above have only partially solved the problem of sampling the fracture component of unsaturated zone water movement. This needs to be done in situ, by isolating water from flowing fractures below the soil but above the water table, i.e. before it mixes with the local lateral groundwater flow. Methods to do this by horizontally-inserted collecting pans can be envisaged, but would be difficult to install without significant disturbance, which could modify and enhance the local fractures and thereby change the unsaturated zone recharge pathways.

Secondly, whilst the soil physics component of the present study has confirmed the earlier findings at nearby Bridgets Farm by Wellings (1984) that conditions which promote unsaturated zone movement through fractures may occur only rarely, the quantification of the fracture flow proportion still remains uncertain. This work also suggested that, on rare occasions, rainfall of very high intensity would exceed the infiltration capacity of the matrix, and fracture flow could result, irrespective of the prevailing matric potential. At this site 30% of the total lysimeter drainage was attributed to fracture flow.

It should be noted that fissure flow from the soil surface reaching the water table directly is more likely where the water table is shallow since fissure flow initiated near the surface may be dissipated into the matrix where the depth to the water table is greater. It could be argued that pesticide ‘hot spots’ in groundwater in the chalk may only occur where the depth to water does not exceed, for example, 5 m. This would represent only about 1% of the surface area of the Chalk outcrop in south-east England (Lewis et al., 1993).

Because of its greater relevance to pollutant transport than volumetric recharge, the quantification of rapid, fracture flow, and the sampling of such flow on the rare occasions it occurs remain critical issues. The present study has, in this sense, not fully achieved its albeit ambitious objectives within the modest resources available, although the sampling methods developed here have been able to detect a component of direct recharge.

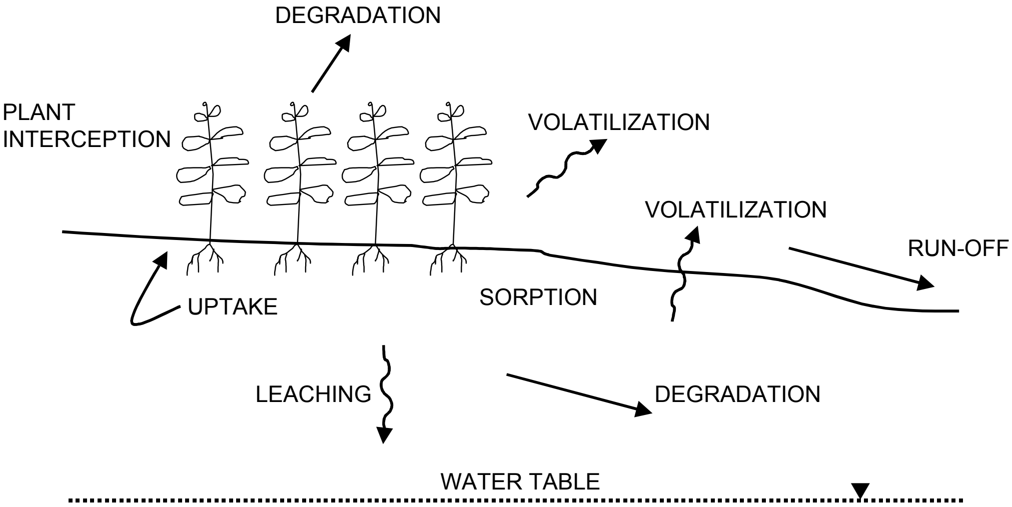

Figure 4.1 Processes of pesticide attenuation and dissipation.

4.2 PESTICIDE PERSISTENCE

The microcosm experiments have shown that there are bacterial communities present in the Chalk aquifer competent to degrade isoproturon, albeit more slowly than in the soil. Half-lives of generally greater than 50 days were obtained, compared to 7–15 days generally for soils (British Geological Survey and Institute of Hydrology, 1996). Degradation rates in the subsurface were variable, and could not be predicted from either TOC levels or the number of bacteria present. Mineralisation of the isoproturon ring structure was incomplete, and loss of the parent compound was associated with the generation of mono- and di-desmethyl-isoproturon metabolites.

However, this degradation potential is not evenly distributed spatially in the Chalk and groundwater and moreover appears to be a somewhat transient quality. This is an important finding, and illustrates how data collected from a single location, on a single date could lead to misleading interpretations about the potential for pesticide degradation. While problematic, it should not be considered surprising, as the factors which determine degradation potential such as bacterial populations, availability of nutrients, moisture conditions and oxygen status are likely to vary spatially, just as the physical properties do, and their distribution may be largely controlled by the physical properties. Even without major fracture flow, the small-scale spatial variability in soil, subsoil, slopes and drainage are likely to produce effects such as local subsurface 'ponding' of flow (Foster et al., 1991), and hence differences in infiltration of water, bacteria, nutrients, colloids and pesticide residues to the subsurface. Given the clear evidence of fracturing from the inspection pit, the scope for uneven distribution of properties and processes is very great.

Hence, the question posed by Johnson et al., (2000): 'will herbicides be degraded in situ in fractured rock aquifers?' is central to the present study. Extensive field studies of the potential for a microbial contribution to denitrification in the major UK aquifers (Lawrence and Foster, 1986; Kinniburgh et al., 1999) suggested that denitrification would be largely restricted to the fractures, and the greatest microbial activity was likely to take place on the fracture walls. This was partly because the very small pore size (about 1.0 µm) of such rocks would exclude most bacteria, but also because some of the requisite nutrients might be more available in the fractures. Given the difficulty of representing such conditions in the laboratory, microcosms containing crushed chalk and groundwater have been used in the present study. This mixture may be poorly representative of conditions in either matrix or fracture environment. If the microcosms are considered to be measuring the degradation potential of the *groundwater* (rather than the solid material), then they certainly can reflect spatial and temporal differences depending on where and when the samples were taken, as shown in Table 3.5. These variations presumably reflect the distribution of factors described in the previous paragraph. It is, however, difficult to say that the present study has fully explored the distribution of degradation potential in both the matrix and fracture environments of the Chalk. The study has indicated, as expected from overall considerations of microbial populations and nutrient status, that degradation would be slower in the underlying aquifer than in soils, and the results summarised in Table 3.5 are the first such data for the Chalk. Questions also remain as to whether the indigenous microflora would degrade isoproturon at 0.1 µg/L in the same way as the 100 µg/L that was used in the microcosms.

4.3 EVOLUTION OF GROUNDWATER PESTICIDE CONCENTRATIONS

Agricultural land on the aquifer outcrop forms the first part of the groundwater flow pathway from recharge at the land surface to discharge by springs, wells, and boreholes or into a river. Thus, whatever pollutants leave the soil form the inputs to the unsaturated zone, and in turn whatever reaches the water table is the starting point for the evolution of groundwater quality en route to discharge points.

Being a similar type of diffuse pollution, the situation for pesticides can be compared to that for nitrate (Table 4.1), which has long been a major groundwater quality concern for the UK water industry. Agricultural soils contain large amounts of nitrogen, to which inorganic and organic fertilisers are added. While nitrogen undergoes complex transformation processes in the soil (Vinten and Smith, 1993), once nitrate is formed it is highly soluble, relatively stable in aerobic conditions and poorly sorbed. As a result, and depending on soil and crop types and cultivation methods, leaching losses for nitrogen from agricultural land often reach 20–30% of the applied fertiliser (Armstrong and Burt, 1993). Resulting nitrate concentrations in the unsaturated zone matrix, as determined by pore water profiling (Chilton et al., 1991) range up to 50–150 mg NO_3/L under most agricultural scenarios (Table 4.1), and up to several hundred milligrams per litre beneath the heaviest applications of organic manure. Once in the unsaturated zone, little further attenuation of nitrate occurs. Given the slow downward movement through the Chalk unsaturated zone of 1–2 m/year, large amounts of nitrate have been 'stored' in the unsaturated zone, eventually to impact on saturated zone groundwater quality. This mechanism has given rise to the 'time-bomb' scenario of the more emotive commentators and writers. What is clear, is that once in the unsaturated zone, this high-nitrate recharge water moves down to the

Table 4.1 Comparison between nitrate and pesticide as a groundwater pollutant.

	Application rates (kg/ha)	Estimated soil concentrations	Percent leached	EC MAC	Observed concentrations	
					Unsaturated zone	Saturated zone
Nitrate	120 – 250		10–30	11.3 mg/L	1 – 150 mg/L	5 – 15 mg/L
Isoproturon	0.25 – 2.5	500–5000 µg/L	<1	0.1 µg/L	0 – 4 µg/L	0 – 0.2 µg/L
Atrazine	1.0 – 2.0		<1	0.1 µg/L	0.1 – 9 µg/L	0 – 0.8 µg/L

saturated zone and to water supply sources, albeit with mixing and dilution on the way.

The results of the present study and that of WRc (Clark et al., 1995) indicate fairly clearly that there are not significant quantities of pesticide residues lodged in the unsaturated zone. The 'time bomb' scenario does not apply in the same way for pesticides, and this is an important finding. Very low concentrations have been consistently observed at the water table, and there is no evidence of likely cumulative rise in concentrations of specific compounds. Further dilution is likely within the saturated zone. It seems very unlikely, therefore, that normal agricultural usage of pesticides in the UK will produce gradually rising concentrations of specific compounds in drinking water supplies. This does not, however, hold for non-agricultural pesticide usage or pesticide disposal, both of which may result in point sources of pollution, with quite different mechanisms and outcomes (Chilton et al., 2000).

While in strictly scientific terms this may be a generally negative finding, in environmental terms it should be considered as highly positive. Several factors may help to explain this outcome:

1. The processes of pesticide attenuation and dissipation in the soil (Figure 4.1) are highly effective in reducing concentrations, leaving little available for leaching.
2. The combination of crop rotations and availability of more than one compound for the same weed control task mean that individual compounds are rarely used on the same field continuously from year to year, greatly lessening the opportunity for residue accumulation. In contrast, most crops will receive nitrogen fertilisers.
3. The widespread adoption of crop rotation practices means that any specific compound is used on a relatively small proportion of agricultural land each year, again in contrast to nitrogen fertilisers.
4. Although more vulnerable to leaching, the lighter and thinner soils which are common over aquifer outcrops may have less vigorous weed development, requiring lower pesticide applications. This may imply that heavier and thicker soils draining to surface waters may be more likely to have higher applications and hence such surface waters may be more vulnerable. The lighter and thinner soils by contrast may need higher nitrogen applications.
5. Successive generations of new pesticide compounds and mixes are effective at lower application rates.
6. The slow unsaturated zone transport through the matrix allows time for further degradation.
7. More rapid, preferential flow in fractures appears to be a relatively uncommon and localised occurrence.
8. Transport of pesticides to the water table may be restricted to areas where the water table is shallow.

Thus, while several important factors contribute to this favourable picture, some words of caution are also appropriate:

1. The discrepancy in unsaturated zone sampling results between solid phase extraction and the ELISA technique raises the possibility that concentrations have been underestimated.
2. The fracture component of unsaturated zone flow has not been fully characterised in terms of quantity or quality.
3. Pesticide persistence has not been fully characterised at ambient temperatures and concentrations, and in relation to matrix/fracture pathways.
4. Current research and UK monitoring take little account of pesticide metabolites, although there is increasing evidence of their environmental occurrence. Kolpin et al. (1996) found in a comprehensive survey of groundwater in Iowa that nine out of ten of the most frequently detected compounds were metabolites. Recent surveys in Netherlands and Germany have begun to show similar pictures. The present study has identified metabolites of isoproturon.

These factors would form the basis for further work on pesticides in groundwater.

5 Conclusions

The results of the study provide some of the first field evidence in the UK for the fate of agricultural herbicides in the Chalk aquifer. Sampling in the unsaturated zone at five sites in southern England has observed low concentrations of atrazine (generally <3µg/L) and almost negligible concentrations of isoproturon in both solid chalk and pore water samples. Regular sampling of groundwater from the uppermost part of the saturated zone has also produced consistently low concentrations (<0.9µg/L atrazine and <0.3µg/L for isoproturon), indicating that relatively little pesticide is reaching the water table. It may be that some short-lived occurrences at the water table could have been missed. It seems unlikely, therefore, that troublesome concentrations of pesticides derived from normal agricultural use will develop in Chalk groundwater if movement through the matrix were the only transport mechanism operating.

While more rapid transport from the soil to the Chalk water table via fractures can be envisaged, evidence from the study suggests that even where conditions which promote such transport occur regularly it in fact only occurs a few times each year. Attempts to sample directly recharging water by the development of novel sampling techniques detected more frequent but still modest pesticide concentrations. Even when fracture flow is encouraged or initiated, this mechanism may carry water and solutes down to the water table only where it is close to the ground surface.

Bacteria capable of degrading pesticides are present in the Chalk aquifer, albeit in smaller populations than in the soil. However, the degradation potential is not evenly distributed in the Chalk, and appears to be a somewhat transient quality. Degradation of isoproturon is slower than in the soil, but still effective in breaking down the parent compound to produce metabolites which can be identified from their chromatography traces. The evidence obtained for mecoprop degradation was inconsistent, and no potential was found for atrazine degradation in the present study. The spatial and temporal variability of isoproturon persistence provides an indication both of the dangers of using data from a single location or time in predictions of pesticide fate and behaviour and of the difficulty and cost of obtaining more applicable data.

A number of important uncertainties remain and further work is required in the following areas:

- developing microcosm studies at observed (low) pesticide concentrations and ambient (low) temperatures
- identification and characterisation of microbial populations, their differing abilities to degrade pesticides and the reasons for spatial variability in degradation potential
- characterising degradation pathways, identification of pesticide metabolites and determining their transport properties
- characterising fracture flow conditions and sampling fracture flow as it occurs.

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Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

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