Fate and behaviour of pesticides in structured clay soils

First Interim Report

1993/058

FATE AND BEHAVIOUR OF PESTICIDES IN STRUCTURED CLAY SOILS

First Interim Report

by

**A.C. JOHNSON, A. HARIA,
C.H. BATCHELOR, J.P. BELL AND R.J. WILLIAMS**

Institute of Hydrology
Crowmarsh Gifford
Wallingford
Oxfordshire
OX10 8BB
UK

Tel: 0491 838800
Fax: 0491 832256
Telex: 849365 Hydrol G

September 1993

Contents

ANNEXES

Executive Summary

This report presents results from the first year of a study of the hydrological and hydrochemical factors and processes that influence the fate and behaviour of pesticides in a clay catchment. The specific objectives of the project are to study pesticide mobility and degradation in relation to soil water dynamics, crop husbandry and climatic factors, and to develop and validate physically-based models of pesticide transport. The wider objectives of the project are to identify practical means of minimising the risk of pollution by pesticides and to develop strategies for monitoring pesticide pollution at the catchment scale.

Experimental studies involved instrumenting and monitoring a new field site on the Oxford University Farm at Wytham. The field selected for the study was underlain with a structured clay soil and planted with winter wheat. Equipment installed at the site included arrays of tensiometers, neutron probe access tubes, run-off traps and measuring devices, soil suction samplers, and a drain flow meter with autosampler. Soil water samples, soil columns and soil samples were collected in the field for analysis and chemical and microbiological experiments in the laboratory.

Drainflow was initiated in response to rainfall events 50 days after isoproturon application. Relatively high concentrations of pesticide, between 200 and 500 μg/l, were found in the drain water during those events, representing a 2.7% loss of available pesticide within 3 days. Other water samples taken manually during this major rain event period also contained high pesticide concentrations (800 μg/l in overland flow and 24 μg/l in the ditch). Drainflow was found to commence soon after the topsoil became saturated. The evidence suggested the drains being filled by water entering from above via macropores, both biopores and cracks. Peak pesticide concentrations in the drain water were interpreted as being related to the intensity of the preceding rainfall once the soil surface had become saturated. In addition differences between peak pesticide and anion concentrations in the drainwater suggested that the drainwater was composed of both water emanating from the surface and from within the profile.

Evidence for lateral interflow was obtained using a bromide tracer. Overall water movement in the field moved via lateral routes; overland flow, lateral interflow and via mole drainflow with interconnections being made by macropores. The high pesticide loss to drainage revealed in this report underlines the potential for surface water contamination in mole drained clay soils. This potential remains even after a considerable time has lapsed since application.

At the time of preparation of this report, a second field season of experiments has started at the Wytham site. The main aims of this second season are to verify the main findings of the first season and to obtain more data on the partitioning both of water movement and pesticide between overland, interflow and drainflow.

Funding has come from a number of sources which include a project funded by the Natural Environment Research Council (NERC) and a project funded jointly by the NERC and the Agriculture and Food Research Council. This second project is being conducted in collaboration with the Soil Survey and Land Resources Centre and Horticulture Research International.

1. Introduction

A number of drinking water sources, both ground and surface waters, in England and Wales have been shown to be contaminated with pesticides (Lees and McVeigh, 1988; Drinking Water Inspectorate, 1992). In many cases levels of individual pesticides are above the maximum acceptable concentration of 0.1 μg/l laid down in the European Community Drinking Water Directive (Council of the European Communities Directive, 1980). In the case of some pesticides contamination may be caused by non agricultural use (Gomme *et al*, 1992). However, two studies of small agricultural clay catchments in England have shown a direct link between agricultural usage and pesticide runoff (Matthiessen *et al.*, 1992, Williams *et al.*, 1991, Harris *et al.*, 1991). The movement of pesticides from agricultural clay catchments is of particular interest, as they account for 45% of the cereal growing area of England and Wales (Cannel *et al.*, 1984). The low matrix conductivity of clay soils should mean that pesticide movement though the soil profile is very slow, thus representing little risk of pollution of water courses. However, as has been stated above, significant losses of pesticides to drainage water have been reported from clay catchments. The processes by which pesticides can be transported from clay soils are therefore of particular scientific and environmental importance.

The hydrology of clay soils is strongly influenced by the presence of macropores consisting of both biopores, created by worm activity, and mechanical fissures resulting from shrink swell processes (Kneale, 1986). The presence of macropores allows the rapid movement of water through the profile, by-passing various amounts of the soil matrix (Kneale and White, 1984, Leeds-Harrison *et al.*, 1986). Clay soils are often drained by a combination of mole and tile drains so as to reduce seasonal water-logging. The drains are designed to intercept lateral flow in the upper horizons; this lateral flow is likely to be augmented by macropore flow both horizontally and vertically. Thus subsurface flow routes will exist for water that may be moving at velocities close to that of overland flow (Bevan and German, 1982), resulting in a rapid movement of water and dissolved solutes to surface waters.

The rapid movement of nitrogen from the upper soil profile, caused by the mineralization of organic-N, observed at Wytham Farm, Oxford during autumn, has been attributed to the action of macropores creating by-pass flow (White *et al*, 1983). A similar flushing effect has been observed following the application of pesticides at ADAS Rosemaund Experimental Husbandry Farm (Mattheissen *et al.*, 1992. Williams *et al.*, 1991). Although the percentage of pesticide lost by this route was only < 1% of that applied, observed concentrations in drains and the receiving stream were often in excess of 10 μg/l, exceeding the current maximum acceptable concentration in drinking water by two orders of magnitude.

It is clear that solutes and in particular pesticides are able to by-pass the soil profile to contaminate surface waters, however, the factors controlling the magnitude of observed concentrations in clay soils are still unclear. In principle the physico-chemical properties of the pesticide are the key to determining its level and persistence in the environment. For example a highly sorbed, rapidly degraded chemical would not be expected, in the normal course of events, to appear in surface or groundwaters. This kind of generalized statement is reasonable for soils in which water flow is through the soil matrix, where there is good contact between soil and water. The nature of by-pass flow is to remove the intimate contact between soil and water thus reducing the possibilities for both sorption and degradation. The extent of the interaction between matric and macropore water, and the hydrological conditions of the soil by which this is controlled are key to understanding, and therefore predicting pesticide transport through structured clay soils.

A detailed hydrological and chemical process study has been set up at Wytham Farm, Oxford, to identify the *in situ* processes of water transport over, within and below the soil in relation to rainfall, antecedent water conditions and agricultural practice. This will provide the information for creating physically-based conceptual models, which should represent realistically the actual conditions of water inputs through various pathways to the outflow from agricultural catchments. The combination of this information with parallel chemical and microbiological studies will make it possible to determine the potential transport of agrochemicals in solution to aquifers and surface waters.

Some of the results given in this report were presented previously as part of a joint report with Alan Walker (HRI) and Andrée Carter (SSLRC) to the Special Topic Steering Committee.

2. Experimental site

2.1 LOCATION AND DESCRIPTION

The clay catchment chosen for this study, located at Oxford University Farm, Wytham in Oxfordshire, is shown in Figure 1. This catchment has previously been used in hydrological studies, such as those conducted by Kneale (1986), and Haigh (1985). It should be noted that Wytham Farm is also being used as the location of studies for the Environmental Change Network (ECN).

The design of the experiments used at Wytham have been based on experience gained at three field process studies that were carried out at ADAS Rosemaund EHF during 1989-1993, (Bell *et al.*, 1991; Williams *et al.*, 1991; Bell *et al.*, 1992). Although the studies at Rosemaund obtained much useful and original information on the hydrological processes that influence pesticide transport, it was clear that a more comprehensive approach was required. The experiments at Wytham and in the laboratories at IH are designed to combine, the hydrological, hydrochemical and microbiological studies information, to provide a clearer picture of the processes which lead to pesticide transport.

The experimental area was on a structured clay soil under arable cultivation of winter wheat that had been moled and ploughed in August, 1992. The ploughing had incorporated the straw and stubble, forming a "buried straw horizon" at a depth ranging from about 0.15 to 0.2 m. The instruments were installed over an area of approximately 25 m by 50 m between field drains 2 and 3 midway up the field. The moles were installed at 3 m intervals, and at a depth of 0.5 m, and drain into the backfill of the field drains, situated 0.75 m below the soil surface (see Figure 2). The site slopes towards the drainage ditch at a gradient of approximately 1:20. The soil within the plot was classified by an SSLRC soil survey to belong to the Denchworth series (Jarvis and Hazelden, 1982). Field instrumentation is described in later sections and a schematic diagram of the Wytham site is shown in Figure 2.

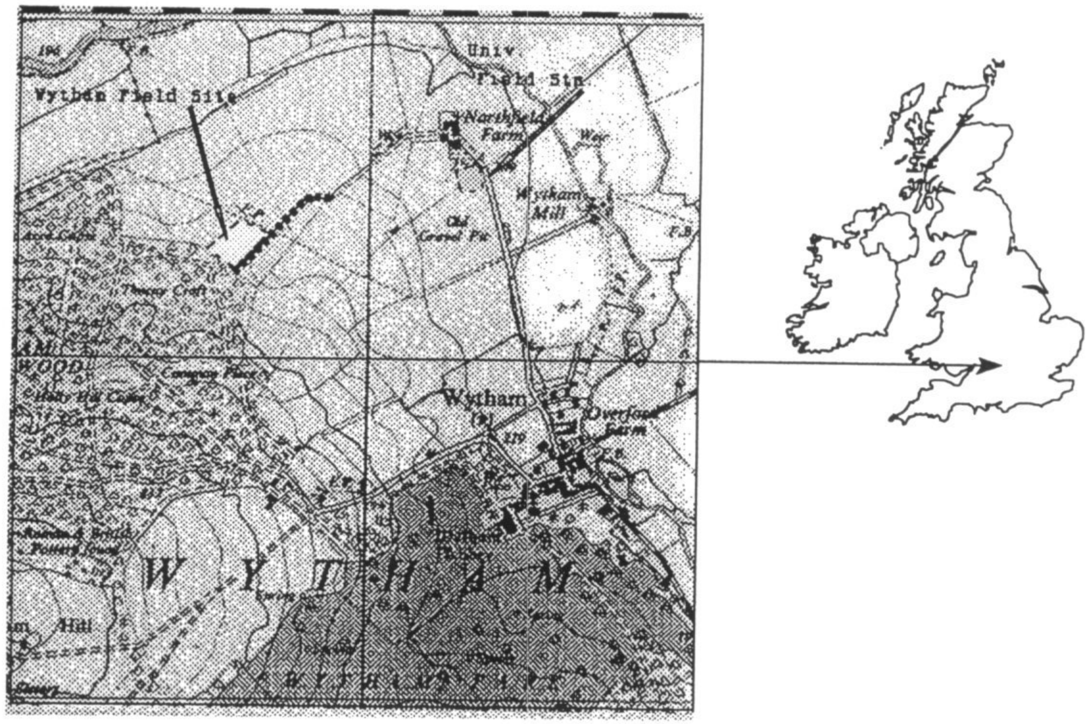


Figure 1. Location of the field site at Wytham

a:wytout1

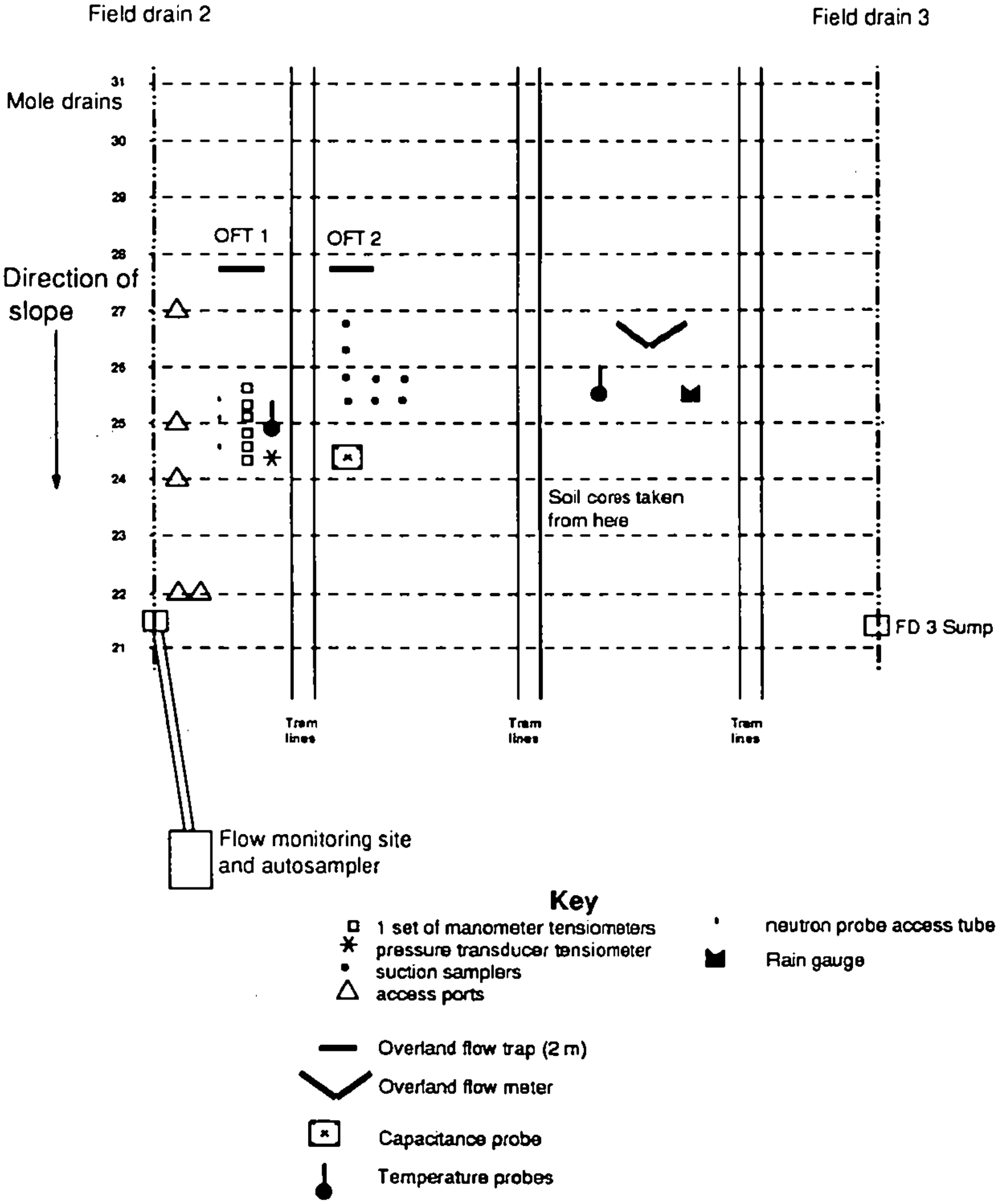


Figure 2. Location of instruments at Wytham for 1992-93 season (superimposed over drain locations)

The initial installation and set-up of the field site proved to be considerably more demanding than had been anticipated, mainly due to the difficulties of working in a waterlogged heavy clay soil during a wet autumn/winter. Rainfall during the winter months was higher than average in December 1992, and in January 1993 was almost double the long term mean monthly rainfall (Figure 8).

2.2 SOIL TYPE

The main profile characteristics of the Denchworth series are a dark brown clayey Apg horizon with a well developed subangular blocky structure. The underlying olive clayey Bg horizon has a strongly developed coarse angular blocky structure. Previous studies report a clay content of approximately 30-40% in the top 30 cm and 60-70% from 40-80 cm, with a bulk density of 1.6 in the upper horizon compared to 1.8-1.9 in the lower horizon. Profiles are very slightly porous and slowly permeable in the subsoil.

The soil is often waterlogged for long periods over the winter, but in dry conditions deep cracks develop which may help to drain autumn rainfall. A closely spaced (20 m) system of pipes supplemented by mole drains is recommended for drainage.

The Total Organic Carbon (TOC) of the top soil and the lower 'B' horizon were analysed to reveal 2.57% in the top soil and 0.48% in the lower horizon, a five fold difference. The dominant clay minerals in the top soil were kaolinite and illite, and in the lower horizon were kaolinite, illite and smectite (see Figure 6). CEC values for the soil series have been given in the range of 35-48 meq/100g (Jarvis and Hazelden, 1982). The combination of a high clay content, with high CEC and a relatively high organic carbon content would suggest that the soil at Wytham would have a relatively high adsorptive capacity for organic compounds.

This soil association covers approximately 1.86% of the total land area of England and Wales but soils with similar hydrology account for 4.95% (including Scotland). Heavy clay soils such as Denchworth series have a tendency to crack and exhibit by-pass flow, and are thought to represent 33% of the land area of England and Wales.

2.3 CROP HUSBANDRY

A winter wheat crop was harvested in August, leaving both stubble and chopped straw on the soil surface. The field was then mole drained. The beam mole plough comprised of a blade leading down to a 3" bullet which was connected to a following ball and chain. The mole depth was approximately 50 cm and the mole drains were at 3 m intervals. The field was then cultivated by ploughing to 15-20 cm. The field was cultivated using a 'Roterra' (powered harrow) and then drilled with winter wheat (variety Haven). Tram lines were set at 12 m intervals. Draza slug pellets (Bayer, active ingredient 4% methiocarb) were applied at 5.5 kg/ha on 11,10,92.

Isoproturon was the active ingredient at 2.5 kg/ha in Javelin Gold (Rhone Poulenc) applied to the field on 10,2,93 to control blackgrass. Nitrate was applied on 6,3,93 in the form of urea (46% N) at a rate of 125 kg/ha. On 15,4,93 the pesticide 'Cheetah' (Hoechst, active ingredient fenoxaprop-ethyl, 60g/l) was applied to control black grass at 2 l/ha in conjunction with 1.5 l/ha Cycocel (a growth regulator) and 1 l/ha LI 700 (adjuvant). On 26,4,93 a further 281 Kg/ha urea was applied to the field. On 30,4,93 0.6 l/ha Starane was applied

(Dow Elenco, active ingredient 200 g/l fluoroxypyr) to control Cleavers and 0.8 l/ha Sportak (Schering) was used as a fungicide. On 18,5,93 1.5 l/ha Cheetah and 1 l/ha Li 700 were again applied to the field. On 21,6,93 1.5 l/ha Impact Excell and 0.5 l/ha Mistral fungicides were applied to the field.

The crop was harvested in mid August, 1993 and the straw baled. The plot was ploughed to a depth of 15-20 cm. On 18,10,93 the plot was cultivated with a 'Roterra' and on the 20,10,93 the field was sown with winter barley, variety Fighter.

2.4 TIMETABLE OF EVENTS

8,92	Winter wheat crop harvested
	Mole drains put in by beam mole plough
	Ploughing and cultivation with powered harrow
9,92	Drilling with winter wheat
11,10,92	Slug pellet application
	Installation of experimental equipment
12,92	Installation completed
10,2,93	Isoproturon applied to control blackgrass
6,3,93	N-fertiliser applied
1,4,93	Significant rainfall and drainflow
12,4,93	No more significant drainflow
15,4,93	Fenoxaprop-ethyl applied to control blackgrass
26,4,93	N-fertiliser applied
22,7,93	Last water samples collected
	Experimental equipment removed
8,93	Crop harvested

3. Methods

3.1 FIELD EXPERIMENTATION

3.1.1 Soil hydrology

The 1992/93 experimental programme comprised of three components:

Monitoring of surface hydrology to determine hydrological inputs and processes.
Rainfall was monitored using tipping bucket rain gauges connected to loggers (Campbell Scientific, USA); effects on surface hydrology being assessed by logging pressure transducer tensiometers (PTTs) and a capacitance probe (Institute of Hydrology, UK) at 10cm depth. Overland flow was collected and measured using guttering lined with damp-proof sheeting inserted into the soil 0.05 m below the surface. Slotted Osma drain and gravel was placed in the gutter, and the whole installation was roofed to prevent the direct entry of rainfall. This was installed in the form of a 4 x 4m 'V', with the 'V' facing upslope. The water collected in the guttering was led to a tipping bucket raingauge by a 8.2 cm drainpipe, the tips being

recorded by a Campbell logger.

Monitoring the influence of rainfall and drainage on the status of the soil water reservoir and related soil water dynamics.
A set of 30 manual mercury manometer tensiometers which straddled mole drain 25 (see Figure 2) were installed at depths of 0.1, 0.3, 0.5, 0.75, and 1.0 m, to give 2-dimensional profiles of potentials around the mole drain. The 0.5 - 1.0 m manual tensiometers were inserted through access tubes and were angled so the profile of porous cups at the different depths were vertically in line. The angled insertion of tensiometers was to reduce the effects of lateral spatial variability. Five pressure transducer tensiometers (PTT) were installed at the same depths at a position 1.5 m from the manual tensiometers. In front of the manual tensiometers 3 neutron probe access tubes were installed to a depth of 1.5 m to enable the employment of a neutron probe (Didcot Instruments, UK), to measure volumetric water contents at 0.1 m increments from the soil surface.

Monitoring the flow of water in field drain 2
Field drain 2 was intercepted at a point equidistant between moles 22 and 21 and the drainage water was fed by an 80 mm pipe to a v-notch weir at the soil surface, some 15 m downslope of the interception point. Pressure transducers were used to determine the height of water in the weir, and by use of a calibration equation the flow rate was deduced.

Monitoring of soil water status commenced in November 1992 and continued throughout the crop cycle.

3.1.2 Soil and water sampling

Suction samplers were installed at three depths (0.25, 0.5 and 0.75 m) through aluminium access tubes to assess isoproturon concentrations in the soil pore water. The augured hole was partially filled with silica flour into which the ceramic pots of the suction samplers were bedded. Two overland flow traps (2 m in length) supplied by SSLRC were installed and connected to 5 l plastic sampling vessels. At the field drain 2 v-notch weir flow gauge site an automatic sampling device was installed (triggered by the height of water collected in the weir box it fills twenty-four 1 l bottles). The 'catchment' of this tile drain prior to its interception was estimated to be 1800 m^2.

Access tubes (110 mm) were positioned directly over mole drains 25, 24 and 22 and small glass beakers (75 ml) installed in the bottom of the moles to act as sumps for water sampling (Figure 2.).

On the same day as pesticide application 1 l of 10000 ppm KBr was applied via a watering can to a 0.5 m^2 area 1.5 m upslope of the 0.25 m suction samplers, and also over the position of mole drain 25, 2 m away from the intersection with field drain 2.

In addition, filter paper discs (Whatman no. 1, 10 cm dia.) were placed across the plot (fastened on wooden battens to keep above the moist soil) to collect the pesticide spray and estimate the true application rate of the pesticide.

Throughout the season water samples were taken manually from the field drain 2 outflow and ditch at the bottom of the field.

As soil coring techniques proved difficult to use due to the sticky consistency of the soil, soil was collected only from the upper 2 cm of the soil with a spatula. At fortnightly intervals 1 kg amounts of soil were collected from 1 m^2 plots, which were sampled in sequence from one end of the experimental plot to the other. Samples were frozen prior to analysis.

3.2 LABORATORY ANALYSIS AND EXPERIMENTATION

3.2.1 Sample preparation, concentration and analysis

Water samples were maintained at 4°C prior to analysis (not more than 1 month). Prior to isoproturon analysis samples were first concentrated using C18 bond elute cartridges (Sorbex) and eluted from the column with a solution of 100% methanol. Analysis of isoproturon was by hplc with a C8 column and acetonitrile/water eluent with detection at 240 nm.

Prior to anion analysis a 5 ml aliquot was taken from the original water sample and filtered using 0.45 um disposable filters (Millipore). Samples were analysed using a Dionex ion chromatograph. The eluent used contained 1.8 mM sodium bicarbonate and 1.7 mM sodium carbonate. The regenerant used was 25 mM sulphuric acid. Detection was by electrical conductivity.

Soil samples were analysed for isoproturon by taking four 30 g samples and extracting with 50 ml methanol prior to determination by hplc.

3.2.2 Total organic carbon analysis

From soil collected from the topsoil and 40 cm, 4 replicate sub-samples of 2 g were placed in small porcelain crucibles. A solution of 4M HCl containing 30 g/l $FeCl_2.4H_2O$ (to prevent any MnO_2 present from indirectly oxidising the organic carbon) was used to saturate the soil in the crucibles to remove carbonates. The crucibles were placed on a hot plate in a fume cupboard for 2 days to evaporate off the solution. The dried soil samples were then weighed accurately in 0.2 g amounts on terracotta crucibles and then analysed with a LECO 444 carbon/sulphur analyser with a furnace temperature of 1400°C.

3.2.3 Clay mineralogy

Soil samples were taken from a soil pit from the top 5 cm and 40 cm depths for analysis. In addition sediment found in tile drain water collected during a rain storm in December was filtered prior to semi-quantitative clay mineral analysis. The equipment used comprised a B-pex goniometer with an EFG X-ray generator.

3.2.4 Total aerobic heterotrophic bacteria

From topsoil and 40 cm soil collected from a soil pit a 1 g sub-sample was placed in a sterile Universal bottle containing 9 ml quarter strength ringer solution (3 replicates). After shaking the sample was diluted 10,000 times in further bottles of sterile ringers solution before plating out using 0.05 ml drops from disposable sterile pastettes onto 0.3% Tryptone Soya Agar (Oxoid) (0.5% agar). The plates were incubated at 20°C for 2 days prior to counting.

3.2.5 Degradation of ^{14}C-labelled isoproturon

Subsamples of topsoil and 40 cm soil samples collected from a soil pit were used to measure moisture content through weight loss after incubation at 105°C overnight. The soil samples were air dried for 2 days so that the samples had lost 10% of their original moisture content. The samples were then ground with a sterile pestle and mortar (flamed in ethanol) and 3 mm sieved. The soils were then placed in 150 ml conical Quickfit flasks and weighed (6 replicates). ^{14}C-ring labelled isoproturon in a 10 mM $CaCl_2$ solution was added to the soil samples to a final concentration of 0.01 μg/g with a disposable pastette. The soils were returned to their original moisture content through the addition of further sterile 10 mM $CaCl_2$; this was 31.5% for the top soil and 21.6% for the 40 cm soil. The Quickfit conical flasks were connected via neoprene tubes to a pump which ran air through a CO_2 trap of soda lime before bubbling through water in a Drechsel flask prior to its introduction to the soil samples. Air from the conical flasks was then bubbled through a CO_2 trapping solution of 70 ml of 50 mM NaOH.

4. Results and discussion

4.1 WEATHER

A major factor influencing the processes of pesticide persistence and transport is the effect of the climate. The two most important factors are rainfall and temperature.

Rainfall data for the 1992/93 crop season is presented in Figure 8, and 10 and temperature data in Figure 11. Figure 8 shows the mean monthly rainfall at Wytham compared with the long term monthly means. December 1992 had slightly above average rainfall, however January 1993 produced almost twice the average monthly rainfall. This created very wet, waterlogged, conditions; and delayed the spraying of pesticide until 10 February 1993.

February and March 1993 proved to be much drier than average, such that desiccation cracks of 2-4 cm depth could be observed at the soil surface. The little rain that did fall over this period produced no significant drainflow events. The first major storm, occurred on 1 April, 1993, and produced the first significant drainflow and pesticide transport. Rainfall between the period of 1-12 April generated a series of drainflow events. No more significant drainflow events occurred after this period.

Temperature data for the 1992/93 crop season (Figure 11) shows the mean daily temperature values after spraying. From the end of April shrinkage cracks were increasingly apparent. Drier conditions in the topsoil is a factor known to reduce microbial activity. Thus, the pesticide may persist for longer than under wetter conditions, but in the absence of transport to the drains it no longer represents an immediate contamination threat to surrounding water courses.

4.2 SOIL STRUCTURE AND HYDROLOGY

4.2.1. Soil profile and physical characteristics

Results presented cover the data assimilated over the initial five/six months from the end of November 1992 to mid July, 1993.

Manometer tensiometer data were analysed to produce 2-D distributions of soil water potentials. These showed the spatial temporal wetting and drying around mole drain 25 during the crop cycle. Data showing total soil water potentials around a mole drain during saturated field conditions in the winter months is presented in Figure 3. Ranges of total soil water potential were represented by different letters defined within the key. Saturation in Figure 3 was shown as the area above the solid line.

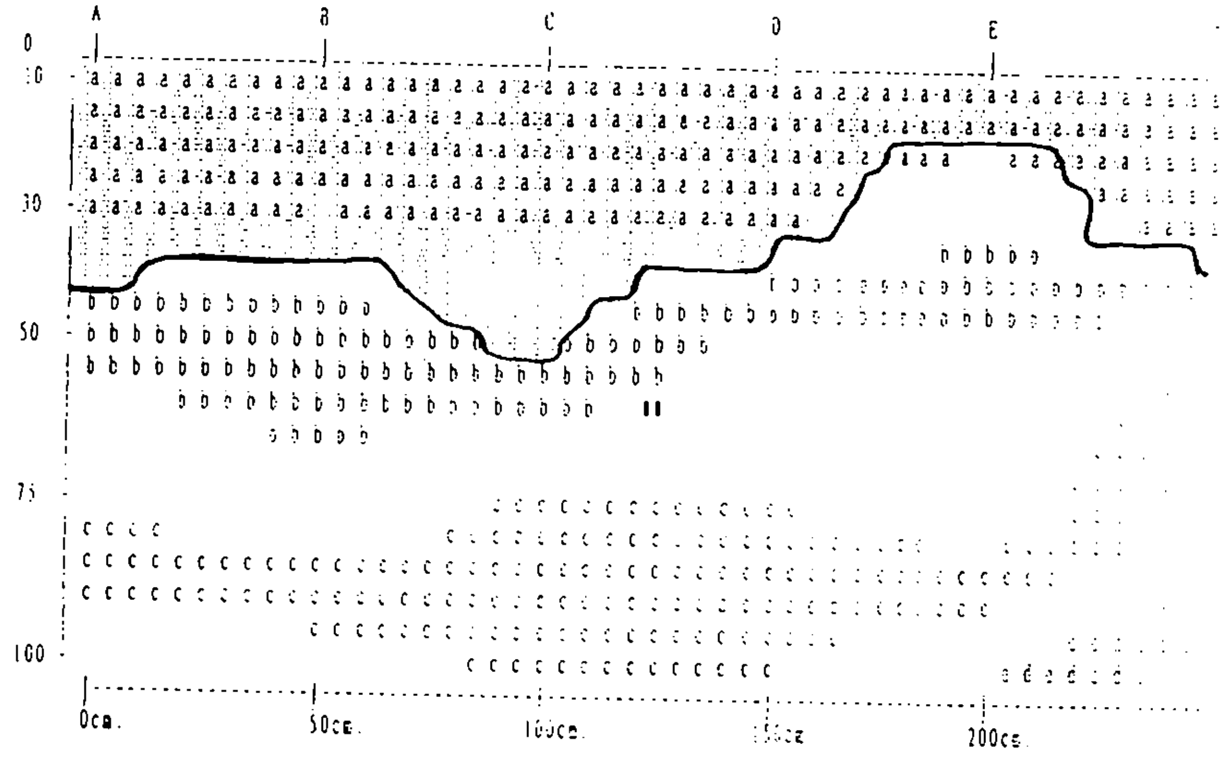
The presence of a saturated zone at 0.3-0.4 m up to the soil surface, resulting from a build up of saturation above a lower horizon of low hydraulic conductivity, was clearly indicated and the evidence was corroborated by pressure transducer tensiometer (PTT) data in Figure 4. Figure 4 showed conditions greater than saturation (ie. a positive head of water) at the soil surface, during and after the storm event on 6/7th December 1992. This was shown by the potential at 0.1 m being greater than -1 kpa, and at 0.3 m greater than -3 kpa.

No evidence of a permanent water table under these wet conditions within the top 1.0 m was seen from the tensiometer data shown in Figures 3 and 4 as total soil water potentials never became greater than -10 kpa during this period.

Data presented by Jarvis & Hazelden (1982) indicated that downward movement of water in the Denchworth series was likely to be severely restricted below the topsoil. An increase in clay content from 38% to 73% between 0.3 m and 0.4 m and a corresponding increase in packing density from 1.6 to 1.9 gcm-3 can be expected. This would present a significant barrier to vertical infiltration within the profile. This boundary (providing the base for the saturated zone) at about 0.35 m corresponds well with changes in soil type and can be attributed to the change from A to B horizons within the profile at Wytham. Another boundary change was seen at a depth of 0.8 m which was indicated by the presence of a wetter zone above 0.8 m than below that depth, shown in Figure 5, from data collected from the manual tensiometers. The profile from 0.35-0.8 m seemed to consist of a higher fine clay content and greater bulk density, and consequently a much lower hydraulic conductivity than the rest of the profile. This can give rise to a secondary saturated zone at this lower depth. The low hydraulic conductivity (K) of the matrix (0.007-0.071 m/day at 0.6 m), associated with the Denchworth series, (Jarvis and Hazelden, 1982) and the presence of macropores suggest that preferential flow mechanisms would be dominant in this soil.

Another feature within the profile is the buried straw layer (at approximately 15 cm depth) resulting from the incorporation of the previous year's straw and stubble. This layer may influence hydrological processes such as lateral interflow and in addition may be a site of increased pesticide sorption.

One of the most important characteristics of this site is its significant shrink/swell capacity. The porosity of this site in terms of hydrology, in the winter months, is almost exclusively governed by biopores consisting of worm and old root channels. During the late spring and summer, extensive soil shrinkage fractures were observed, some extending to well below



⁞ = SATURATED

a = 0 to -2.5 kPa

b = -5.0 to -7.5 kPa

c = -10.0 to -12.5 kPa

d = -15.0 to -17.5 kPa

II: ESTIMATED DRAIN POSITION

% OF CROSS SECTION ABOVE 30cm. WHICH IS SATURATED : 26.6 %

% OF CROSS SECTION ABOVE 50cm. WHICH IS SATURATED : 29.2 %

% OF TOTAL CROSS SECTION WHICH IS SATURATED : 29.2 %

Fig. 3. Total potentials at 10-100 cm depths measured across mole drain 25 by manual tensiometers on 7,12,92

a:ptdest

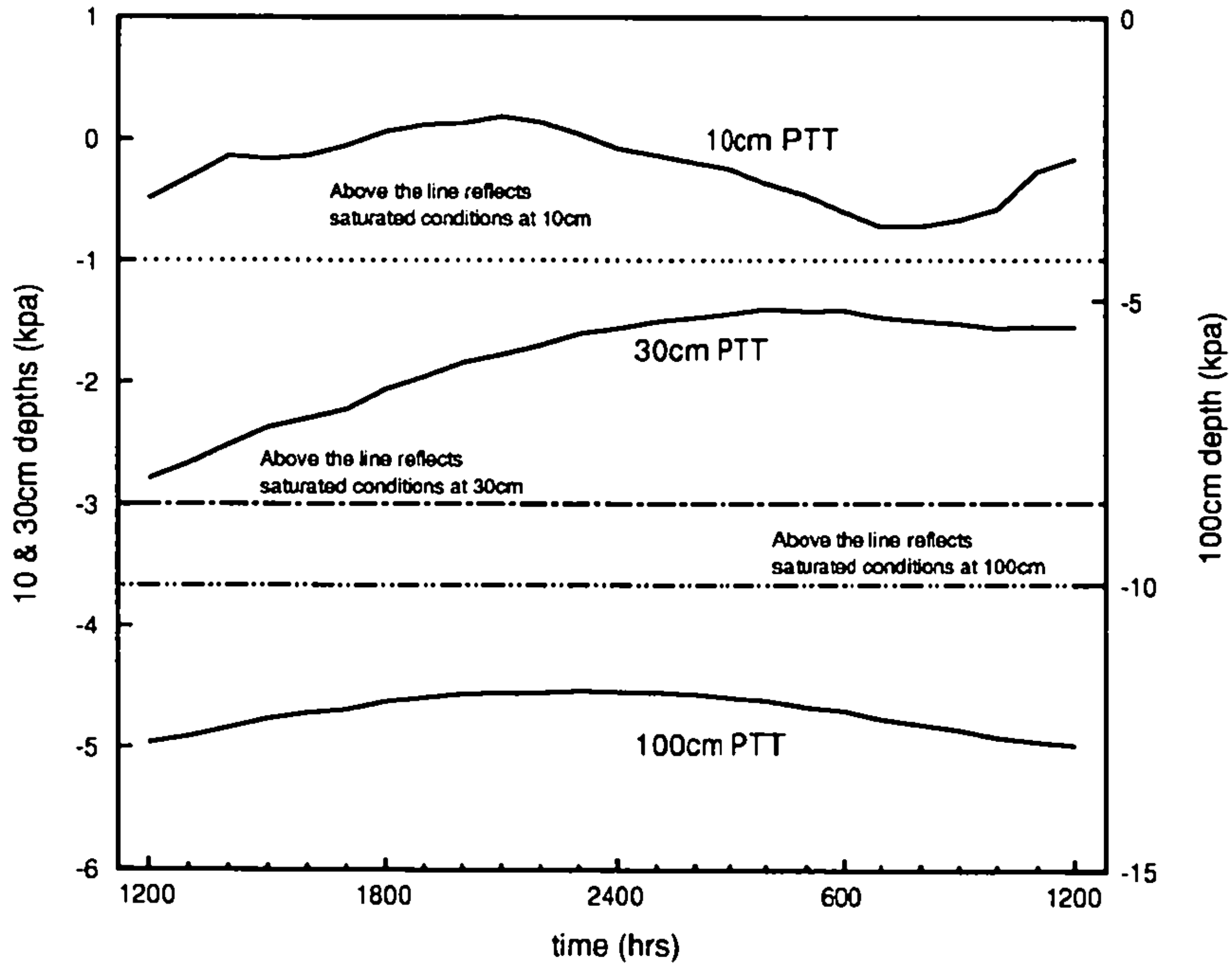
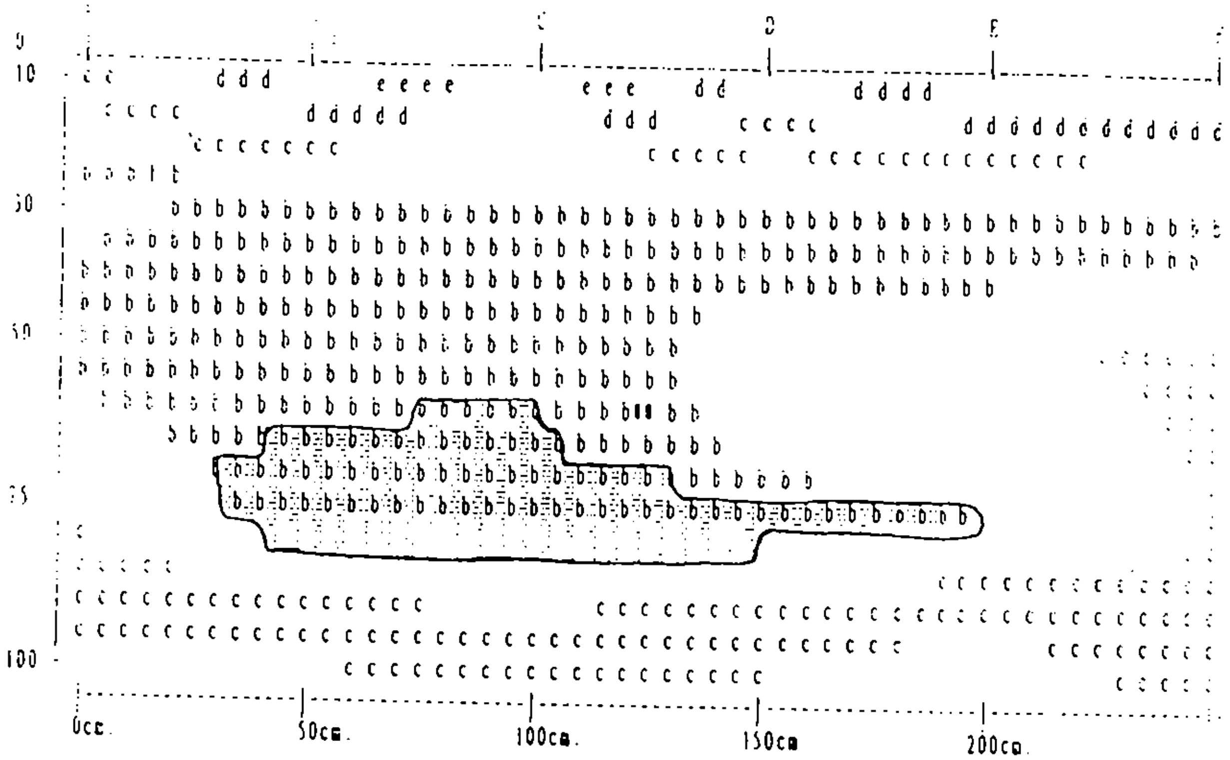


Figure 4. Total potentials at 10, 30 and 100 cm depths during rainfall event of 6th/7th December 1992



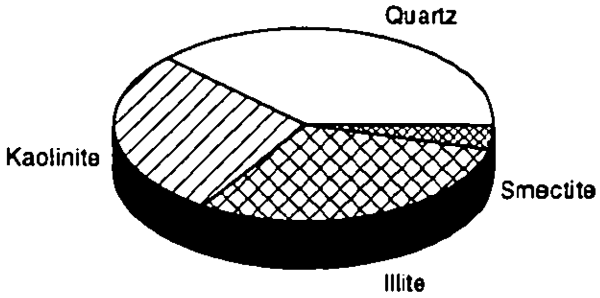
: = SATURATED
a = 0 to -2.5 kPa
b = -5.0 to -7.5 kPa
c = -10.0 to -12.5 kPa
d = -15.0 to -17.5 kPa
e = -20.0 to -22.5 kPa

II= ESTIMATED DRAIN POSITION

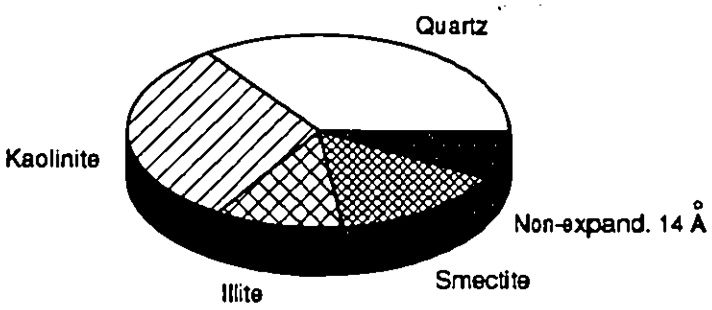
% OF CROSS SECTION ABOVE 30cm. WHICH IS SATURATED : 0.0 %
% OF CROSS SECTION ABOVE 50cm. WHICH IS SATURATED : 0.0 %
% OF TOTAL CROSS SECTION WHICH IS SATURATED : 9.5 %

Figure 5. Total potentials at 10-100 cm depths measured across mole drain 25 by manual tensiometers on 4,5,93.

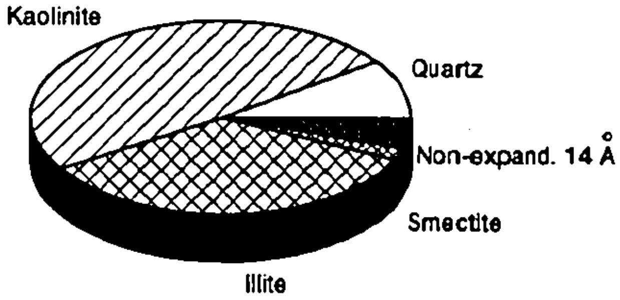
Claywy3



Soil surface



'B' horizon



Sediment found in field drain 2
from rainfall event 3,12,92

Figure 6. Clay mineralogy at Wytham

1m in depth at the height of the summer. As explained in the following section the water fluxes within the profile are determined by these macropores, both biological and physical in nature.

4.2.2. Observed flow pathways and antecedent conditions

Flow pathways were studied largely from data collected from a variety of instruments from a series of discete drainflow events. Data for the capacitance probe is not presented due to problems with calibration. This was possibly due to a 'salinity effect' whereby ions effect the frequency readings presented by the probe. Therefore, the relationship between frequency and water content is difficult to establish. Readings with the neutron probe were taken only in the latter part of the project, after April, 1993.

Storm event 1 (SE1) - 6/7th December 1992, 65 days before spray day.

Figure 7 describes SE 1 and shows the relationship between rainfall, overland flow (surface runoff), and drain flow from the field drain. Under surface saturated field conditions recorded rainfall events showed an immediate reaction in terms of drainflow. Due to this rapid response, and the absence of a water table/wetting front at mole drain depth, the drain flow events have been attributed to macropores providing water for the drains from the soil surface. This is in contrast to the more normal situation of the water table in periods of field capacity falling to a level controlled by the depth of the mole drains.

Studies have shown that macropore flow is the predominant process in the heavy clay soil at Wytham (Kneale and White, 1984; Kneale, 1986) and in other heavy clay soils (Beven and Germann, 1982; Bouma *et al.*, 1981). By-pass flow has been shown to occur in the noncapillary interpedal pore space whenever application rate exceeded the infiltration rate of the individual microaggregates (Radulovich *et al.*, 1992). At Wytham during the winter to early spring period by-pass flow was thought to be through macropore channels consisting of earthworm burrows and also most probably moling fissures, unlike the late spring and summer months which were dominated by shrinkage cracks. This is because during the winter cracks were not observed at the soil surface, however large numbers of open worm burrows were apparent at the surface.

Overland flow is thought to be produced by rainfall excess which occurs at the ground surface when the rainfall intensity exceeds the infiltration capacity (Pilgrim *et al.*, 1978). This is demonstrated clearly in Figure 7 where significant overland flow occurred 2 hours (approx.) after the start of rainfall. At this point one can assume that the macropores were working at maximum capacity, and unable to accept more water. The start of overland flow coincided with peak drain flow. It is important to note that significant overland flow, or sheet flow, is chronologically the secondary factor in the removal of excess precipitation. If the macropore infiltration capacity has not been reached then significant overland flow will not begin. During this storm event the volumes of overland flow were beyond the recording capability of the tipping bucket flow meter.

Unfortunately the drain flow measurement method in December, 1992 was artificially restrictive to flow and as a result the peak drain flow, as demonstrated by the plateau in Figure 7, is artificial. Therefore the percentage rainfall exiting as drain flow given in Table 1 for SE 1 is an underestimate. For SE 1 the water flow from the field drain to the V-notch weir was along a pipe whose internal diameter proved to be the dominant restrictive factor

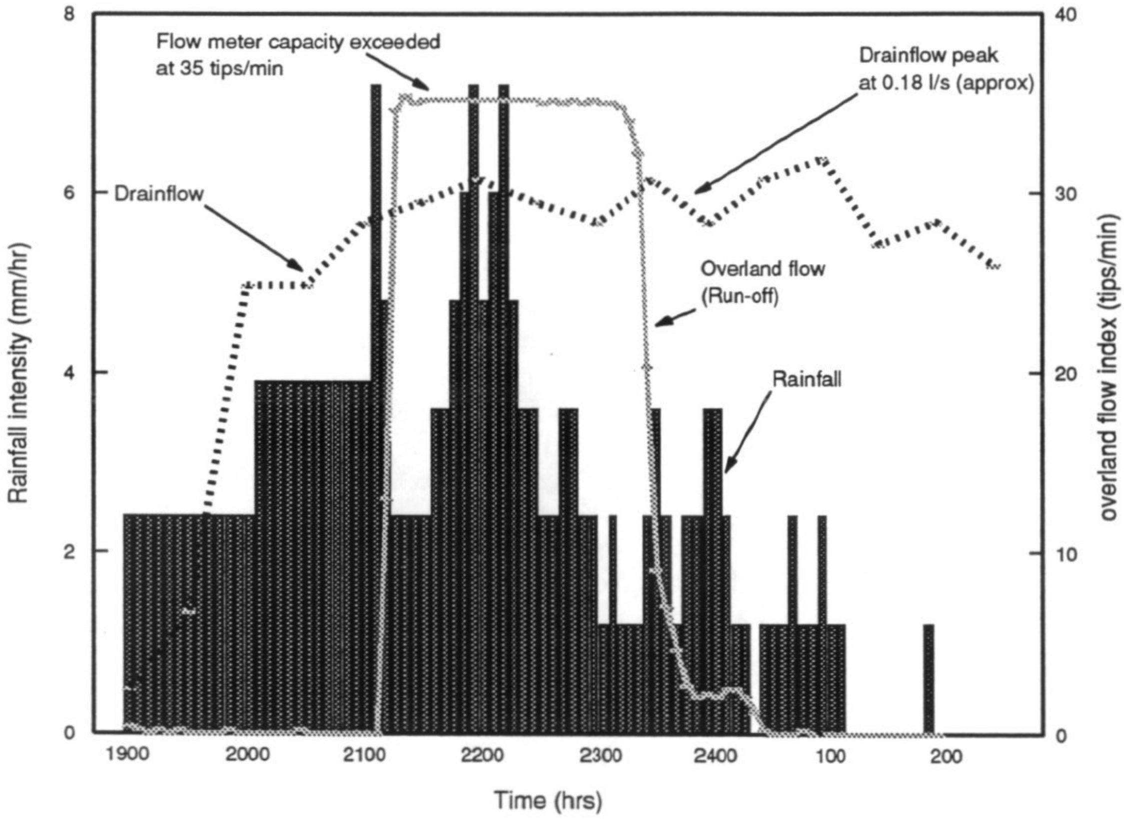


Figure 7. A comparison of rainfall, overland flow and drainflow at Wytham
6th/7th December 1992

to flow. This pipe was replaced with one whose internal diameter was equal to that of the field drain in late December, 1992. The presence of a saturated zone at 0.3-0.4 m depth immediately after SE 1 shown in Figure 3 suggests sub-surface lateral flow was also a feature during and after the storm event.

The clay mineral composition of sediment found in the field drain water is shown in Figure 6. Whilst it is difficult to ascertain the origin in the soil profile of all the sediment collected, the presence of a non-expandable 14 Å fraction suggested that some of the sediments had originated from the B horizon because the non-expandable 14 Å fraction did not occur in the other horizons.

Observed changes in conditions between December, 1992 and April, 1993

The topsoil remained close to saturation until early February 1993, at which time the absence of rainfall and the still conditions allowed the farmer onto the field to apply the pesticide. The period between the spraying of pesticide on 10/02/93 (day 0) and SE 2 on 01/04/93 (day 50), the first recorded significant drainflow event, was relatively dry as shown by data for February and March 1993 (Figure 8). The rainfall events that did occur at this time seem to have been sufficient to raise the matric potential at 10 cm to saturation, but for only brief periods (Figure 9), but ceased before any significant drain flow events were initiated. Rainfall and temperature data collected from 1 April, 1993 onwards are shown in Figures 10 and 11.

Storm event 2 (SE 2) - 1st April 1993, 50 days after spray day.

Figure 12 represents SE 2 which was the first recorded incidence of significant drainflow since spraying on 10th February 1993. The drainflow associated with that rainfall event has been plotted, along with the concentration of isoproturon present in water samples collected every 30 minutes by the triggered autosampler.

Overland flow was not picked up by the overland flow meter, however this equipment was believed to be out of commission during the April period. Water was collected in the overland flow traps (Figure 13); however the amount of overland flow could not be quantified.

The delay between the initiation of drainflow and rainfall was related to the drying of the topsoil that occurred from 10th February 1993 resulting in an increased soil water deficit (SWD) in the surface layer (0-0.05 m). Shallow cracks during this period were clearly visible at the soil surface. The rainfall that fell before the start of drain flow was assumed to be used to satisfy this SWD, although the entire deficit within the profile down to drain depth was not reduced to zero before drain flow occurred. This is demonstrated in Figure 14 where PTT data showed the surface 10 cm to have a positive head of water, and the soil at 30 cm to be unsaturated, when the field drain was flowing during SE 2.

Robinson *et al.* (1987) also showed 42% of storm rainfall passing through mole drains despite the soil moisture content being well below "field capacity". Although the soil profile was not completely saturated, the major pathways, ie. macropores, had to be surrounded by soil at a soil water content which was conducive to those pathways functioning. This would also include the soil surface as a major pathway of water supply to macropores (Beven and Germann, 1982).

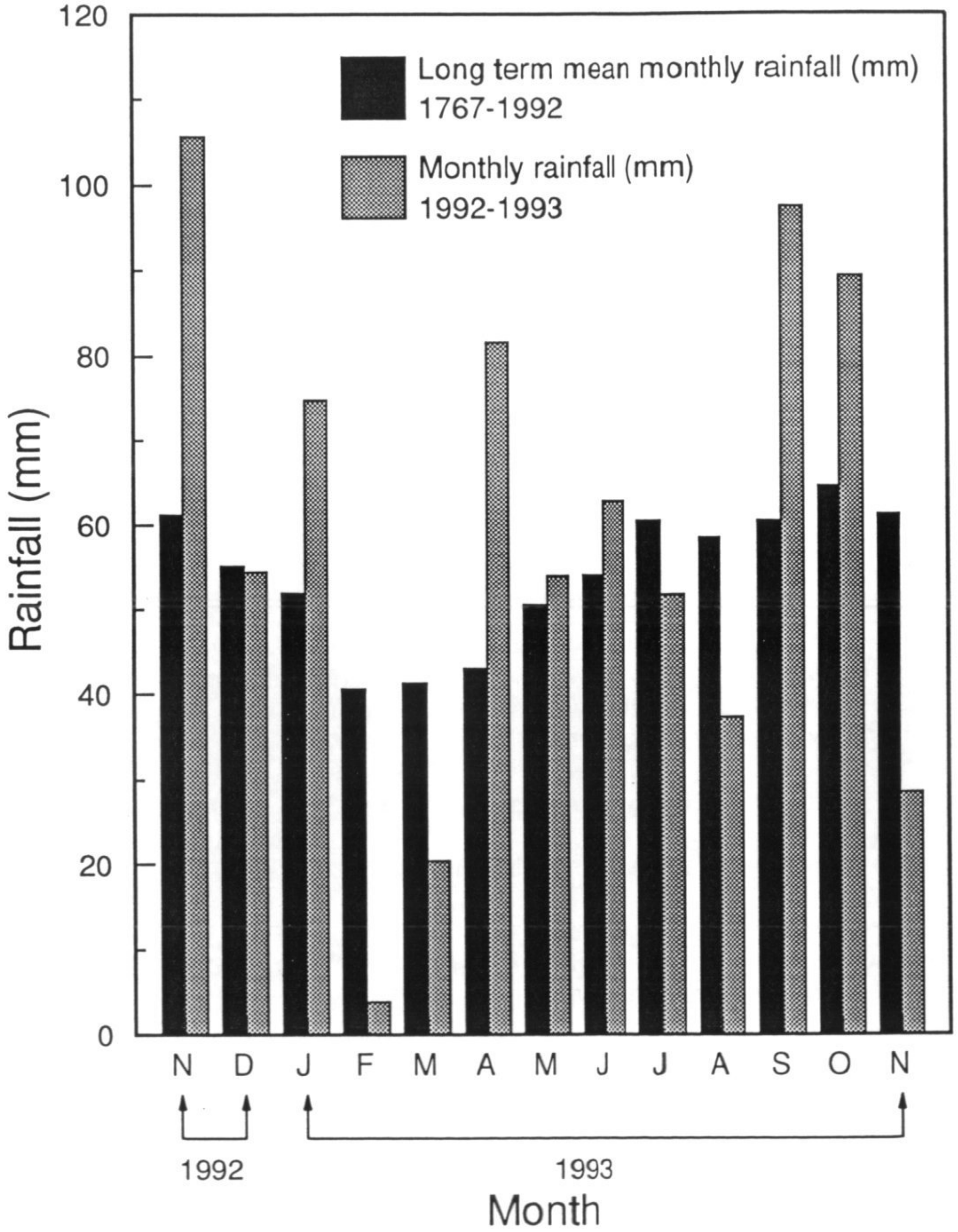


Figure 8. Comparison of long term mean monthly rainfall with monthly rainfall in 1992/3

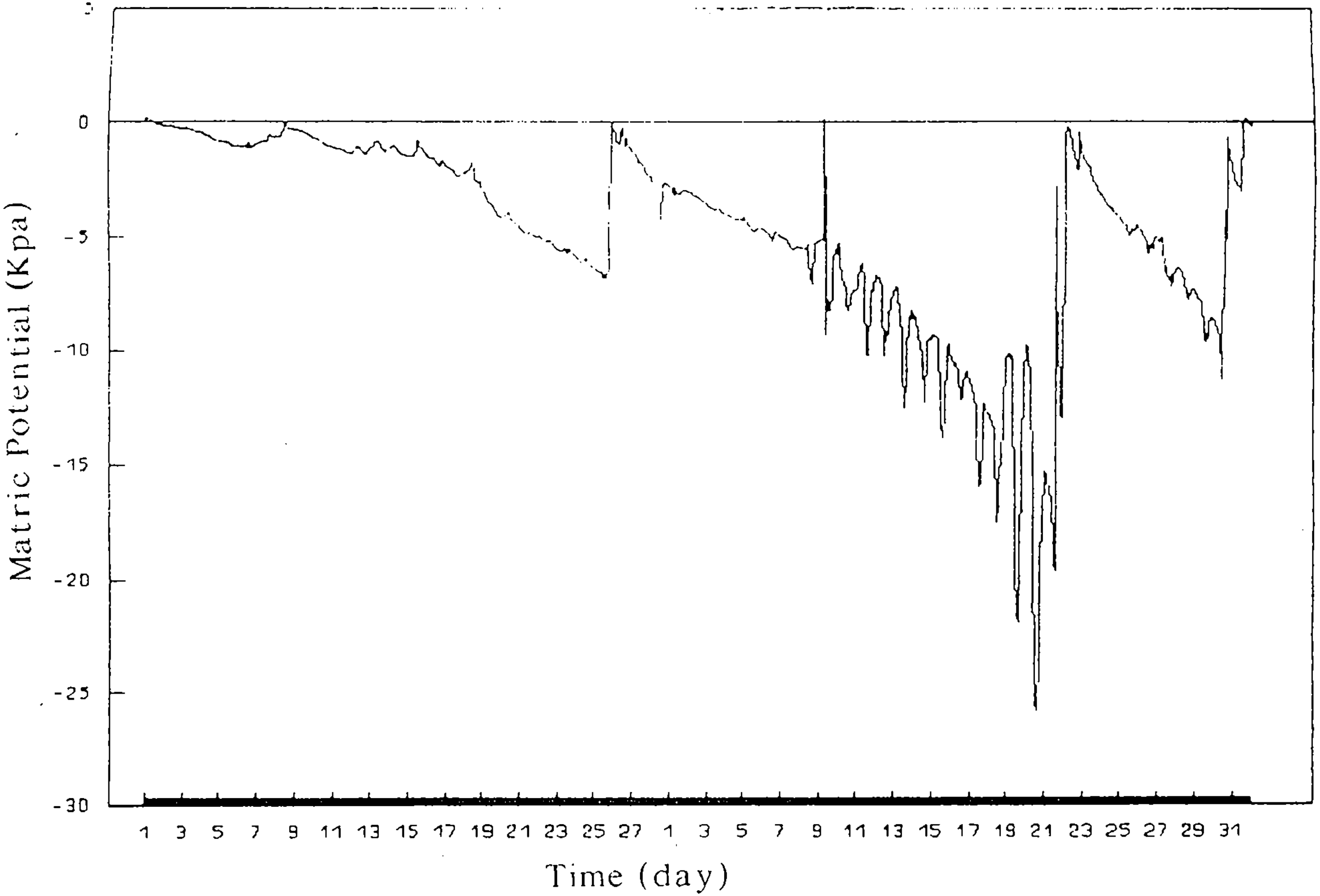


Figure 9. Matric Potentials at 10cm Depth at Wytham From 1st February to 31st March 1993.

a:cumrain

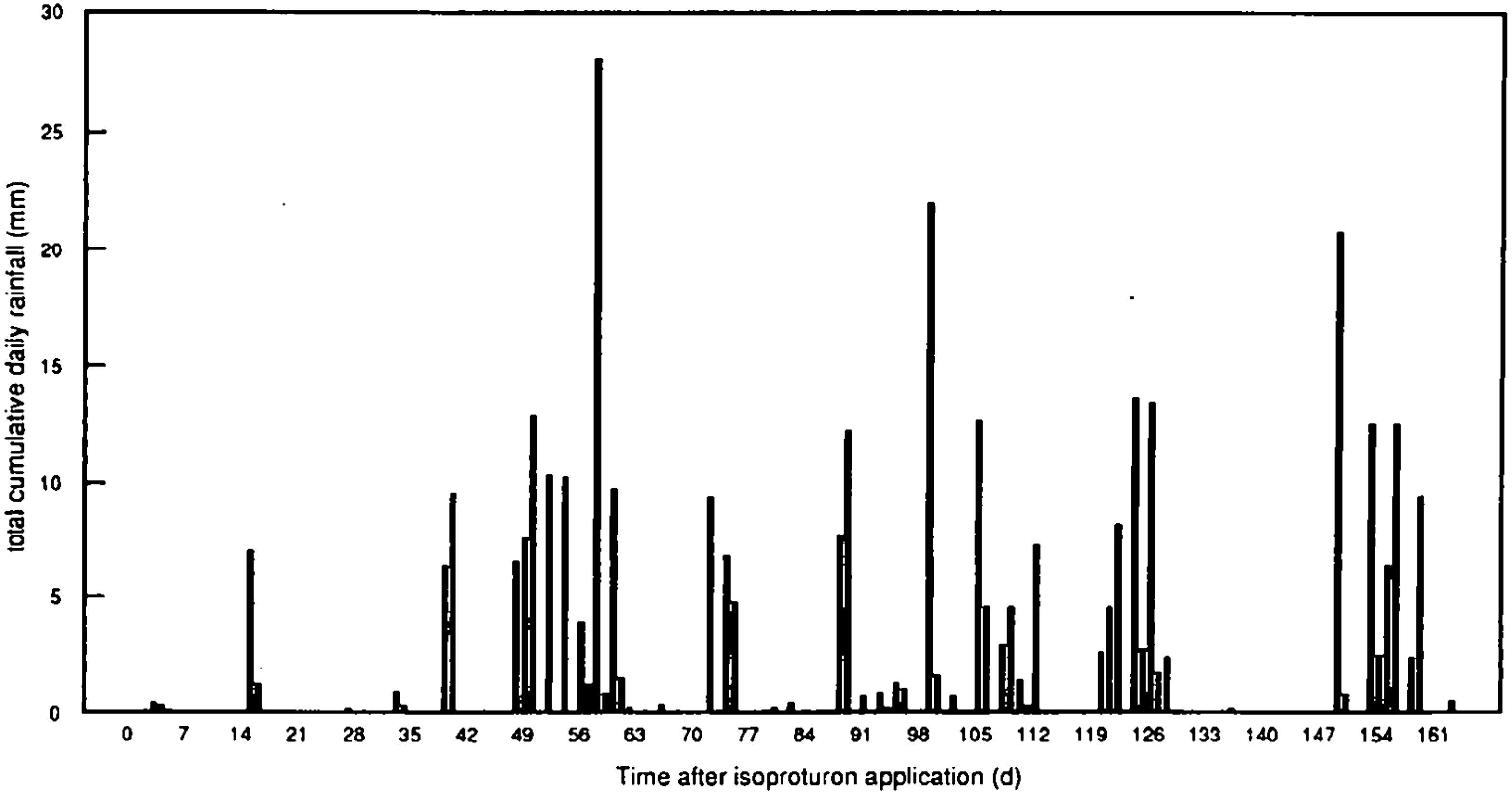


Figure 10. Rainfall data for Wytham beginning 1 April, 1993

a:cumtemp

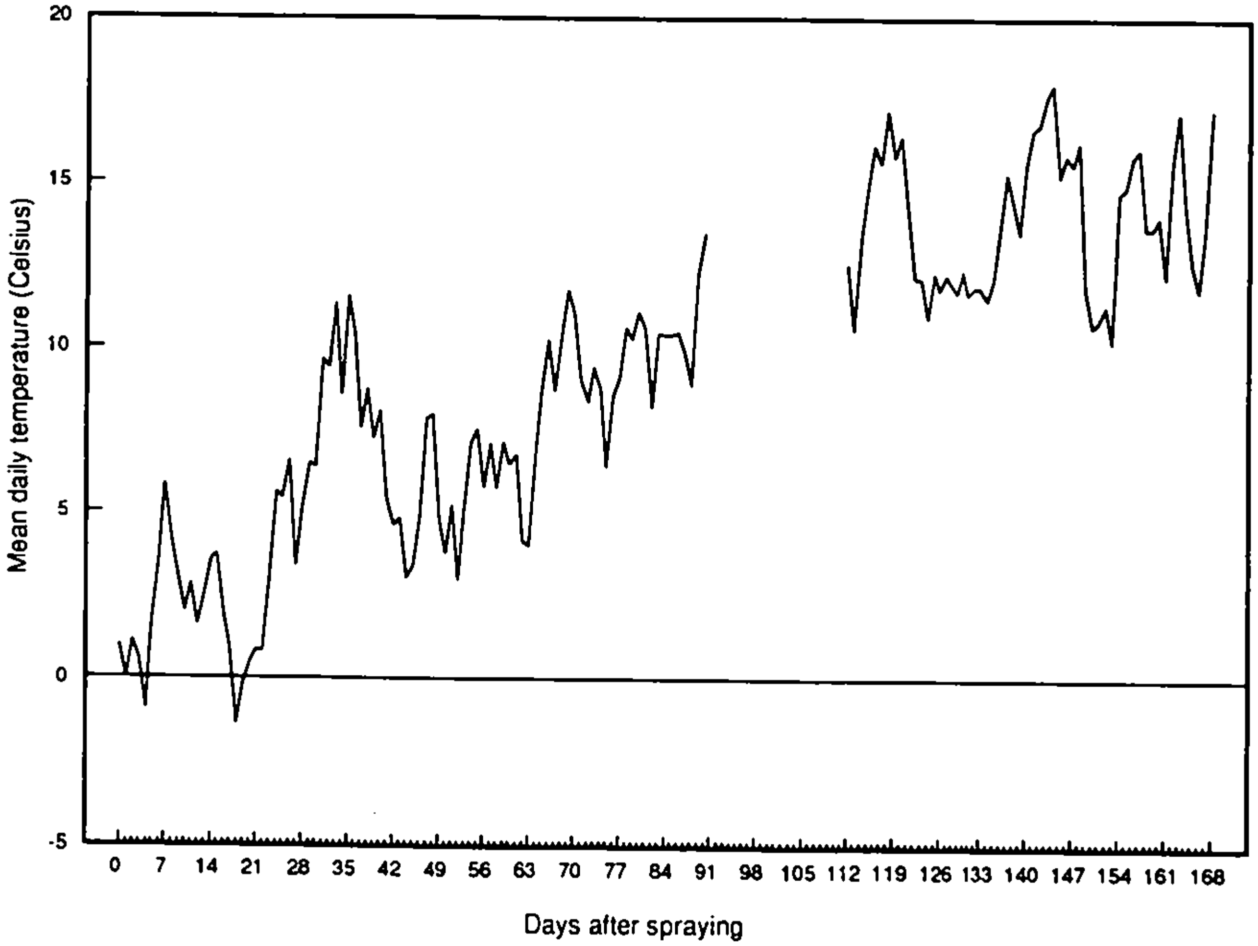


Figure 11. Mean daily temperatures, beginning 10 February, 1993

a:storm1

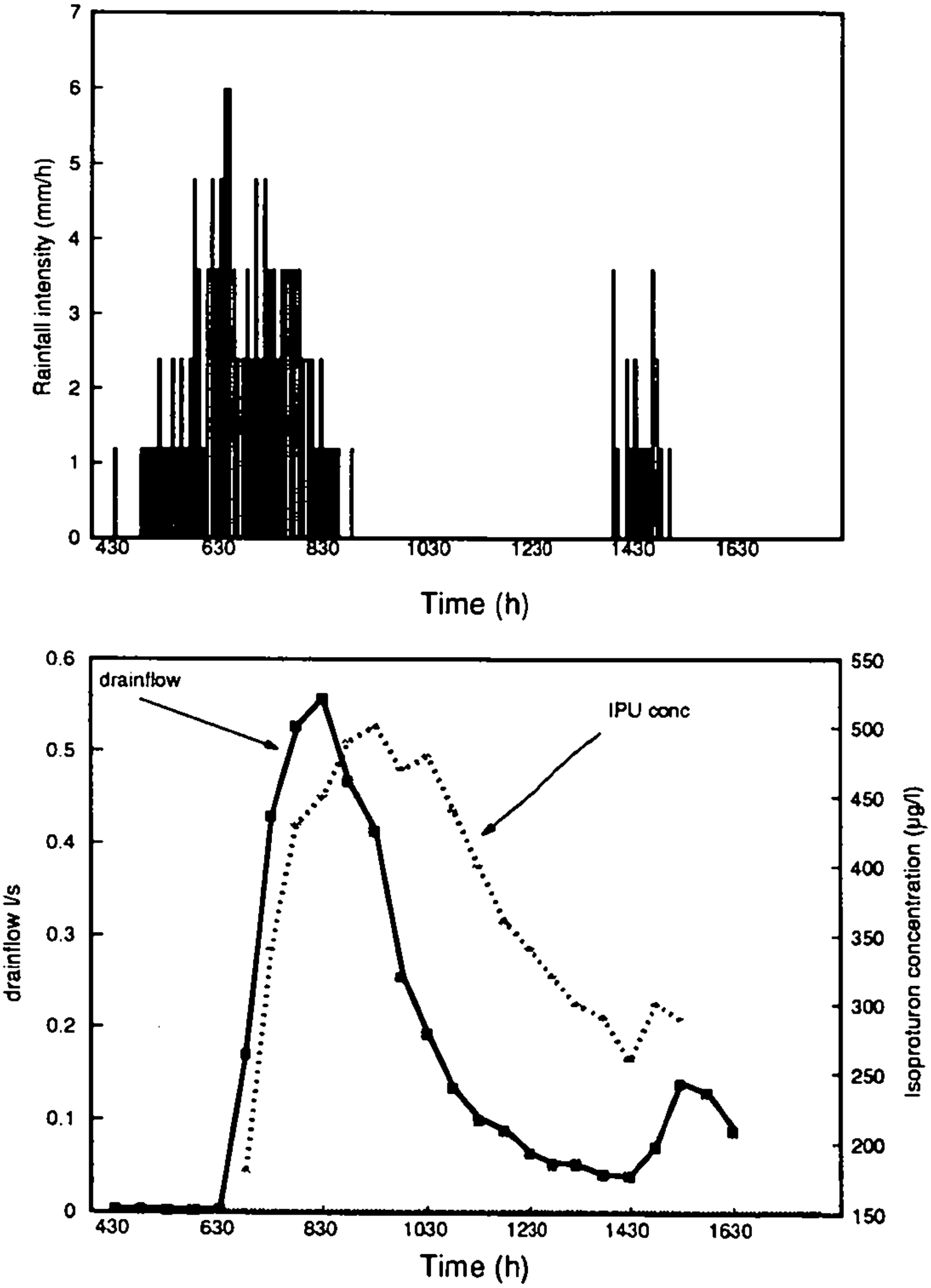
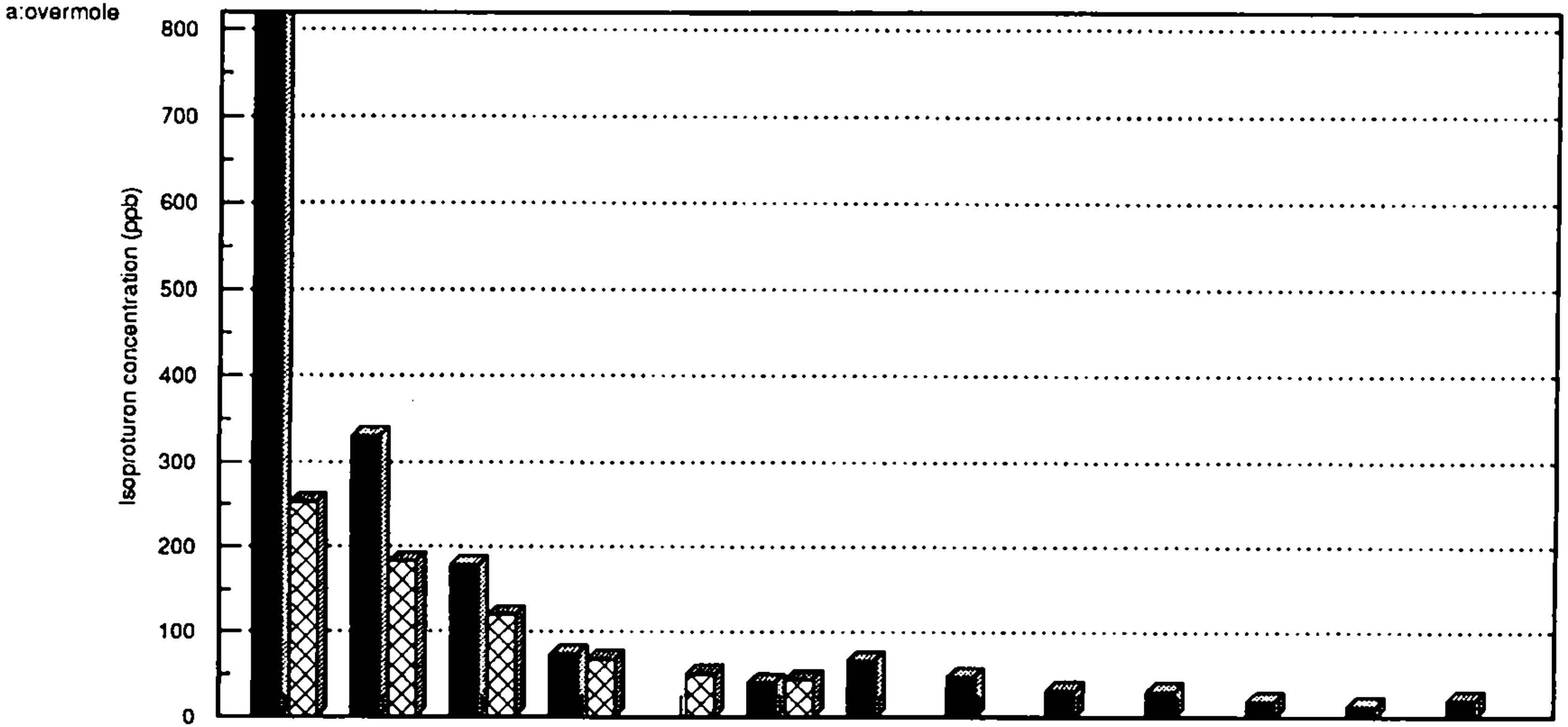


Figure 12. Relationship between rainfall, drain flow and ipu concentration 50 d after ipu application (1,4,93)



Time after isoproturon application (d)	50	56	64	75	78	90	100	106	113	120	124	127	162
overland flow ■	817	330	179	73	0	40	68	47	31	30	19	13	20
mole drain ⊠	252	183	120	67	50	44	* N/A	N/A	N/A	N/A	N/A	N/A	N/A

Figure 13. A comparison of isoproturon concentrations found in overland flow and mole drainage water (2 replicates for overland flow and 1-3 for mole drains)

* N/A No water available to collect

A:IPUPTT1

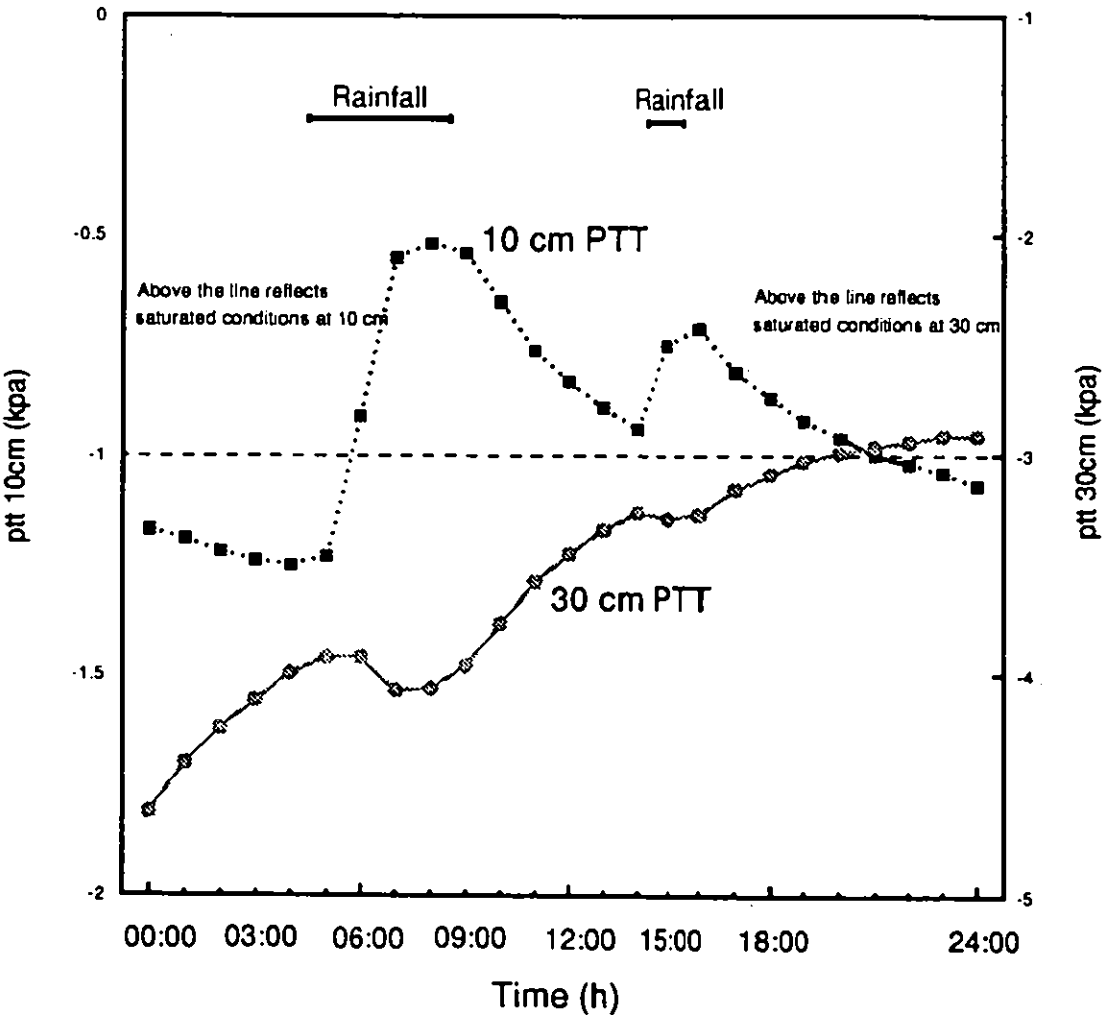


Figure 14. Total Potentials at 10 & 30cm Depths during storm event 50 d after ipu application (1,4,93)

On this occasion the drain flow did not plateau out, suggesting that the maximum capacity for infiltration had not been reached. The field drain demonstrated the typically peaked hydrograph (rapid response to rainfall) which have been noted by (Kneale, 1986; Robinson *et al.*, 1987; Robinson and Beven, 1983) as a characteristic of underdrained clay soils of this type.

Storm event 3 (SE 3) - 3rd April 1993, 52 days after spray day.

Figure 15 describes SE 3 which occurred 2 days after SE 2. Again, as with SE 2, the drainflow associated with that rainfall event has been plotted, along with the concentration of isoproturon present in the drain water.

As with SE 2 there was a delay in the initiation of drain flow after the start of rainfall. It is interesting to note that the rain storm two days previously did wet up the profile and change the antecedent soil moisture condition. PTT data in Figure 16 clearly shows the increase in wetting from unsaturated to saturated conditions at 30 cm. Thus as the drains were flowing under both these conditions, it suggests that drain flow was not influenced directly by soil antecedent moisture status below approximately 10cm from the soil surface.

A further drainflow event occurred (data not shown) which coincided with saturated conditions being measured by the 10 cm PTT on day 54, shown in Figure 16.

Observed conditions after 12 April, 1993 (day 62)

No significant drain flow events were measured from day 62 despite a greater than average amount of rainfall (Fig. 8). The possible reasons for this include the much higher SWD that had to be satisfied, and large cracks, visible through the mole access ports, running lengthways along the base of the mole drains. In addition, the higher radiation at this time of year means a greater potential evaporation rate. The crop being at a mature growth stage would have lead to greater extraction of water from the soil. As shown in Figure 17, which describes the matric potentials at 0.1 m depth during May and June 1993, the rainfall was only enough to bring the point at 10 cm below the surface to saturation for short periods without the creation of a significant "head of water" as observed in previous drainflow events. Although drainflow was not observed during this period some limited overland flow did occur as water was collected from the overland flow traps (Figure 13). Neutron probe data which was collected during this period is shown in Figure 18. A general decrease in water content of the soil can be seen over this period. The occasions on which a transient increase in water content was seen at all depths may be related to rainwater running down the cracks around the neutron probe access tubes.

Leeds-Harrison *et al.* (1986) suggested that the hydraulic conductivity, (K), of cracked soils is much greater than saturated soils, and that the fall in K is very rapid initially as a soil begins to swell under constant saturation. Thus one would expect in saturated conditions the percentage of rainfall bypassing the soil matrix to become drain flow to be far less than in drier conditions. However our data did not show increased amounts of rainwater going to drainflow during the drier period. In the summer other factors as mentioned may prove to dominate in the restriction of drain flow, more so than the swelling of pores associated with wetting.

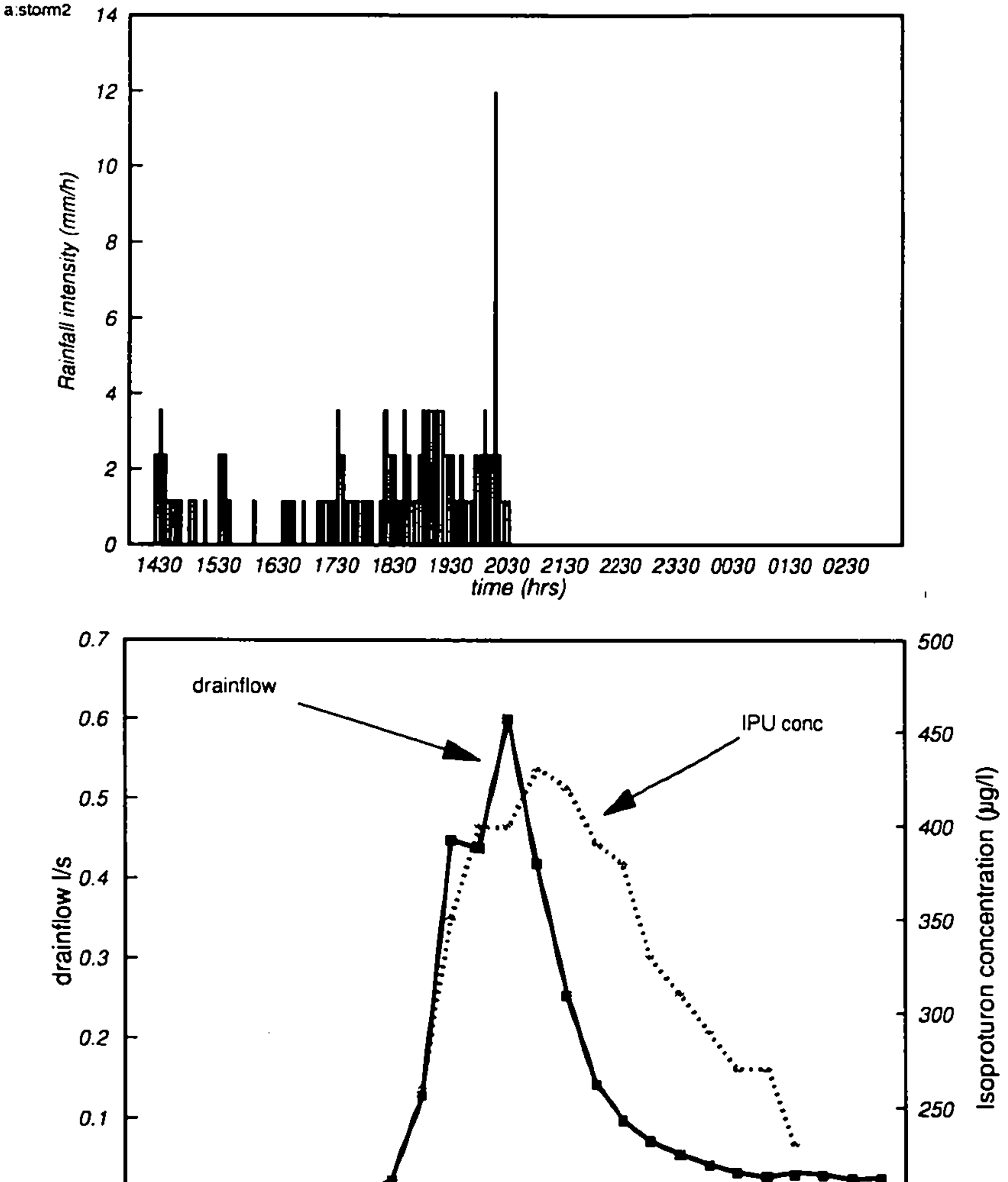


Figure 15. Relationship between rainfall, drain flow and ipu concentration 52 d after ipu application (3,4,93)

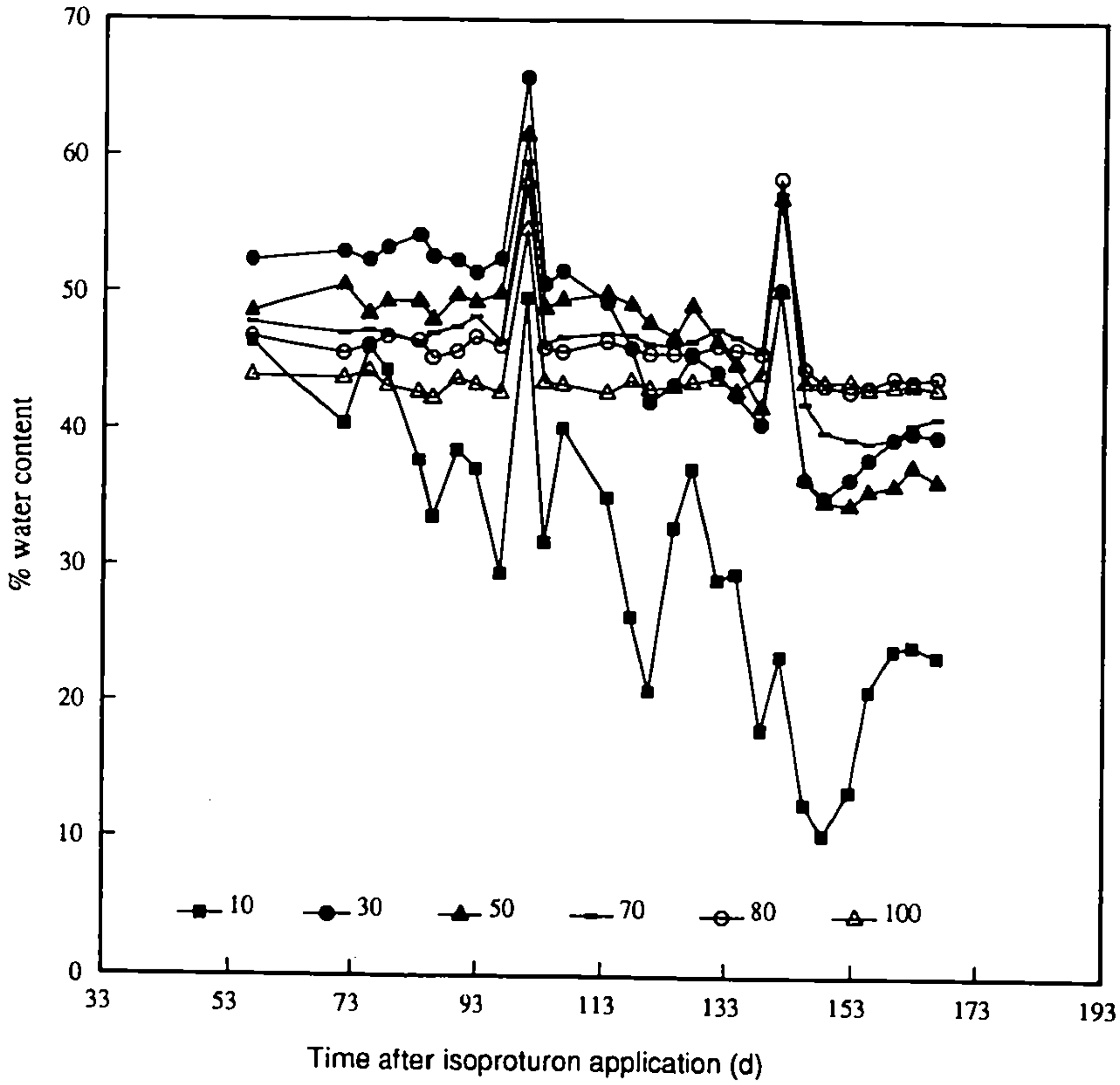


Figure 18. Changes in water content over time as measured by twice weekly neutron probe readings beginning 4 April, 1993.

Table 1 *Comparison of hydrological data from storm events 1, 2 and 3.*

	STORM EVENT 1 **6th/7th December 1992**	**STORM EVENT 2** **1st April 1993**	**STORM EVENT 3** **3rd April 1993**
Total Storm Rain (mm)	18.3	12.7	10.3
Rainfall exiting as drain flow (%)	17.6	31.9	28.1
Rainfall that satisfies SWD before drain flow can start	-	39% = 4.95 mm	45% = 4.64 mm
% Rainfall accounted for	-	71%	73%

Table 1 gives a comparison between the three storm events, showing the percentages of rainfall that were used to satisfy the SWD, and that which exited as drain flow. This was for a catchment estimated to be 1800 m^2 in size. As can be seen, similar amounts of rainfall (4.5 - 5.0 mm) were needed to satisfy the SWD before drainflow was initiated in April. This is despite the much wetter antecedent conditions below the topsoil for SE 3. The data suggests that soil water antecedent conditions below the surface 10 cm (approx.) are irrelevant to drain function. Approximately 70% of the rainfall for the storm events in April can be attributed to these two processes, leaving 30% still unaccounted for. This 30% may be accounted for by overland flow, sub-surface lateral flow or deep drainage. Process studies in the forthcoming 1993-94 season will attempt to improve our understanding of the in-field soil water balance.

4.2.3 Discussion of factors influencing flow mechanisms

Figures 19 and 20 are attempts to obtain an estimate of the antecedent conditions required to initiate overland flow and drain flow, all flow data being plotted against the equivalent matric potentials at a depth of 0.1 m below the soil surface.

All overland flow events monitored by the overland flow meter occurred only when the matric potential at 0.1 m was greater than zero, ie. when the surface 0.1 m is saturated. The same was true for the drainflow data. Therefore if the surface soil is anything less than saturated, overland flow and drainflow will not occur.

Specifically looking at drainflow it can be seen in Figure 20 that the majority of the points for all drainflow events of > 0.15 l/s (approx.) are located when the soil at 0.1 m depth had on it a positive head of 0.5 kpa. If rainfall is separated into that which did and did not initiate drain flow and plotted against the antecedent soil surface moisture conditions as represented by 0.1 m PTT, Figure 21 can be presented. This figure demonstrates that most rainfall that fell when the soil matric potential at 0.1 m was less than 0.4 kpa did not initiate drain flow; and that rain falling at a surface matric potential greater than 0.4 kpa did initiate drain flow.

However, it can be seen that on some occasions rainfall events caused drainflow when the surface was less than saturated, and some rainfall at surface saturation caused no drainflow. The former can be explained in that the PTT located to monitor surface conditions is at 0.1 m below the soil surface. In reality the conditions for drain flow may require saturation in only a:NP1

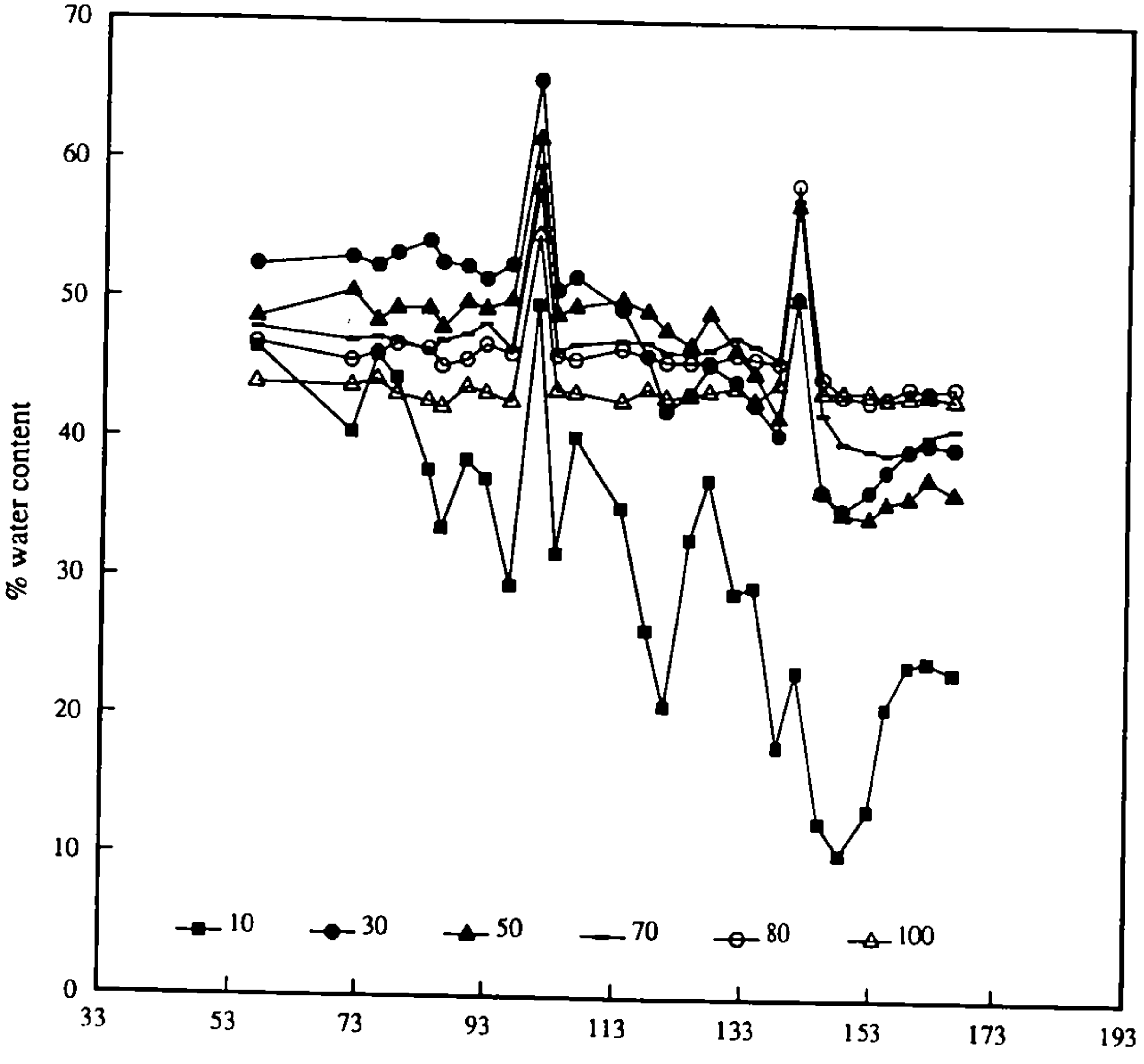


Figure 18. Changes in water content over time as measured by twice weekly neutron probe readings beginning 4 April, 1993.

Table 1 *Comparison of hydrological data from storm events 1, 2 and 3.*

	STORM EVENT 1 6th/7th December 1992	STORM EVENT 2 1st April 1993	STORM EVENT 3 3rd April 1993
Total Storm Rain (mm)	18.3	12.7	10.3
Rainfall exiting as drain flow (%)	17.6	31.9	28.1
Rainfall that satisfies SWD before drain flow can start	-	39% = 4.95 mm	45% = 4.64 mm
% Rainfall accounted for	-	71%	73%

Table 1 gives a comparison between the three storm events, showing the percentages of rainfall that were used to satisfy the SWD, and that which exited as drain flow. This was for a catchment estimated to be 1800 m^2 in size. As can be seen, similar amounts of rainfall (4.5 - 5.0 mm) were needed to satisfy the SWD before drainflow was initiated in April. This is despite the much wetter antecedent conditions below the topsoil for SE 3. The data suggests that soil water antecedent conditions below the surface 10 cm (approx.) are irrelevant to drain function. Approximately 70% of the rainfall for the storm events in April can be attributed to these two processes, leaving 30% still unaccounted for. This 30% may be accounted for by overland flow, sub-surface lateral flow or deep drainage. Process studies in the forthcoming 1993-94 season will attempt to improve our understanding of the in-field soil water balance.

4.2.3 Discussion of factors influencing flow mechanisms

Figures 19 and 20 are attempts to obtain an estimate of the antecedent conditions required to initiate overland flow and drain flow, all flow data being plotted against the equivalent matric potentials at a depth of 0.1 m below the soil surface.

All overland flow events monitored by the overland flow meter occurred only when the matric potential at 0.1 m was greater than zero, ie. when the surface 0.1 m is saturated. The same was true for the drainflow data. Therefore if the surface soil is anything less than saturated, overland flow and drainflow will not occur.

Specifically looking at drainflow it can be seen in Figure 20 that the majority of the points for all drainflow events of > 0.15 l/s (approx.) are located when the soil at 0.1 m depth had on it a positive head of 0.5 kpa. If rainfall is separated into that which did and did not initiate drain flow and plotted against the antecedent soil surface moisture conditions as represented by 0.1 m PTT, Figure 21 can be presented. This figure demonstrates that most rainfall that fell when the soil matric potential at 0.1 m was less than 0.4 kpa did not initiate drain flow; and that rain falling at a surface matric potential greater than 0.4 kpa did initiate drain flow.

However, it can be seen that on some occasions rainfall events caused drainflow when the surface was less than saturated, and some rainfall at surface saturation caused no drainflow. The former can be explained in that the PTT located to monitor surface conditions is at 0.1 m below the soil surface. In reality the conditions for drain flow may require saturation in only a:ptflow

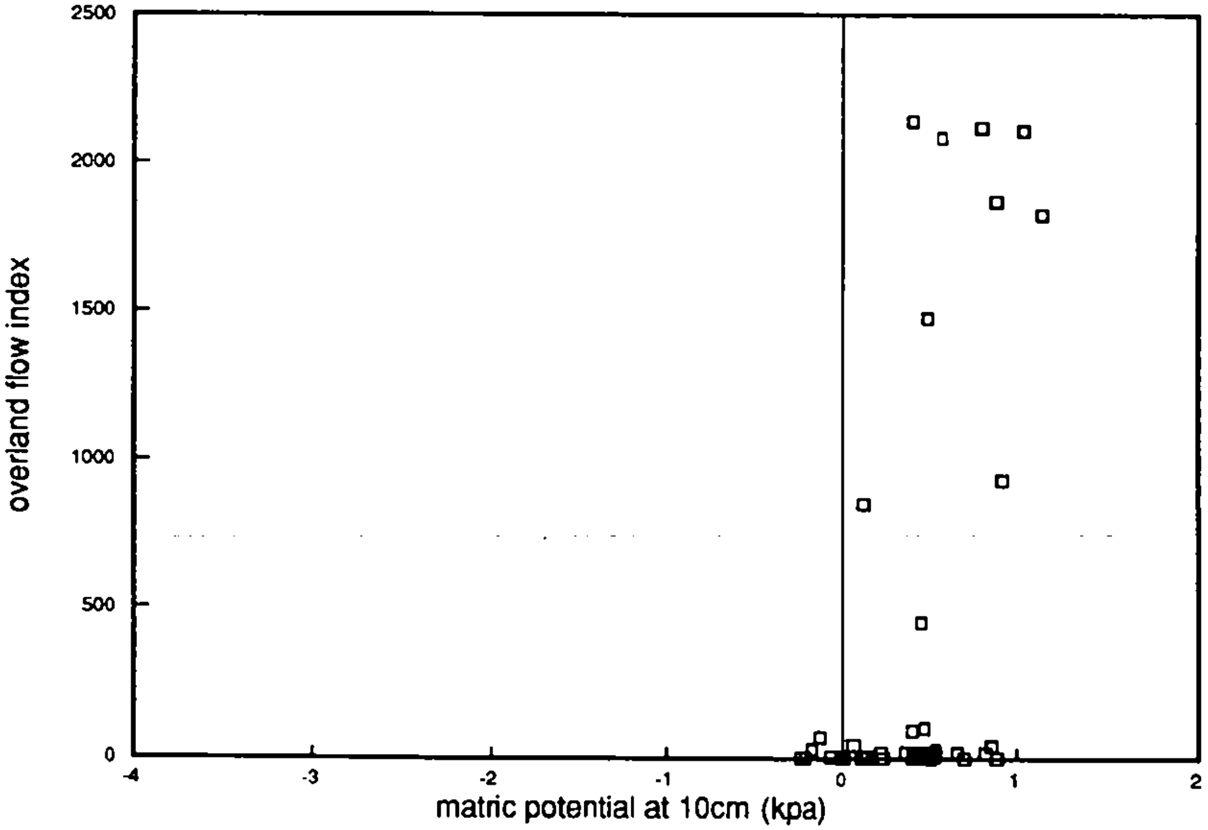


Figure 19. Overland flow events and related soil matric potentials at 10 cm depth

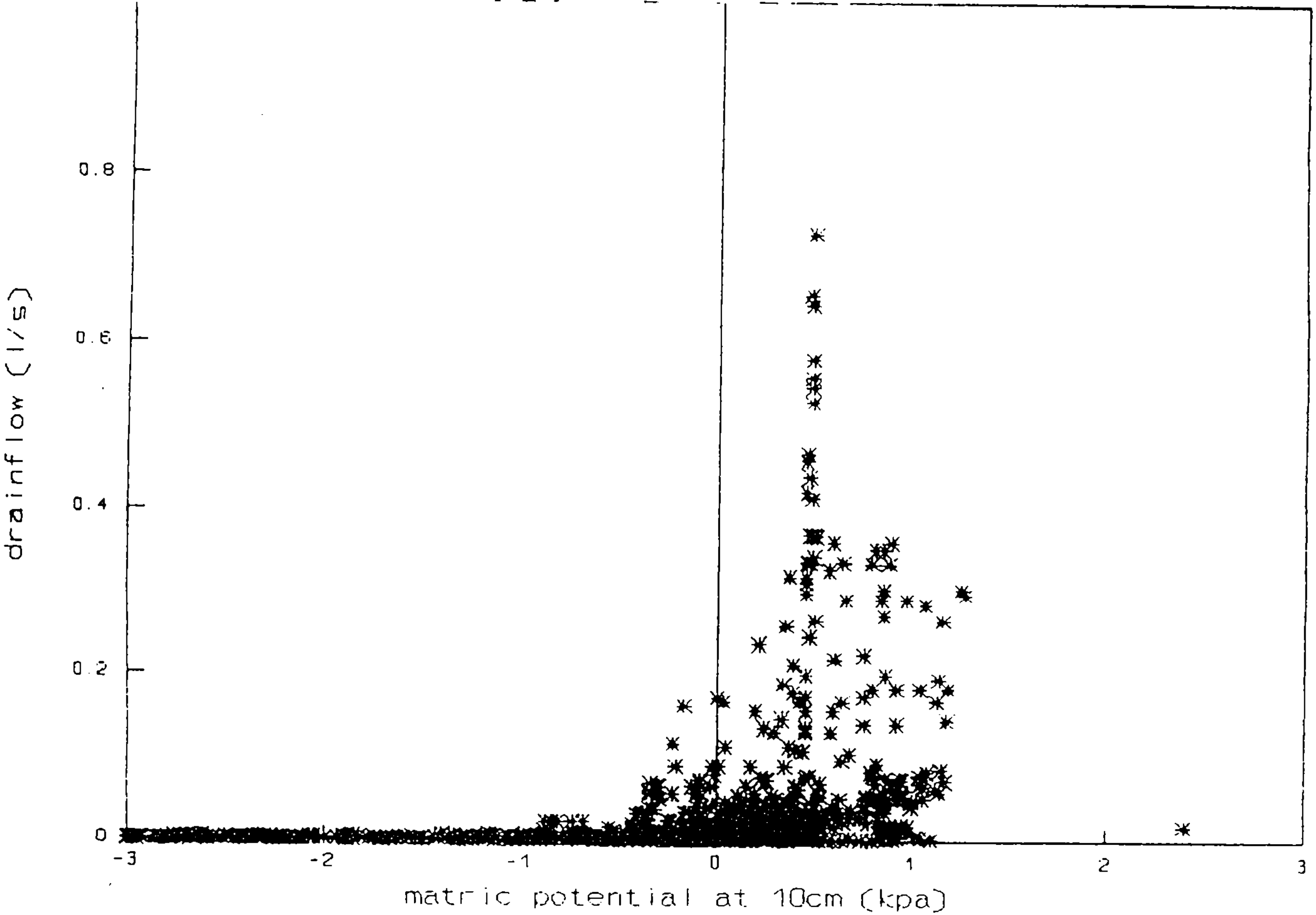


Figure 20. Drain Flow Occurence and Related Soil Matric Potentials at 10 cm Depth.

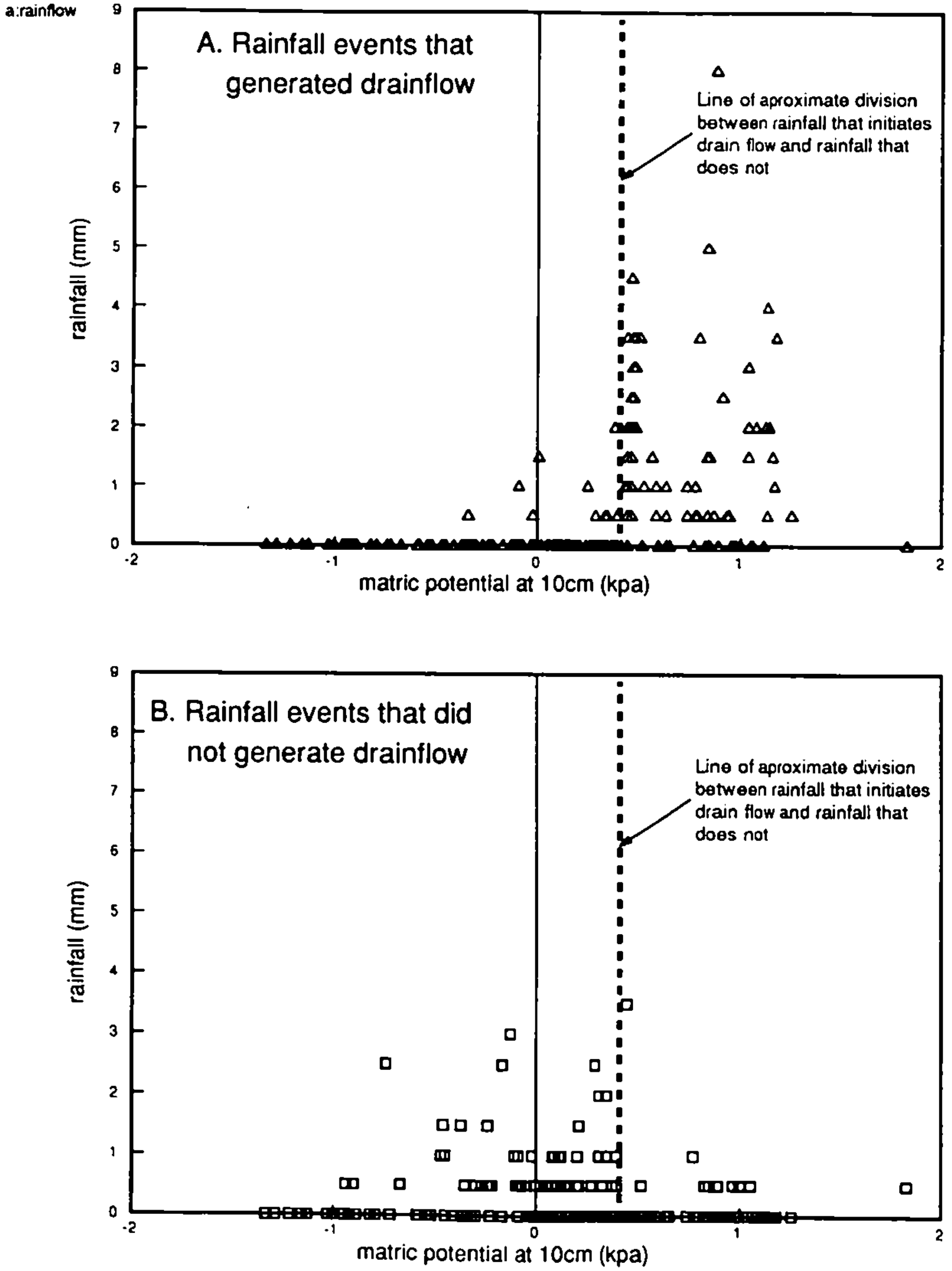


Figure 21. Examination of the relationship between rainfall, antecedant soil moisture conditions at 10 cm and the initiation of drainflow.

the top 0.05 m (for example); surface saturation that would not be monitored by the 0.1 m PTT. The rainfall events at surface saturation that did not cause flow could possibly be secondary rainstorms a few hours after major events when the surface was very wet. A small volume of water would then only initiate trickle flow that would not be recorded.

The distinction between the two groups of rainfall events is shown by the vertical dashed line in Figure 21 and suggests the initiation of a saturated layer before major water fluxes to the mole drains can begin. The presence of this saturated layer is likely to form the locus for lateral interflow, even under largely unsaturated conditions at depth, which may divert excess water laterally towards the moling fissures. This induction of lateral flow in the topsoil, by the rise in potential, towards the fissures over the mole drains has been noted by Leeds-Harrison *et al.* (1982).

Evidence that water in the saturated topsoil moves laterally was provided by use of bromide as a tracer at Wytham. 1 l of 10,000 ppm bromide placed 1.5 m upslope of the 25 cm suction samplers can be detected 56 days after application following the major rainfall events beginning on day 50 (see Figure 22). In addition the same amount of tracer placed over mole drain 25 could also be detected in the sump placed in the mole drain during the main rain events 49-50 days after application. A small proportion of the tracer appeared to have moved laterally to the next mole drain 3 m downslope from where the tracer was applied (see Table 2).

Table 2 *Vertical movement of tracer into mole drains*

Time after application (d)	50	56	64
mole 25	13,600	6,000	3,100
mole 24	1,000	400	50
mole 22	50	100	50

Concentrations given in ppb

10,000 ppm Bromide tracer applied directly above mole 25. The mole drains are 50 cm below the surface. Mole drains 24 and 22 were 3 and 9 m respectively downslope

Figure 23, which is based on results from this first field season, gives a schematic overview of the principal routes of water flow over, within and below the soil at Wytham; and thus shows the possible routes of pesticide transit to the catchment surface and sub-surface drainage systems.

4.3 PESTICIDE PERSISTENCE AND TRANSPORT

4.3.1 Variation in pesticide degradation with depth

Detailed pesticide sorption studies have not yet commenced with Wytham material. A preliminary experiment on isoproturon degradation (Figure 24) has been carried out using ^{14}C labelled isoproturon with topsoil (upper 3 cm) and soil from the 'B' horizon (40 cm).

a:su25br

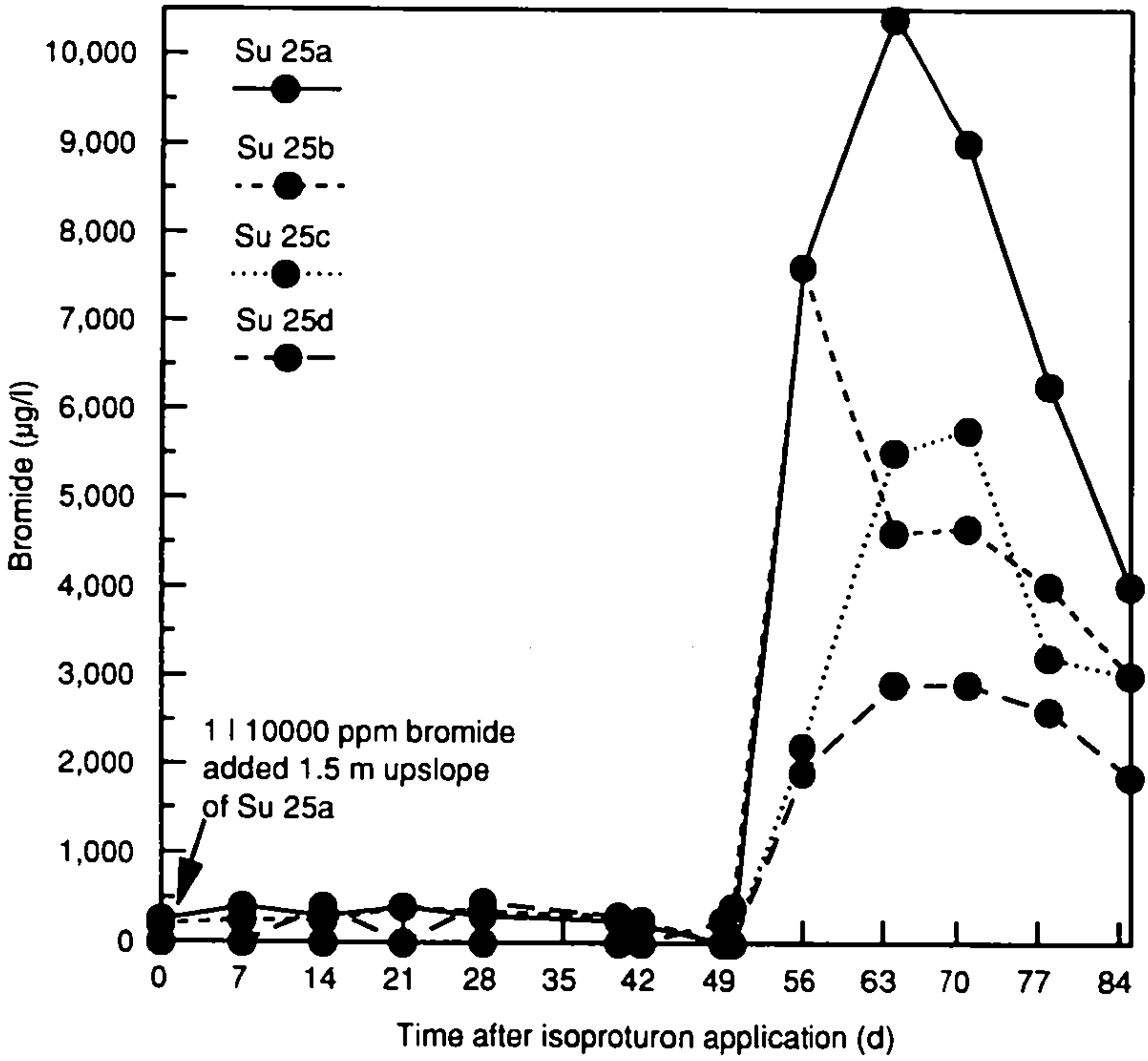


Figure 22. Lateral tracer movement towards 25 cm suction samplers

a:wyflow3

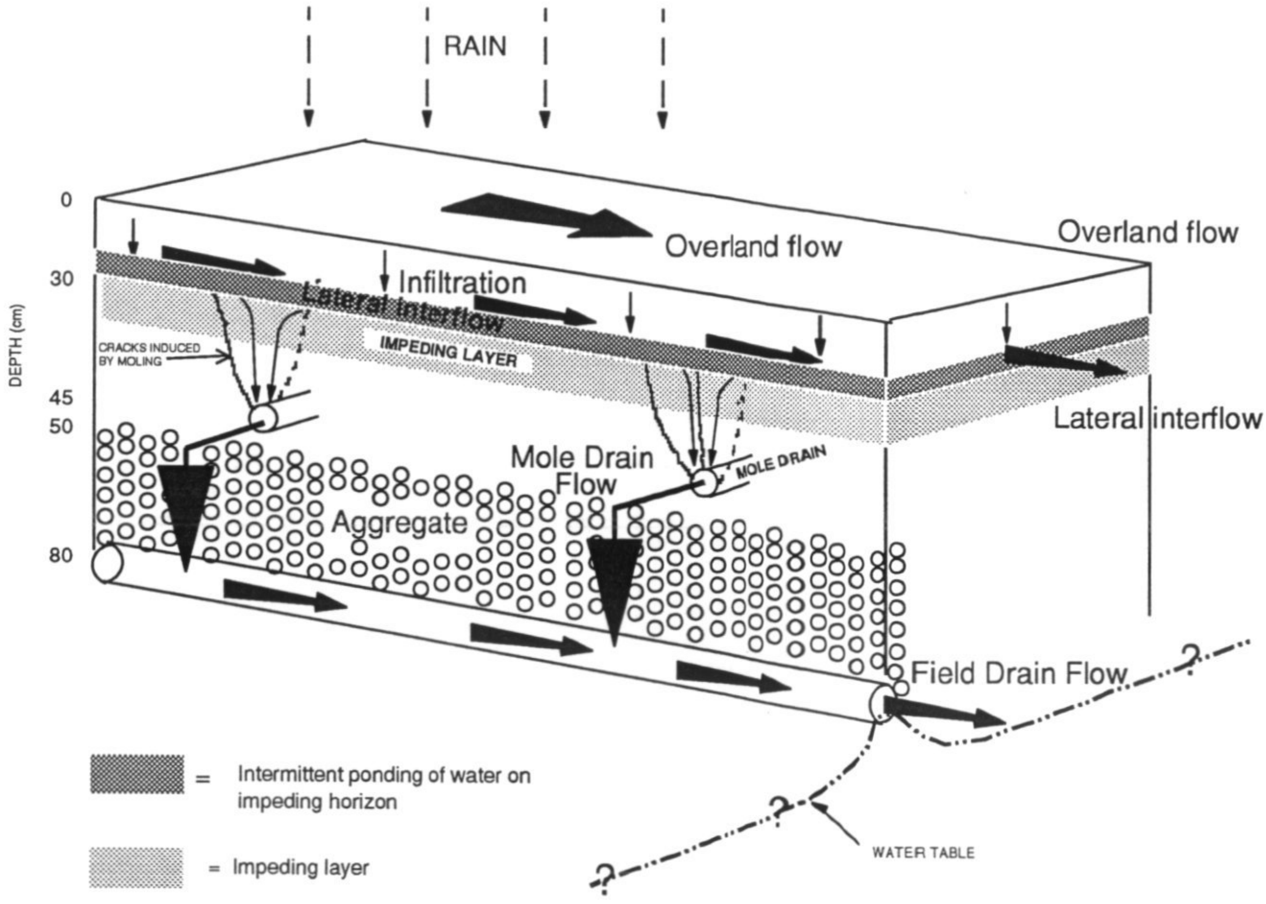


Figure 23. Schematic diagram of principal flow routes of water through and over the soil at Wytham

a:wydeg2a

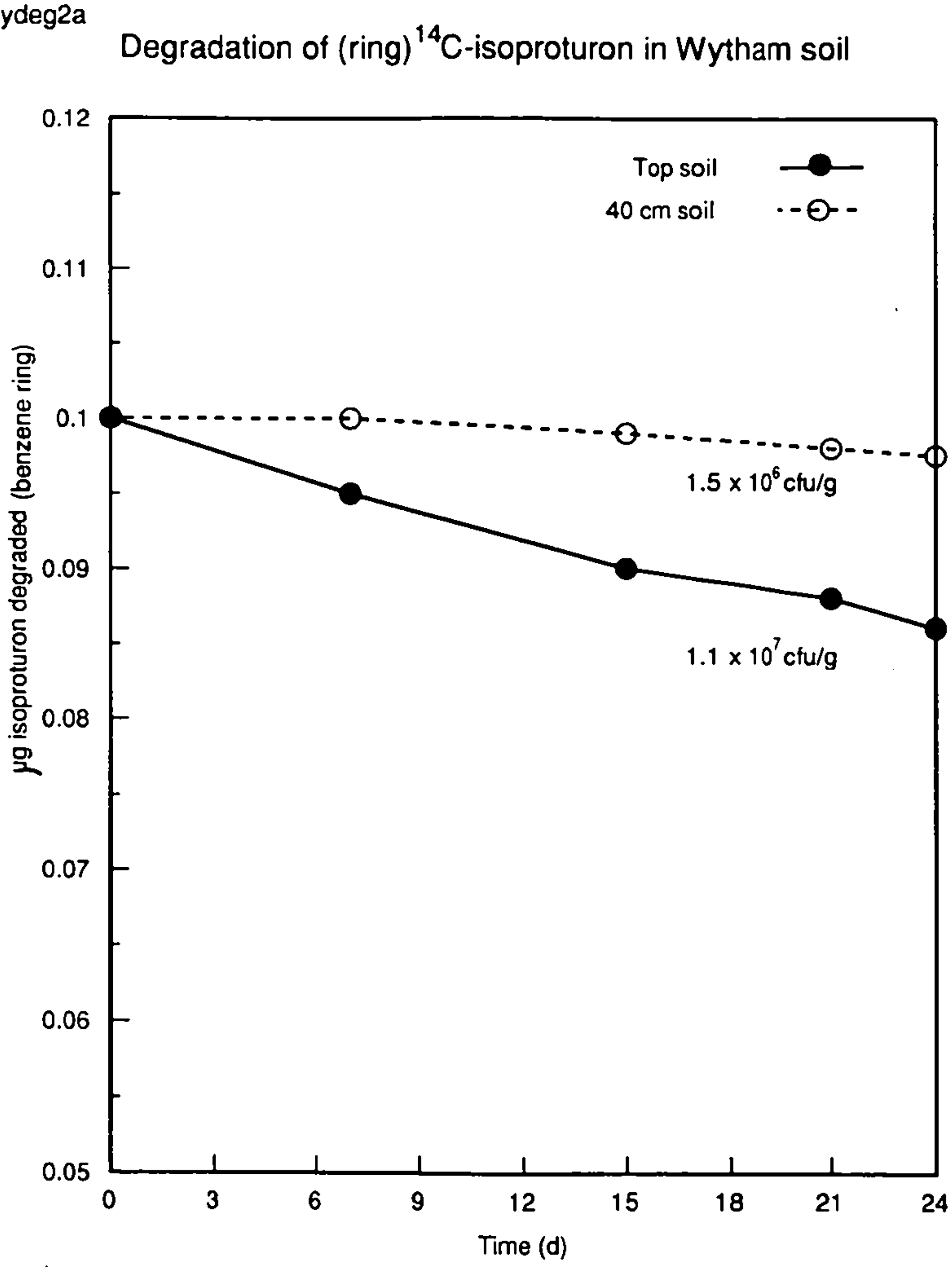


Figure 24. Degradation of ^{14}C-isoproturon (0.01 mg/kg) at 20 °C . Soil was air-dried before re-wetting to original moisture content (31.5 % for top soil and 21.6 % for 40 cm soil) with a solution of 10 mM $CaCl_2$ containing ^{14}C-isoproturon
(6 observations per mean)

Degradation is signalled by the complete metabolisation of the benzene ring and the release of $^{14}CO_2$, so the degradation rates cannot be compared to true half-lives. However, the potential to degrade the compound in the lower horizon is much reduced in comparison to the topsoil, only 2 of the 6 replicates showing any degradation. This also suggests that the degradation potential at depth is likely to be much more variable in a lateral sense when compared to the topsoil. It may be appropriate to study the anaerobic degradation also at this depth.

Analysis of the number of viable aerobic heterotrophs at depth shows a tenfold reduction with depth from 1.1×10^7 to 1.5×10^6 cfu/g. The higher clay content at depth (Jarvis and Hazelden, 1982) particularly of smectite (Figure 6) may also influence degradation through adsorption of the pesticide, making it less available to bacteria as noted by Sims *et al.*, (1992).

4.3.2 Mini-lysimeter data on pesticide transport

Intact soil cores were taken from Wytham but considerable problems were encountered due to the shrink-swell nature of the clay soil and the propensity of the rain/irrigation water to move down the edge of the column. The methods being used are now being improved by the use of vaseline to reduce preferential flow of water and solutes down gaps between the soil core and the PVC or aluminium containers in which the soil is held.

4.3.3 Persistence of residues in the field

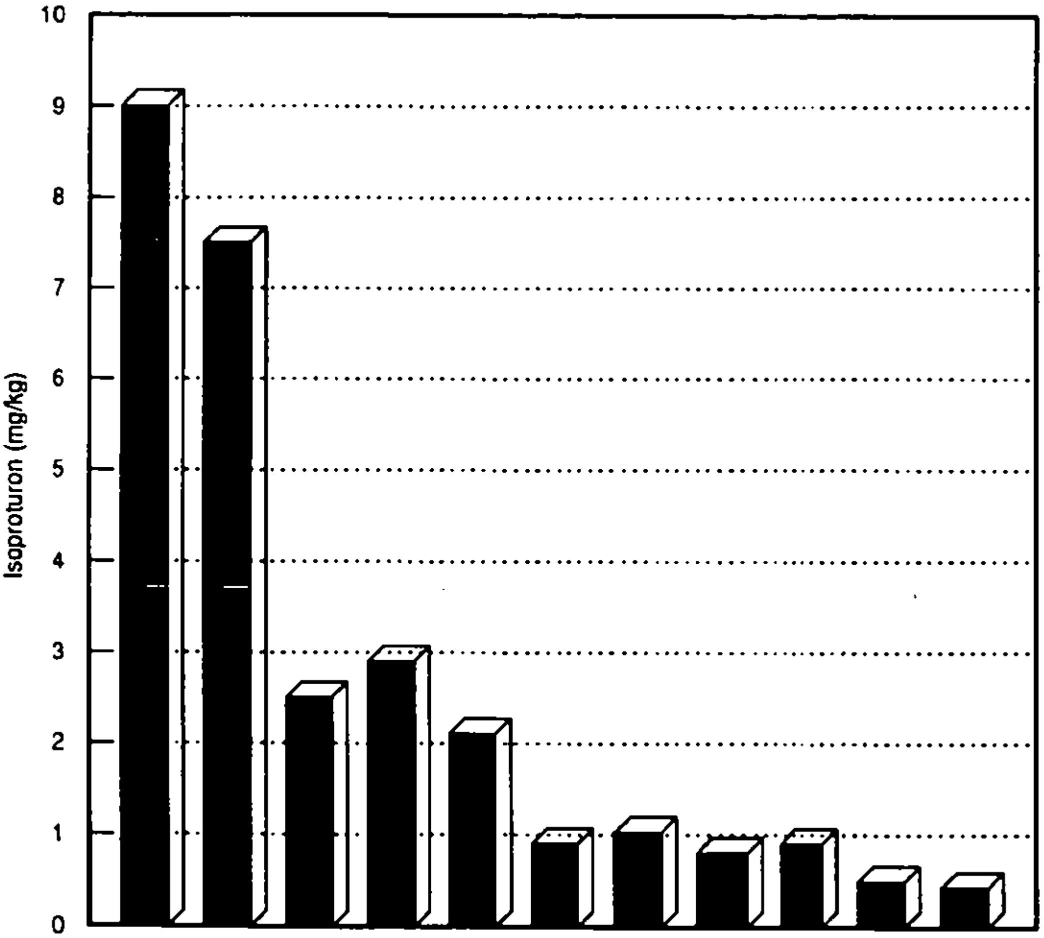
Table 3 shows the even distribution of pesticide over a 12 m long sampling area on the spraying day, which indicated a remarkably even application. The measurement of soil residues showed a good agreement between the replicates within each square metre that was sampled. The decline in amount over time (Figure 25, see also Table 10) gives a curve which suggests a DT_{50} in the region of 30 days, as expected. However, when the pesticide concentration was reduced to the 1 mg/kg level in soil it persisted for a longer period than would have been predicted by the DT_{50} assumption of 30 d. This phenomena of increased persistence of a small proportion of the soil residues was also observed with isoproturon by Mudd *et al.* (1983) in a sandy loam soil. This may be because this residual pesticide is protected in some way from degradation and is not bio-available. An alternative explanation is that degradation was reduced due to increasing moisture stress in the drier summer months.

Table 3 *Distribution of isoproturon (expressed as kg/ha) at Wytham on spray day, 10th February 1993, measured by a series of filter paper discs spread across the plot (30 m).*

	A	B	C	D	E
1	2.67	2.25	2.95	2.62	2.17
2	2.43	2.61	3.06	2.53	1.92
3	2.71	2.37	2.76	2.26	1.91
4	2.59	2.12	2.79	2.38	1.97

Overall mean = 2.45 kg/ha
SD = 0.33

a:residue2



Time after application (d)	7	21	35	49	64	78	100	113	127	141	155
Isoproturon concentration (mg/kg) ■	9.00	7.50	2.50	2.90	2.10	0.90	1.03	0.80	0.90	0.49	0.43

Figure 25. Isoproturon present in the top 2 cm of soil at Wytham

4.3.4 Isoproturon in overland flow water

Whilst data were collected on isoproturon concentrations in overland flow water, the total loss of pesticide from the field plot by this route cannot be estimated, as the overland flow traps collected water from an unknown and variable area. The data does, however, give an indication of the amounts of pesticide that could be mobilised and transported from the soil surface. This is potentially the same water that could enter a macropore and find its way to the drainage system. Between day 50 and 90, rainfall events generated both overland flow and drainflow, but from 90 d, rainfall generated overland flow without drainflow (see Figure 13). The chloride and sulphate concentrations found in the overland flow water were lower than that in the soil water (up to 50% less for chloride) collected by the suction samplers (see Tables 4, 5 and 6). Clearly the overland flow that occurred during this period of May to July would have been limited in its extent by the large shrinkage cracks that were developing during this period. The small volumes of 500-100 ml collected by the 2 m traps during this period would probably have been from rainwater that collected immediately in front of the traps. It is interesting to speculate on the fate of the isoproturon carried in overland flow water and deposited within shrinkage cracks. The potential for isoproturon degradation in the lower horizon would appear to be very low, as indicated by the ^{14}C-isoproturon degradation experiment (see Fig. 24). Possibly this isoproturon is trapped within the matrix for many years, it may possibly reach the groundwater or leak into the drains in succeeding seasons.

Table 4 *Isoproturon and anions in the overland flow traps*

Days from isoproturon application	**50**	**56**	**64**	**75**	**90**	**100**	**106**	**113**	**120**	**124**	**127**
OFT1 isoproturon	1,100	330.0	200	95.0	61.0	102.0	62.0	NA	30.0	NA	NA
OFT1 chloride	11	6.5	3	3.5	4.0	5.0	4.0	NA	10.5	NA	NA
OFT1 sulphate	26	16.5	8	6.5	8.0	13.5	11.0	NA	11.0	NA	NA
OFT1 nitrate	>50	>50.0	>25	>25.0	4.6	>25.0	>25.0	NA	21.0	NA	NA
OFT2 isoproturon	535	330.0	158	52.0	20.0	30.0	33.0	31	NA	18.8	13.0
OFT2 chloride	10	6.0	3	4.5	2.5	3.5	2.5	50	NA	7.0	5.5
OFT2 sulphate	23	14.5	2	7.0	6.0	7.5	9.0	7	NA	8.5	7.0
OFT2 nitrate	>50	>25.0	>25	>25.0	0.6	>25.0	8.6	>25	NA	5.2	5.2

Key

NA	No determination possible
>25.0	Above highest standard

Concentrations given as μg/l for isoproturon and mg/l for anions

Table 5 *Anions in 25 cm suction samplers*

Days from ipu application	28	40	42	49	50	56	64	71	78	85	100	113
(a) bromide	0.30	0.25	0.20	NA	NA	7.6	10.4	9.00	6.25	4.00	2.70	0.8
(a) chloride	37.00	30.00	31.00	NA	NA	23.0	16.5	16.50	15.00	18.50	16.00	4.0
(a) sulphate	46.00	42.00	44.00	NA	NA	31.0	31.0	31.00	26.00	26.00	22.00	19.0
(a) nitrate	19.00	>25.00	>25.00	NA	NA	>200.0	176.0	120.00	63.00	20.00	>50.00	6.2
(b) bromide	0.36	0.30	0.25	NA	0.4	NA	4.6	4.60	4.00	3.00	2.05	NA
(b) chloride	28.00	30.00	28.00	NA	33.0	NA	25.0	23.00	19.00	18.00	19.00	NA
(b) sulphate	19.00	27.00	28.00	NA	30.0	NA	28.0	27.00	22.00	18.50	17.50	NA
(b) nitrate	3.40	>25.00	>25.00	NA	>50.0	NA	>100.0	>75.00	50.00	17.00	>25.00	NA
(c) bromide	NA	NA	NA	0.25	NA	2.7	5.5	5.75	3.20	3.00	NA	NA
(c) chloride	NA	NA	NA	27.00	NA	26.0	21.0	22.00	13.00	15.00	NA	NA
(c) sulphate	NA	NA	NA	34.00	NA	31.0	27.0	25.00	18.00	19.00	NA	NA
(c) nitrate	NA	NA	NA	>25.00	NA	>50.0	>125.0	>125.00	42.00	26.00	NA	NA
(d) bromide	0.45	0.30	NA	NA	NA	1.9	2.9	2.90	2.60	1.85	0.75	NA
(d) chloride	30.00	29.00	NA	NA	NA	20.0	18.5	18.50	16.50	17.50	10.00	NA
(d) sulphate	23.00	29.00	NA	NA	NA	26.0	24.0	25.00	15.50	15.50	17.50	NA
(d) nitrate	1.80	>25.00	NA	NA	NA	>25.0	>50.0	44.00	1.60	0.50	>25.00	NA

Key

NA	No water collected
>25.00	Above highest standard

Concentrations given as μg/l

4.3.5 Isoproturon in the soil water collected by the suction samplers

Data from the suction samplers showed the presence of large amounts of pesticide at depth after the rain event 16 days after application (see Table 7). The suction sampler data must be viewed with great caution as bromide tracer added on day 35 in the immediate vicinity around the 50 and 75 cm suction samplers was detected after only 5 days by all of these samplers. This suggested that water could enter their silica flour 'pots' by running down along the length of the suction sampler directly from the soil surface. In other words, the suction samplers themselves acted as macropores. However, the suction samplers must have interacted to some degree with the surrounding soil pore water as the anion concentrations detected by these instruments were greater than those found in overland flow (see Tables 5 and 6).

Table 6 *Anions (mg/l) in 50 and 75 cm suction samplers*

	28	35	40	42	49	50	56	64	71	78	85	100
50 (a) bromide	NA	0.20	24.0	22.00	NA	12.4	5.00	NA	NA	NA	NA	NA
50 (a) chloride	NA	32.00	26.0	27.00	NA	31.0	17.50	NA	NA	NA	NA	NA
50 (a) sulphate	NA	33.00	28.0	27.00	NA	30.0	29.00	NA	NA	NA	NA	NA
50 (a) nitrate	NA	>25.00	30.0	32.00	NA	88.0	>100.00	NA	NA	NA	NA	NA
50 (b) bromide	0.15	NA	NA	4.50	NA	2.9	NA	2.05	NA	1.50	NA	1.05
50 (b) chloride	35.00	NA	NA	38.00	NA	36.0	NA	40.00	NA	32.00	NA	33.00
50 (b) sulphate	36.00	NA	NA	42.00	NA	37.0	NA	50.00	NA	48.00	NA	41.00
50 (b) nitrate	18.40	NA	NA	23.00	NA	>50.0	NA	>25.00	NA	>25.00	NA	>25.00
75 (a) bromide	0.10	0.10	1.2	1.05	0.65	NA	2.05	0.95	2.9	1.60	0.80	0.65
75 (a) chloride	26.00	27.00	32.0	32.00	34.00	NA	21.00	11.00	18.5	24.00	21.00	24.00
75 (a) sulphate	38.00	38.00	42.0	39.00	50.00	NA	39.00	29.00	25.0	48.00	26.00	29.00
75 (a) nitrate	>25.00	>25.00	>25.0	>25.00	>25.00	NA	>25.00	>25.00	44.0	>25.00	64.00	>25.00
75 (b) bromide	0.10	0.15	31.0	25.00	NA	8.8	NA	1.40	0.9	0.85	1.45	1.10
75 (b) chloride	41.00	50.00	50.0	47.00	NA	31.0	NA	13.00	16.0	17.50	28.00	37.00
75 (b) sulphate	>50.00	50.00	100.0	90.00	NA	65.0	NA	27.00	32.0	25.00	56.00	>50.00
75 (b) nitrate	>25.00	>25.00	45.0	72.00	NA	110.0	NA	>25.00	>25.0	>25.00	42.00	>25.00

Key
NA No water collected
>25.00 Greater than highest standard

Concentrations given as μg/l

Table 7 *Isoproturon in the suction samplers*

Days from Ipu application	7	14	21	28	35	40	42	49	50	56	64	71	78	85	100	113
Su 25a	19.8	9.3	73.0	350.0	NA	340.0	200.0	80	NA	170	129	151	163	112	44.0	22
Su 25b	18.1	6.9	NA	500.0	NA	230.0	250.0	NA	NA	185	118	135	122	109	61.0	NA
Su 25c	NA	NA	NA	15.0	NA	110.0	NA	NA	NA	220	195	126	98	96	NA	NA
Su 25d	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	180	NA	136	113	47.0	NA
Su 25 mean	18.7	8.1	73.0	288.0	NA	227.0	225.0	80	NA	192	155	137	129	107	51.0	22
Su 50a	4.6	5.8	2.4	6.5	5.6	10.6	10.6	NA	79	240	30	NA	59	54	29.0	NA
Su 50b	0.0	NA	NA	NA	NA	NA	NA	NA	83	NA	NA	NA	NA	NA	NA	NA
Su 50 mean	4.6	5.8	2.4	6.5	5.6	10.6	10.6	NA	81	240	30	0	59	54	29.0	NA
Su 75a	0.9	4.6	1.5	1.3	1.0	1.1	1.1	NA	250	50	67	151	99	30	15.6	NA
Su 75b	4.3	NA	102.0	290.0	210.0	175.0	180.0	NA	NA	NA	102	29	37	92	56.0	NA
Su 75 mean	2.6	4.6	51.7	146.0	105.0	88.0	90.0	NA	250	50	84	90	68	61	35.8	NA

Key
NA No water collected

Concentrations given as μg/l

4.3.6 Isoproturon in mole drainage water

Three mole drains, 25, 24 and 22 contained 75 ml capacity sumps from which water was collected on a routine basis. It would be difficult to establish whether the drainage water collected in the sump reflected the initial drainage water, the penultimate drainage water or an average of the two. Comparison with the field drain isoproturon concentrations for 50 d would suggest that the water in the sump reflects the 'tail' of the event. Water was collected from all three sumps on days 50, 56 and 64, with concentrations of 185 to 290 μg/l on day 50 to 108 to 129 μg/l on day 64 (see Figure 13 and Table 8). It is interesting to note that the mole with the highest concentration of pesticide varied depending on the event. Water could be collected from only one or two of the three moles from days 75 to 90, and none subsequently. The reduction in water reaching the mole drains (and also the field drain) from day 75 onwards can be ascribed to an increasing water deficit in the soil, influenced mainly by crop water use and evaporation. It is interesting to note the similarity in pesticide concentrations in overland flow and mole drain water from the day 75 period. Soil surface residues also remained stable over this period, at around 1 mg/kg.

Table 8 *Isoproturon and anions in mole drain water*

Days after isoproturon	50	56	64	75	78	90
Mole 25 isoproturon (ppb)	280.0	134.0	108.00	67.0	65.00	44.0
bromide (ppm)	13.6	6.0	3.10	2.7	3.00	4.0
chloride (ppm)	18.0	24.0	14.50	21.0	21.00	5.5
sulphate (ppm)	32.0	33.0	23.00	29.0	22.00	16.5
nitrate (ppm)	208.0	>100.0	>50.00	36.0	0.20	>50.0
Mole 24 isoproturon (ppb)	290.0	205.0	124.00	NA	NA	NA
bromide (ppm)	1.0	0.4	0.05	NA	NA	NA
chloride (ppm)	14.0	13.0	4.50	NA	NA	NA
sulphate (ppm)	29.0	26.0	16.00	NA	NA	NA
nitrate (ppm)	>50.0	>25.0	>25.00	NA	NA	NA
Mole 22 isoproturon (ppb)	185.0	210.0	129.00	NA	36.00	NA
bromide (ppm)	0.1	0.1	0.05	NA	0.05	NA
chloride (ppm)	13.0	8.5	5.50	NA	8.00	NA
sulphate (ppm)	26.0	17.0	12.00	NA	17.50	NA
nitrate (ppm)	>50.0	>25.0	>25.00	NA	21.00	NA

Key

>50.0	Above highest standard
NA	No water collected

4.3.7 Isoproturon in main field drainage water

The first rainfall event which triggered the autosampler is shown in Figure 12 and the second in Figure 15. A number of observations can be made from these storm events:

- In both events the delay between the onset of rainfall and drainflow appeared to be related to the development of a positive head in the topsoil recorded by the 10 cm PTT (Figure 16), as described in section 4.1.2.
- Isoproturon and drain flow velocity appear to be closely related, although the peak pesticide concentration lags behind peak drainflow by 1 h and pesticide concentrations decline more slowly with time with respect to drainflow. This hysteresis effect can be seen for both storm effects in Figure 26. Possible explanations are given below.
- Isoproturon concentrations and anion concentrations show an inverse relationship in both storm events (see Figures 27 and 28). In other words as isoproturon concentrations increase, so anion concentrations decrease, and vice versa.

The main field drain catchment for the plot was estimated to be 1800 m^2 and together with the amount of pesticide known to be available in the soil surface at that time (2.9 mg/kg, giving approximately 167 g in 1800 m^2), in 8 h of rainfall on 1,4,93 drain efflux was 7000 l. A cumulative loss of 2.5 g is suggested, this would mean a loss of 1.5% to the drainage in the first event. The second event based on the same parameters yielded 2 g, an equivalent of 1.2%. Therefore in the combined events, 2.7% of the pesticide was lost to the drainage in a matter of 3 days. It was estimated that 30% of the rainfall that fell in the events entered the tile drain.

4.3.8 Isoproturon in the ditch at the bottom of the field

Water samples were taken on a routine basis (once a week on average) both from the field drain 2 outfall and from the ditch 1 m upstream from the field drain 3 outfall. Unfortunately the field and adjacent ditch at Wytham do not comprise a hydrologically defined catchment. A component of the water in the ditch would have come from the nearby Wytham wood and therefore would have diluted the field/pesticide component, but the figures are of interest in terms of revealing pesticide concentrations in a ditch which ultimately enters the Thames.

Pesticide concentrations in the ditch from the spraying day until 100 days after spraying were routinely above 0.1 μg/l (see Figure 29 and Table 9). The highest concentrations of 16.8 and 23 μg/l corresponded to rainfall events on or prior to days 42 and 50.

4.4. MODELLING WORK

Only a very preliminary attempt has been made to model the Wytham soil water processes. At this point in time it is not certain that the processes controlling pesticide runoff have been defined and a suitable conceptual model formulated. The model developed to describe pesticide movement at Rosemaund (Williams and Volkner, 1993) has been modified in a first attempt to simulate the perceived Wytham soil flow routes.

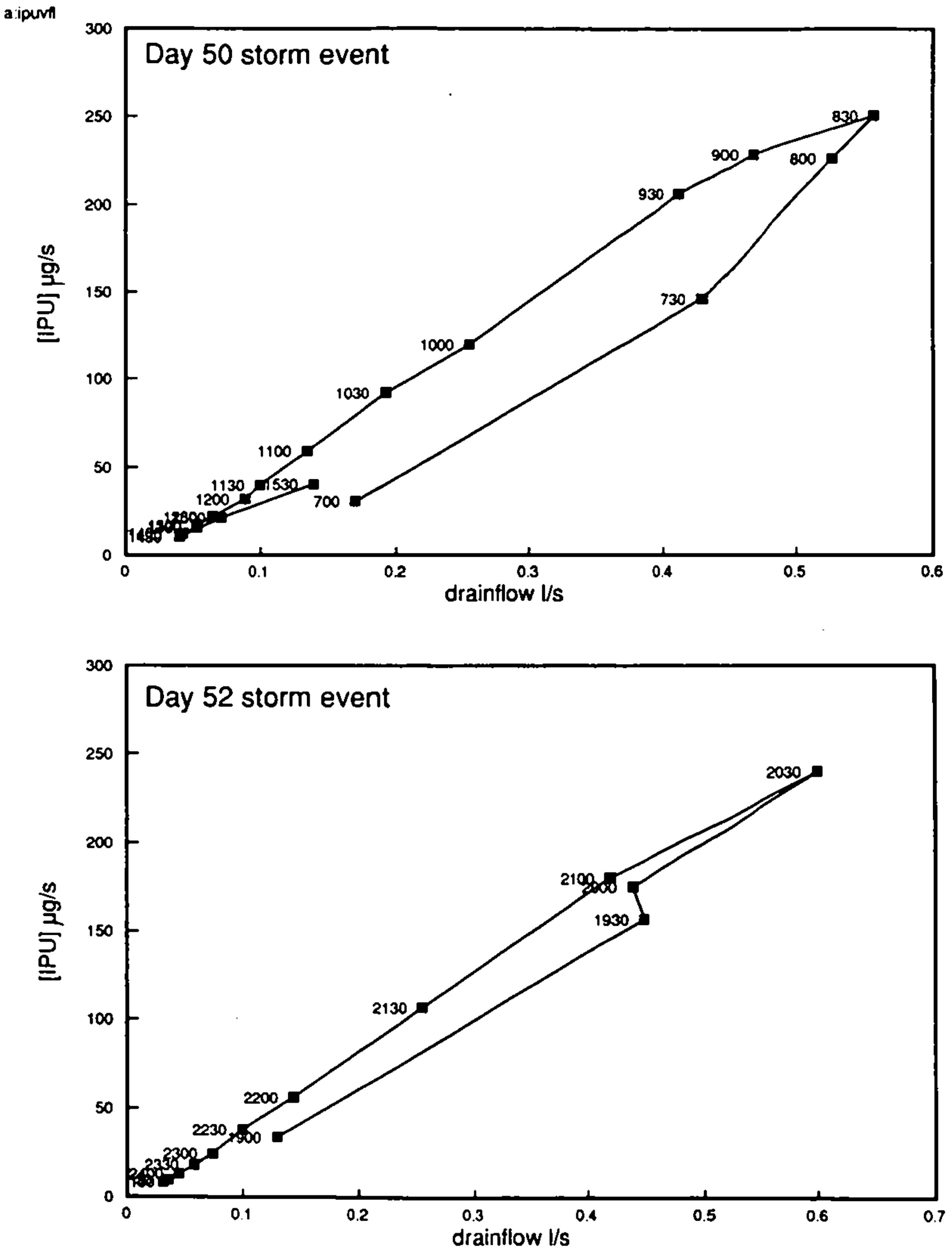


Figure 26. Comparison of isoproturon concentration with drainflow

a:50dsaltb

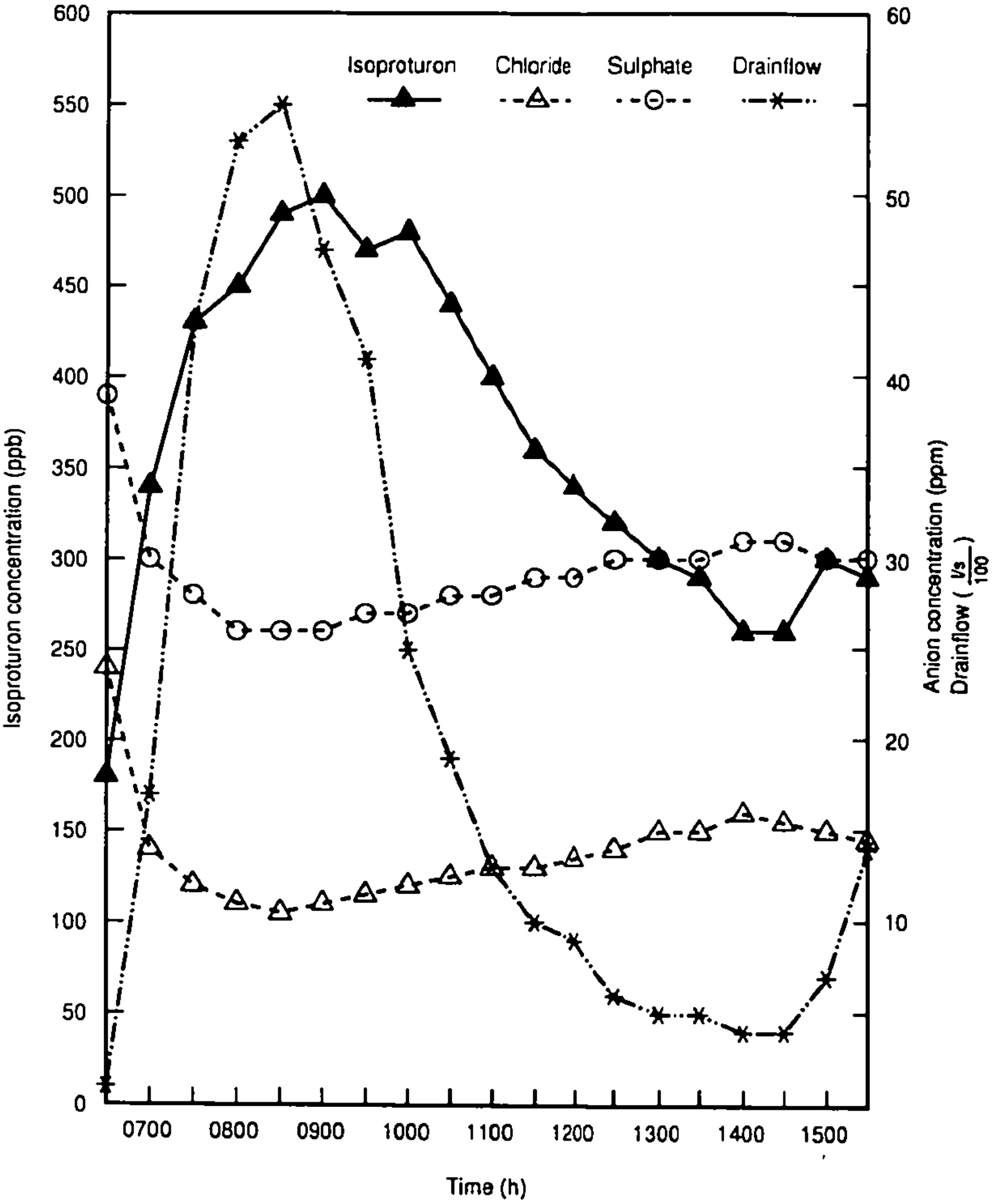


Figure 27. Comparison of solute concentrations with drainflow for the 50 d storm event

a:52dsaltb

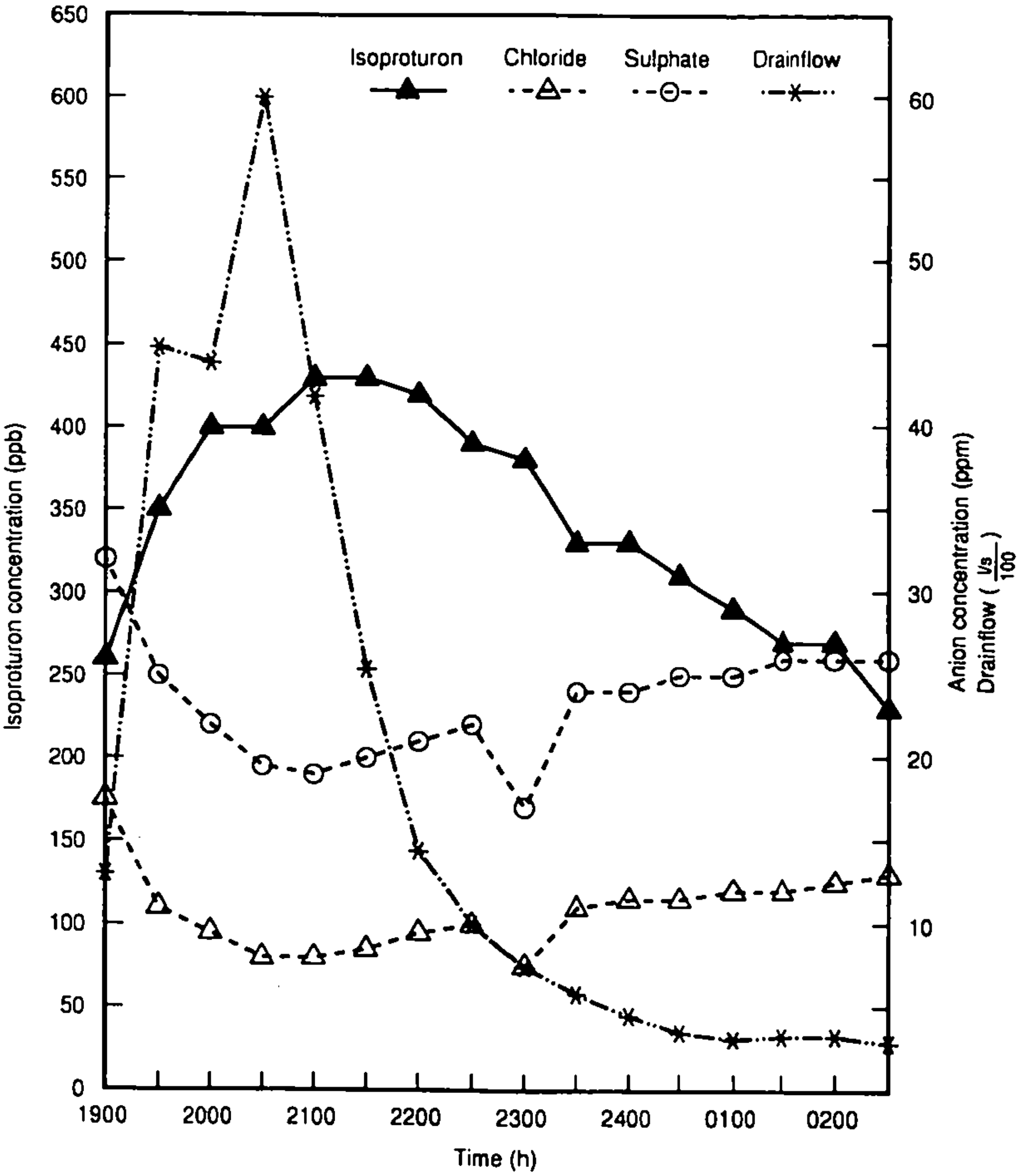


Figure 28. Comparison of solute concentrations with drainflow for the 52 d storm event

a:ditch

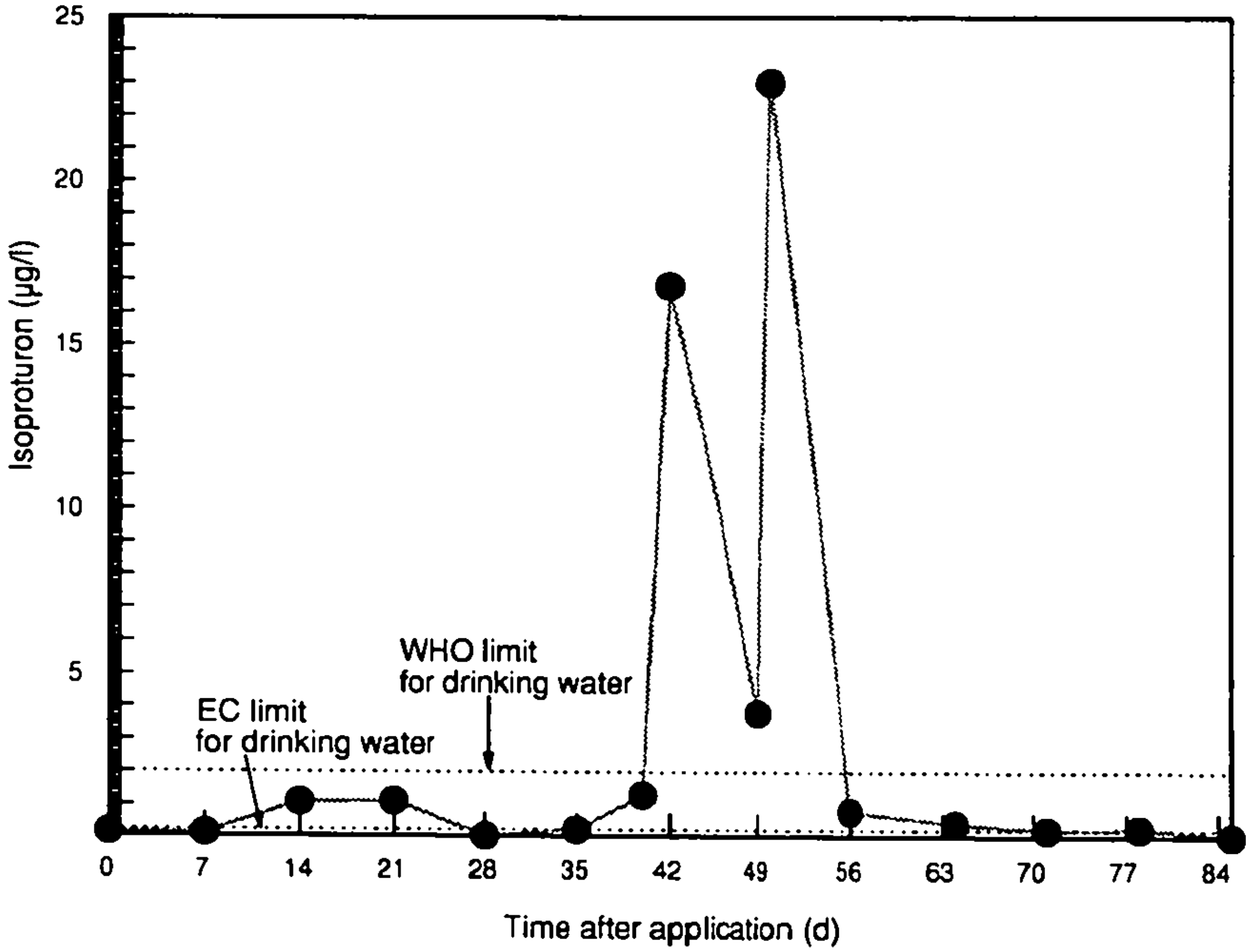


Figure 29. Isoproturon concentrations in water samples taken during routine sampling from the ditch at Wytham

Table 9 *Isoproturon and anions in ditch and field drain 2 outfall water*

Days from isoproturon application	**-69**	**0**	**7**	**14**	**21**	**28**	**35**	**40**	**42**	**49**	**50**	**56**	**64**	**71**	**78**	**85**	**100**	**113**
Ditch isoproturon (ppb)	(0.1)	0.16	0.15	1.10	1.12	(0.08)	0.25	1.31	16.80	3.8	23	0.81	0.43	0.24	0.28	(0.08)	0.14	(0.10)
Ditch chloride (ppb)	ND	ND	ND	ND	ND	ND	ND	ND	33.00	31.0	24	30.00	27.00	28.00	28.00	29.00	28.00	31.00
Ditch sulphate (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	>50.00	>50.00	>50.00	>50.00	>50.00	>50.00	>50.00	84.00	>50.00	>50.00
Ditch nitrate (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	7.00	11.0	>25	10.40	10.00	8.80	6.40	6.40	4.20	4.20
FD2o isoproturon (ppm)	(0.1)	0.18	1.53	1.16	0.80	0.95	(0.08)	26.00	0.32	122.0	NA	2.10	0.83	0.86	0.99	0.38	0.92	0.09
FD2o chloride (ppm)	ND	ND	ND	ND	ND	ND	ND	28.00	32.00	23.0	NA	28.00	25.00	26.00	26.00	27.00	24.00	29.00
FD2o sulphate (ppm)	ND	ND	ND	ND	ND	ND	ND	50.00	>50.00	>50.00	NA	>50.00	>50.00	>50.00	>50.00	74.00	>50.00	>50.00
FD2o nitrate (ppm)	ND	ND	ND	ND	ND	ND	ND	9.20	1.60	>25	NA	6.60	4.40	2.40	3.00	1.60	9.00	1.40

Key

ND	No determination made
NA	No determination possible
>50.00	Above highest standard
(0.10)	Below detection limit

Note for isoproturon: EC limit for drinking water is 0.1 ppb
WHO limit for drinking water is 2 ppb

The model consists of a number of connected boxes which describe the changing properties of the soil both vertically through the soil profile and horizontally as they are influenced by the presence of drains. Macropore flow is allowed through cracks that penetrate through the soil layers and whose extent is defined by the percentage of volume the macropores occupy. Cracks close as the soil water content increases in a linear manner up to a minimum value which represents the volume of biopores. The model is designed to represent a drainage element of the soil which is considered as the area from one drain mid point to the next. For this exercise the mole drains were considered to be the relevant drainage mechanism. The model is driven by hourly rainfall with the rate of movement of water out of a given box being proportional to its water content.

Pesticide is distributed between the soil and the soil water using a single valued instantaneous adsorption isotherm. The partition coefficient was calculated from the product of the koc and the organic carbon content. Degradation of pesticide occurs at a uniform rate throughout the profile, the rate being proportional to the pesticide concentration. Pesticide is transported through the soil profile dissolved in the soil water.

The model was set up so that the main flow path was lateral through the near surface (to 40 cm), this flow being intercepted by a high conductivity area representing the mole drains. Once in the mole the water was transported immediately to the tile drain. Water was not able to move vertically other than in the area immediately above the drain. Lateral flow below 40 cm was also not allowed.

A preliminary simulation of the first two rainfall event described earlier was carried out with no site calibration other than to establish the flow paths described above. The results achieved were encouraging, with the model predicting concentrations in the drains of a few hundred μg/l for both events; the first higher than the second. It is too early to say whether this modelling approach has been valid or useful in describing the pesticide processes at Wytham, however, it is heartening that such high concentrations as those observed at Wytham can be simulated.

5. Preliminary conclusions on pesticide persistence and transport at the field site

5.1 DEGRADATION

The degradation of isoproturon as deduced from the reduction in concentration in the soil surface was as expected. A DT_{50} of 30 d was estimated from the decline in residues. The increased persistence of residues from 78 d after application suggests that these residues may have an enhanced protection from biodegradation. This may be due to a strong sorption with the organic matter fraction of the soil. However, rainfall during the 80-162 d period did elicit small-scale overland flow which contained isoproturon in the range of 13-60 μg/l. Clearly the pesticide does not become completely unextractable so why does the degradation rate 80 d after application decline to an approximate DT_{50} of 70 d from an initial value of 30 d? Walker (personal communication) has shown with alachlor that the proportion of aqueous

Table 10 *Isoproturon present in top 2 cm of soil at Wytham (mg/kg)*

Days after isoproturon spraying	7	21	35	49	64	78	100	113	127	141	155
Replicates											
1	7.80	6.96	2.29	2.91	1.85	0.83	0.92	0.89	1.02	0.41	0.37
2	8.24	6.82	2.02	2.95	1.78	0.86	1.26	0.84	1.06	0.57	0.50
3	9.69	7.60	2.76	2.92	2.35	1.13	0.91	0.79	0.77		
4	10.43	8.50	2.98	2.82	2.35	0.94		0.69	0.80		

available pesticide as opposed to total declines with time. Degradation must therefore become increasingly limited by desorption kinetics over time. An alternative explanation is a decline in microbial activity due to a reduced moisture content in the soil surface, an important factor in degradation rate (Walker, 1991).

5.2 THE RELATIONSHIP BETWEEN SOIL RESIDUES AND THE PESTICIDE AVAILABLE FOR TRANSPORT

The mechanism of pesticide transport to the drains via macropores studied by this project, is based on the assumption that the majority of water entering the macropores is from the immediate soil surface. In this case the pesticide in the top few cm of the soil (mixing zone) is that which is primarily responsible for contamination of the drainage water. The pesticide in the soil may be considered as belonging to one of three groups: aqueous, weakly sorbed (aqueous extractable) and strongly sorbed (methanol extractable). Sorption experiments for isoproturon and Wytham soil have not yet been carried out, so it cannot yet be predicted how much of the pesticide belongs to each category in the field. However by day 50 the aqueous phase is likely to be by far the smallest component. It may be that only the aqueous phase pesticide is involved in transport in the storm events. This pool would appear to be replenished between the events by desorption from the solid phase. It is not clear whether desorption occurs on a significant scale during a storm event (Note: pesticide may also be transported whilst sorbed onto sediments).

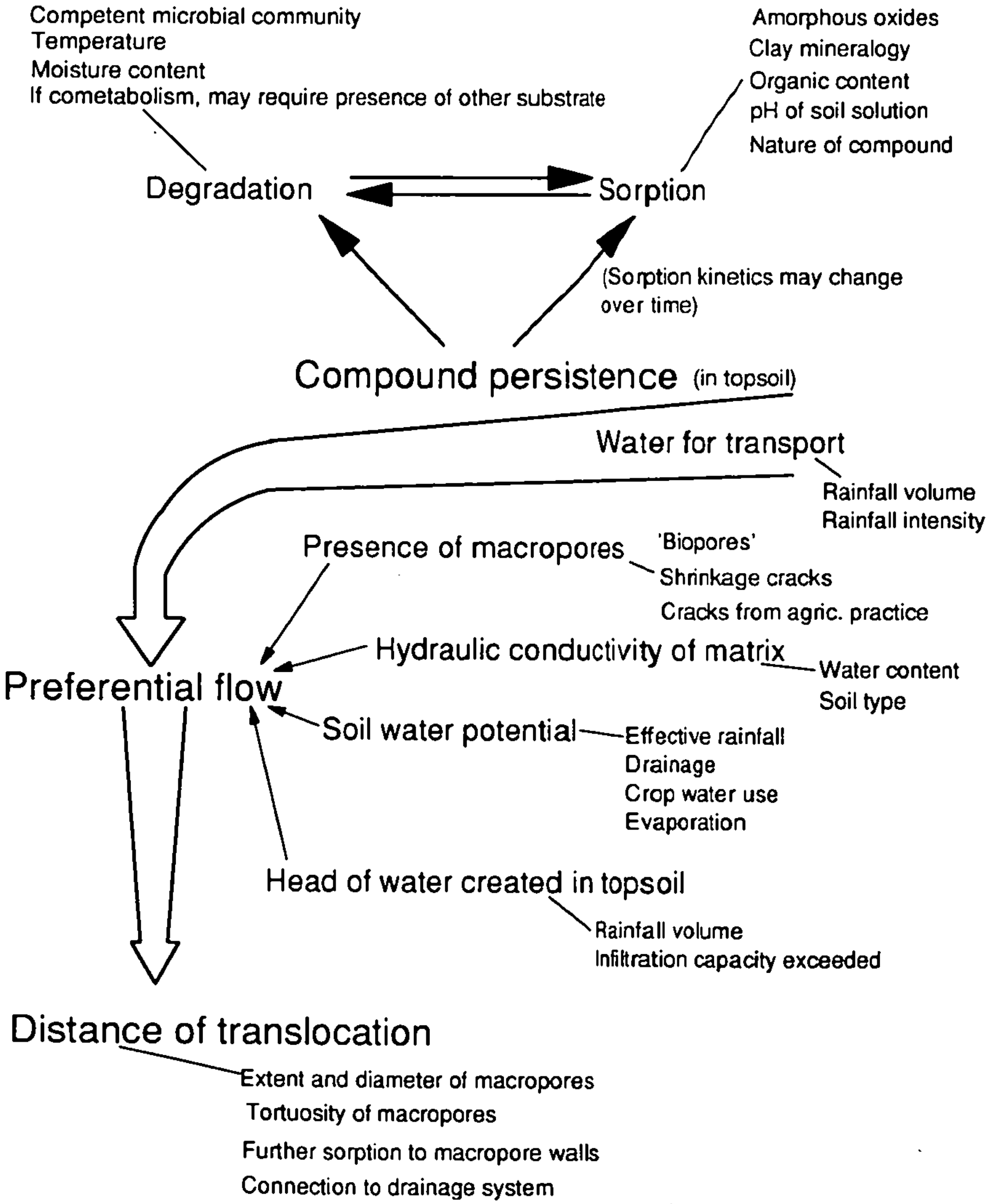
The amount of rainwater mixing with soil water at the soil surface (once matrix infiltration capacity had been exceeded) must also influence the concentration of pesticides found in drainage water (probably related to rainfall intensity). This will dilute the pesticide concentration of the original soil porewater. A schematic diagram which illustrates some of these factors is shown in Figure 30.

5.3. SUGGESTED MECHANISM FOR PESTICIDE TRANSPORT TO DRAINAGE

Data shown in Figures 27 and 28 together with soil hydrology data (Figure 16) may be interpreted in the following way:

a:concept1

Figure 30. Factors involved in pesticide transport by vertical by-pass flow



(1) Prior to rainfall the majority of pesticide is distributed throughout the top few cm of the soil, whilst the anions are distributed throughout all of the topsoil, as natural components of the soil porewater, possibly anions may also be concentrated on some of the macropore walls due to water evaporation (Figure 31).

(2) Rainfall wets up the topsoil from the top down, nothing happens until a positive head is achieved in the topsoil (top 10 cm). Some of the pesticide may be moved to below the surface 'mixing zone' during this period. In this case the longer the delay between inception of rainfall and initiation of drainflow, the less pesticide may be available for transport by preferential flow mechanisms (Baldwin *et al.*, 1975).

(3a) When the topsoil becomes saturated and cannot accept any more rainwater, lateral water movement is initiated, possibly both within the top 10 cm and at the soil surface. Some of this water connects to vertical macropores.

From experimental work on mole drain flow and solute movement at Wytham, Haigh (1985) suggested that water entered the macropores in the B horizon from within the topsoil, rather than directly from the soil surface.

(3b) The macropore walls become saturated as water moves down from the surface.

(3c) Water runs down a combination of macropores to reach the drains, and re-adsorption of pesticide onto worm burrow walls may occur (Edwards, 1991; Stehouwer *et al.*, 1993). The function of the macropores to transport water may be inhibited by trapped air unable to escape and thus prevent further water entry. Water and pesticide are now moving from the soil surface to the drains, driven only by the positive head of water generated by the rainfall, subsequent to topsoil saturation having been achieved. The first water to arrive at the drains may (a) flush out old soil water in the profile, (b) transport salts from the macropore walls, or (c) mix thoroughly with mobile soil water (with a high salt concentration) in the upper horizon (Haigh, 1985).

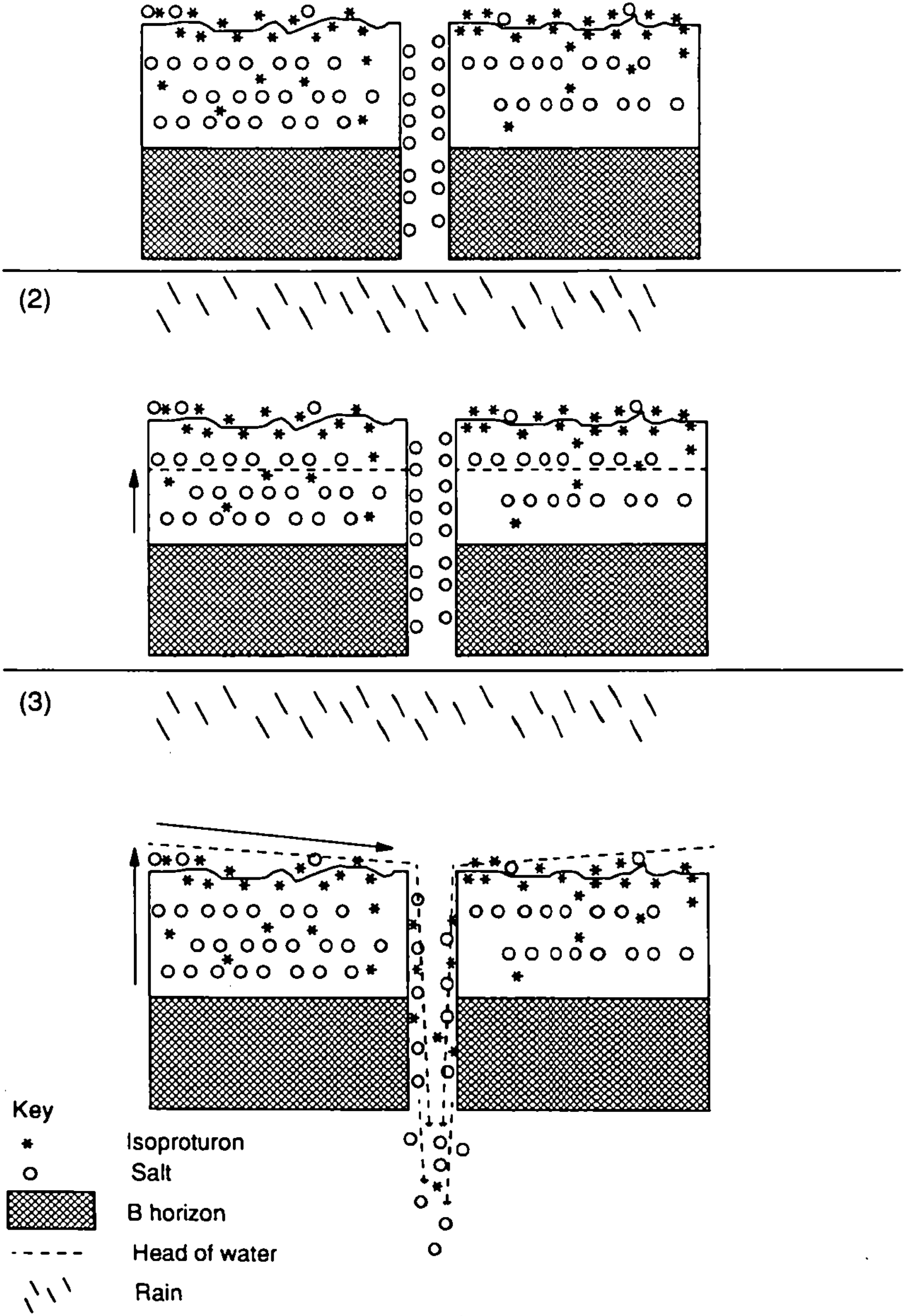
(4a) As more water arrives from the soil surface, where the majority of pesticide is concentrated, so the pesticide concentration rises. The anion concentrations decline (possibly to the same concentration of the rainwater/overland flow water).

(4b) Subsequent rainfall events during the drainflow period are rapidly translated to changes in drainflow velocity and higher pesticide concentrations. Pesticide concentration may, however, be reduced due to depletion of the available pool during the event.

(4c) Overland flow must occur at least to a limited extent to feed the macropores, whilst significant overland flow probably also occurs during the rainfall period and takes pesticide off the plot, as water was collected from the overland flow traps during this period. It is believed that the overland flow meter was not working correctly over this period.

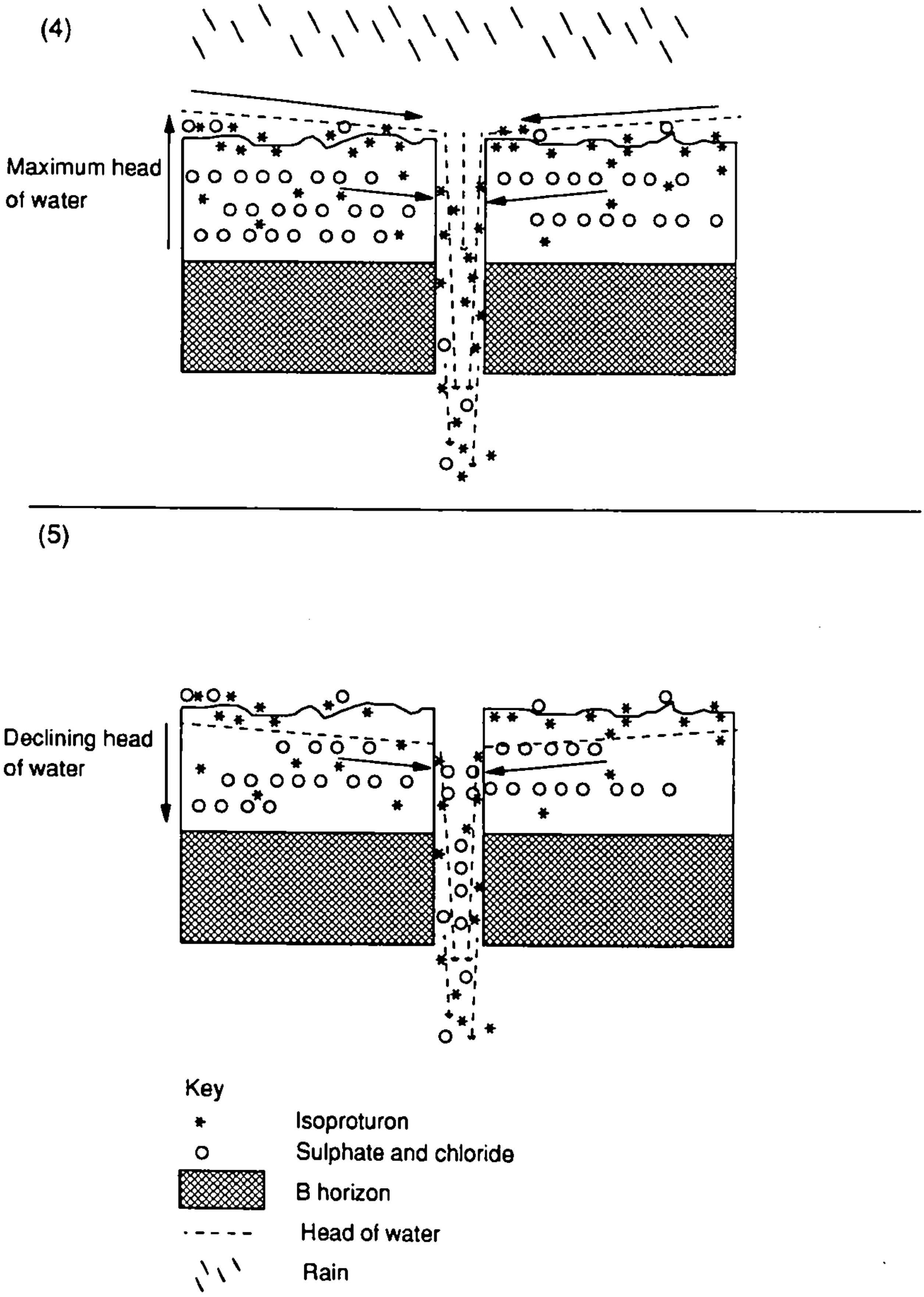
(4d) Lateral interflow is also likely to occur within the saturated soil at the top 10 cm, although no water sampler was in place to confirm this. Lateral movement of bromide tracer from mole 25 to mole 24 may be an indication of lateral interflow (see Table 2).

Figure 31. Suggested mechanism for pesticide and salt transport to drainage



a:saltcon2

Figure 31. continued



(5) As drainflow declines, the proportion of water arriving directly from the soil surface (with high pesticide concentration) is reduced, but water continues to arrive laterally through the topsoil, bringing water with a higher salt and lower pesticide concentration.

Therefore, data from these storm events suggest that changes in pesticide and anion concentrations may be attributed to the different origins of the water entering the drains.

I) Some water may have entered from the soil surface with a steady pesticide concentration, of perhaps 600 μg/l, and low anion concentrations similar to that found in overland flow water (see Figure 32)

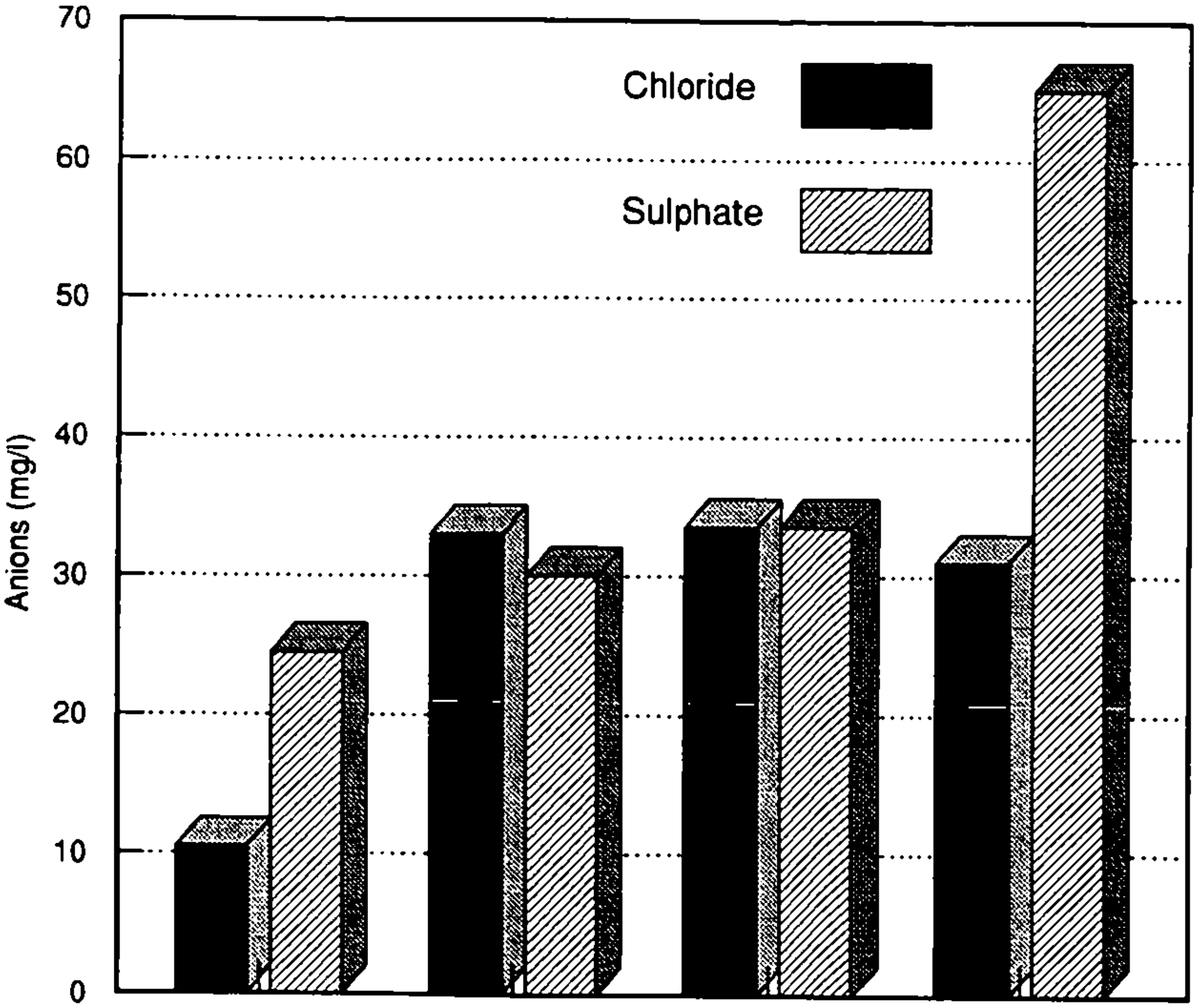
II) Other water may have moved into the macropores from a lateral direction from 10 cm and above. It may have contained little or no pesticide (not having penetrated to this depth in appreciable quantities) but an anion concentration similar to that found in the suction samplers (see Figure 32). This water was possibly the last to start entering the macropores and the last to stop, although Haigh (1985) suggested that lateral water movement into macropores in the B horizon was the major component throughout a drainflow event.

Initially, water may first flow down from the soil surface and lose pesticide by readsorption on the macropore walls whilst salts on the macropore walls go into solution (thus raising the salt concentration). Then water from the soil surface becomes the dominant component of drainwater, with a high pesticide and low salt concentration. Towards the end of the event as drainflow decreases, water entering the vertical macropores from lateral macropores within the 'A' horizon may become an important component, introducing water with a higher salt and a lower pesticide concentration then that from the soil surface. A variation on this theory is provided by Haigh (1985), who suggested that the relationship between anion concentrations in the drainwater was related to increases and decreases in mixing of rainwater (input water) and a mobile soil water component within the A horizon. Thus during low flow periods the maximum mixing occurs between the new and old water in the A horizon.

In Figure 26 a hysteresis effect can be observed. Pesticide concentration was found to lag slightly behind the peak drainflow, such that for any given drainflow velocity the pesticide present was greater as drainflow was decreasing rather than increasing. In other words less pesticide was carried at the beginning of the rainfall event than at the end. There are a number of possible explanations:

- Readsorption of pesticide on macropore walls in the initial phase of the event. Once this capacity has been satisfied, less of the pesticide travelling down to the drains is retained.
- Increasing mixing and transport of pesticide at the soil surface.
- The changing ratio of old water to new water (rainfall) ie initally drainwater is largely old soil porewater. Rainfall interacting with the surface soil becomes a larger and larger component until the ratio declines as rainfall stops and more old water comes in again.

It seems probable that the mole drain network, ie artificial drainage, is the main culprit in contamination of the nearby surface water. Whether water enters the mole drain primarily via a combination of 'the slot' left by their manufacture and biopores, or by biopores only, a:anion50d



Source of sample	OFT	Su 25	Su 50	Su 75
Chloride	10.5	33.0	33.5	31.0
Sulphate	24.5	30.0	33.5	65.0

Figure 32. Comparison of anion concentrations found in water samples taken from the overland flow traps and the 25, 50 and 75 cm suction samplers 50 days after isoproturon application (mean of 2-4 observations)

has yet to be established. Lateral interflow and overland flow also occur, but their effect on direct contamination of the ditch is less clear. Bromide tracer evidence suggests that water can move across the 'inter-mole area' either above or below the surface. Figure 30 lists the main factors which are believed to influence pesticide transport by vertical by-pass flow. An opportunity to test the theories described above, and to see whether the same phenomena are repeated should arise in the 1993-94 season.

The evidence, therefore, from the first season of fieldwork at Wytham, suggests that a mole drained heavy clay soil poses a serious threat in terms of pesticide contamination to the surrounding water courses. The results so far demonstrate that high contamination of drainage water can occur for a considerable period after pesticide application to the field.

6. Future work

6.1 FIELD EXPERIMENTATION

A hydrologically defined plot will be constructed in which the proportion of rainwater and pesticide in overland flow, lateral interflow and drainflow can be calculated (see Figure 33). It is not possible to quantify movement of water to below drain depth in the field, but this component is not thought to be large, based on this year's tensiometer data. Through the employment of additional pressure transducer tensiometers, flow meters with data loggers and autosamplers, it is hoped to build a more complete picture of water and pesticide movements through the soil during a storm event.

6.2 LABORATORY EXPERIMENTATION

The soil profile and characteristics will be described in greater detail. SSLRC will describe the soil profile in physical terms, including particle size analysis. HRI will study the aerobic degradation potential of the different soil depths, as well as adsorption potential studies for isoproturon. If the appropriate equipment is available, IH will study anaerobic degradation potentials at different soil depths.

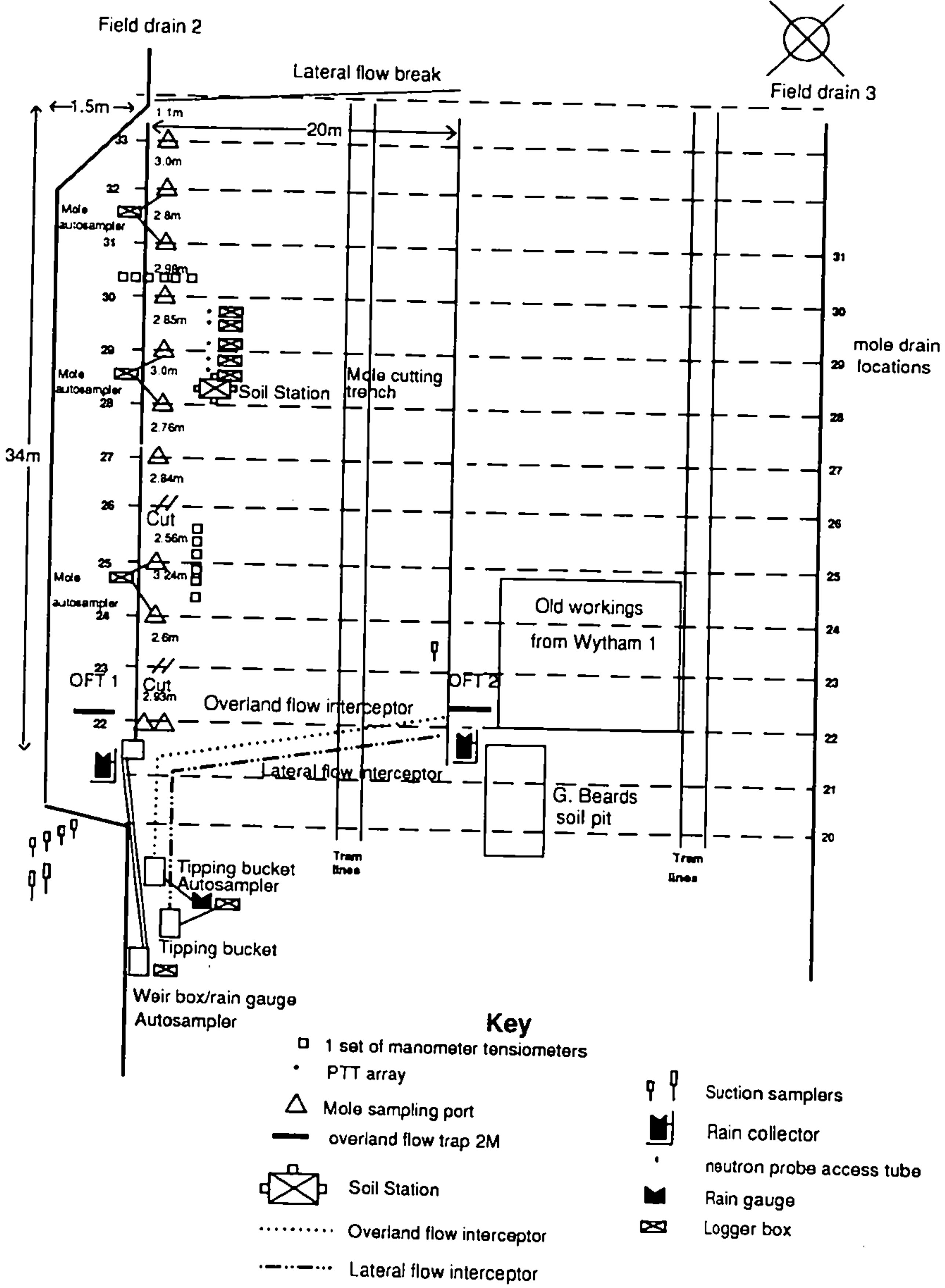
Both repacked soil columns and undisturbed soil columns containing soil from Wytham will be used to study macropore transport of solutes. A number of parameters will be manipulated, including irrigation rate, position of tracers in the column, and the presence of macropores. In essence, the columns will be used to verify suppositions on macropore flow which come from interpretations of field data.

6.3 MODELLING STUDIES

The data collected from Wytham in the first year confirm the importance of by-pass flow in heavy clay soils. Thus models of flow, and the transport of solutes through systems that are controlled by Darcian flow through the matrix, are not appropriate. Attempts to model the system at Wytham will concentrate on developing modules that describe by-pass flow and its a:newwyt3b

Figure 33. Wytham location of instruments

(superimposed over the location of the field and mole drains)



link with the matrix. The following processes are likely to be of key importance in such a model:

i) The commencement and cessation of by-pass flow. This can be controlled either by the conditions in the soil matrix or by rainfall intensity.

ii) The interaction between by-pass flow and the matrix. Here the depth of penetration of by-pass flow must be considered, especially as it is controlled by the dryness of deeper soil layers. Additionally, the interaction of solute in the by-pass flow with the matrix will have implications for sorption/desorption.

iii) The nature of the by-pass flow routes will change with time e.g. shrink/swell cracks will change diameter with water content.

iv) The connectivity of the by-pass flow routes will obviously influence the depth and speed of movement of water and solutes by-passing the matrix.

The development of conceptual models to describe this processes will be undertaken as follows:

a) The literature will be reviewed with respect to modelling of by-pass flow carried out by other workers. There has been a great deal written concerning the flow of water in by-pass flow routes, but little on the movement of solutes.

b) The interaction between the matrix and the by-pass flow route will be considered in a simplified form, a single macro-pore passing through an homogeneous matrix. This situation can be set up in the laboratory under controlled conditions and thus generate vital information for the conceptualization of this system.

c) Through b) above, several types of by-pass flow route can be investigated i.e. structural cracks, earthworm channels and shrink swell cracks.

The aim is to develop a model of a simplified system so as to isolate individual or small groups of processes within the system. The expansion of the model to a field scale will need much thought, particulary with regard to the distribution and connectivity of macropores.

ACKNOWLEDGEMENTS

The authors wish to thank NERC and AFRC for providing financial assistance for this project. The authors also wish to thank Oxford University for permission to work at Wytham farm, and in particular David Sharpe, the farm manager, whose assistance was and is vital to the success of the field experiment. The assistance of IH personnel with chemical analysis, in the workshop, site services and instrument section is gratefully acknowledged. The authors are grateful for helpful discussions on the work from Tim Burt (Oxford University) and the principal collaborators in the component of the project that is funded as part of the NERC\AFRC Special Topic, Alan Walker (HRI) and Andrée Carter (SSLRC). The help given by Tim Burt in obtaining permission to locate the experiment at Wytham was much appreciated.

7. References

Ahuja, L.R. & O.R. Lehman. 1983. The extent & nature of rainfall-soil interaction in the release of soluble chemicals to runoff. Journal of Environmental Quality 12: 34-40.

Allen, R. & A. Walker. 1987. The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. Pesticide Science 18: 95-111.

Baker, J.L. & J.M. Laflen. 1979. Runoff losses of surface-applied herbicides as affected by wheel tracks and incorporation. Journal of Environmental Quality 8: 602-607.

Baldwin, F.L., P.W. Sandlemann, & J.M. Davidson. 1975. Movement of fluometuron across and through the soil. Journal of Environmental Quality 4: 191

Bell, J.P., Abbott, C.L. and Batchelor, C.H. 1991. The soil hydrology of 'Longlands', Rosemaund EHF, Herefordshire, First Interim Report - Crop Year 1989/90, Institute of Hydrology report.

Bell, J.P., Abbott, C.L. and Batchelor, C.H. 1992. The soil hydrology of 'Longlands', Rosemaund EHF, Herefordshire, Second Interim Report - Crop Year 1990/91, Institute of Hydrology report.

Beven, K. & P. Germann. 1982. Macropores and water flow in soils. Water Resources Research 18: 1311-1325.

Blair, A.M., T.D. Martin, A. Walker & S.J. Welch. 1990. Measurement and prediction of isoproturon movement and persistence in three soils. Crop Protection 9: 289-294.

Bouma, J. & J.L. Anderson. 1977. Water and chloride movement through soil columns simulating pedal soils. Soil Science Society of America Journal 41: 766-770.

Bouma, J., L.W. Dekker & C.J. Muilwijk. 1981. A field method for measuring short-circuiting in clay soils. Journal of Hydrology 52: 347-354.

Buttle, J.M. 1990. Metolachlor transport in surface runoff. Journal of Environmental Quality 19: 531-538.

Cameron, K.C., D.F. Harrison, N.P. Smith & C.D.A. McLay. 1990. A method to prevent edge-flow in undisturbed soil cores and lysimeters. Australian Journal of Soil Research 28: 879-886.

Cannel, R.Q., M.J. Goss, G.L. Harris, M.G. Jarvis, J.T. Douglas, K.R. Howse & S. LeGrice. 1984. A study of mole drainage with simplified cultivation for autumn-sown crops on a clay soil. 1: Background, experiment and site details, drainage systems, measurement of drainflow and summary of results, 1978-1980. Journal of Agricultural Science Cambridge 102: 539-559.

Clark, L. & J. Gomme. 1992. Pesticides in a Chalk catchment in Eastern England. Hydrogéologie 4: 169-174.

Council of the European Communities. Directive of the 15th July 1980 relating to the quality of water intended for human consumption. 80/778/EEC; 05 01 229, 30th August 1980.

Czapar, G.F., R. Horton & R.S. Fawcett. 1992. Herbicide and tracer movement in soil columns containing an artificial macropore. Journal of Environmental Quality 21: 110-115.

Dao, T.H. 1991. Field decay of wheat straw and its effect on metribuzin and S-ethyl metribuzin sorption and elution from crop residues. Journal of Environmental Quality 20: 203-208.

Dictor, M.C., G. Soulas, K. Takagi, J.P.E. Anderson, K. Lewis & F. Lewis. 1992. Subsoil microbiology: microbial activity and potential for pesticide degradation in the unsaturated zone. In Proceedings of the International Symposium on Environmental Aspects of Pesticide Microbiology in Sigtuna, Sweden pp 284-290.

Drinking Water Inspectorate (1992). Nitrate, Pesticides and Lead 1989 and 1990. DoE Report.

Edwards, C.A. 1991. Long-term ecological effects of herbicides: Field studies. In Proceedings of British Crop Protection Conference pp 883-890. Published by BCPC.

Edwards, W.M., M.J. Shipitalo, L.B. Owens & L.D. Norton. 1989 Water and nitrate movement in earthworm burrows within long-term no-till cornfields. Journal of Soil and Water Conservation 44: 240-243.

Ela, S.D., S.C. Gupta & W.J. Rawls. 1992. Macropore and surface seal interactions affecting water infiltration into soil. Soil Science Society of America Journal 56: 714-721.

Fermanich, K.J. & T.C. Daniel. 1991. Pesticide mobility and persistence in microlysimeter soil columns from a tilled and no-tilled plot. Journal of Environmental Quality 20: 195-202.

Ghodrati, M. & W.A. Jury. 1990. A field study using dyes to characterise preferential flow of water. Soil Science Society of America Journal 54: 1558-1563.

Ghodrati, M. & W.A. Jury. 1992. A field study of the effects of soil structure and irrigation method on prefential flow of pesticides in unsaturated soil. Journal of Contaminant Hydrology 11: 101-125.

Gomme, J., L.R.S.C. Shurvall, S.M. Hennings, & L. Clark. 1992. Hydrology of Pesticides in a Chalk Catchment: Groundwater, J. IWEM, 6, 172-178.

Graham-Bryce, I.J. 1981. The behaviour of pesticides in soil. In The Chemistry of Soil Processes (Ed. D.J. Greenland & M.H.B. Hayes), pp 621-671. Published by John Wiley and Sons Ltd, Chichester.

Grossmann, J. & P. Udluft. 1991. The extraction of soil water by the suction-cup method: a review. Journal of Soil Science 42: 83-93.

Guo, L., T.J. Bicki, A.S. Felsot & T.D. Hinesly. 1993. Sorption and movement of alachlor in soil modified by carbon-rich wastes. Journal of Environmental Quality 22: 186-194.

Haigh, R.A. 1985. Water balance and water quality studies in an underdrained clay soil catchment. PhD thesis, University of Oxford.

Hance, R.J. 1987. Herbicide behaviour in the soil, with particular reference to the potential for groundwater contamination. In Herbicides (Ed. D.H. Hutson & T.R. Roberts). pp223-247. Published by John Wiley and Sons Ltd.

Hance, R.J. & F. Fuhr. 1992. Methods to study fate and behaviour of pesticides in the soil. In Lysimeter Studies of Pesticides in the Soil. BCPC Mono No. 53 (Ed R.J. Hance and F. Fuhr) pp 9-18. Published by British Crop Protection Council.

Harris, G.L. 1991. Soil drainage and crop management strategies to minimise pesticide leaching. In The Brimstone experiment, proceedings of a conference on collaborative work by ADAS Field Drainage Experimental Unit and Rothampstead Experimental Station, October 15-16, 1991 (Ed J.A. Catt) pp55-69. Published by Lawes Agricultural Trust.

Harris, G.L., M.J. Goss, R.J. Dowdell, K.R. Howse & P. Morgan. 1984. A study of mole drainage with simplified cultivation for autumn-sown crops on a clay soil. 2. Soil water regimes, water balances and nutrient loss in drain water 1978-1980. Journal of Agricultural Science Cambridge 102: 561-581.

Harris, G.L., S.W. Bailey & D.J. Mason. 1991. The determination of pesticides losses to water courses in an agricultural clay catchment with variable drainage and land management. In Brighton Crop Protection Conference, Weeds vol. 3, pp 1271-1278. Published by British Crop Protection Council.

Harris, G.L., A.B. Turnbull, A.J. Gilbert, D.G. Christian & D.J. Mason. 1992. Pesticide application and deposition - their importance to pesticide leaching to surface water. In British Crop Protection Conference, Pests and Diseases, pp 477-486. Published by British Crop Protection Council.

Harris, G.L., R.A. Hodgkinson, C. Brown, D.A. Rose, D.J. Mason & J.A. Catt. 1993. The influence of rainfall patterns and soils on losses of isoproturon to surface waters. Proceedings Crop Protection in Northern Britain pp 247-252.

Hellpointner, E., R. Fritz, K. Scholz & M. Spiteller. 1992. Lysimeter studies relevant to the fate of pesticides in the soil, experimental limitations/conclusions. In Lysimeter Studies of Pesticides in the Soil, BCPC Mono No. 53 (Ed R.J. Hance and F. Fuhr) pp 141-144. Published by British Crop Protection Council.

Isensee, A.R. & A.M. Sadeghi. 1992. Laboratory apparatus for studying pesticide leaching in intact soil cores. Chemosphere 25: 581-590.

Jarvis, M.G. & J. Hazelden. 1982. Soils in Oxfordshire 1, Soil Survey Record No. 77 (Ed. M.G. Jarvis & J. Hazelden), pp 53-64. Soil Survey of England and Wales, Rothampstead Experimental Station, Harpenden.

Kneale, W.R. 1986. The hydrology of a sloping, structured clay soil at Wytham, near Oxford, England. Journal of Hydrology 85: 1-14.

Kneale, W.R. & R.E. White. 1984. The movement of water through cores of a dry (cracked) clay-loam grassland topsoil. Journal of Hydrology 67: 361-365.

Kookana, R.S., L.A.G. Aylmore & R.G. Gerritse. 1992. Time-dependent sorption of pesticide during transport in soils. Soil Science 154: 214-225.

Lee, K.E. 1985. Earthworms their ecology and relationships with soils and land use. Published by Academic Press, Sydney.

Leeds-Harrison, P., Spoor, G., & Godwin, R.J., 1982. Water flow to mole drains. J. Agric. Engineering Research. 27: 81-91.

Leeds-Harrison, P.B., Shipway, C.J.P., Jarvis, N.J. & Youngs, E.G., 1986. The influence of soil macroporosity on water retention, transmission and drainage in a clay soil. Soil Use And Management. 2: 47-50.

Lees, A & K. McVeigh. 1988. An investigation of pesticide pollution in drinking water in England and Wales. Special Report, Friends of the Earth, London.

Leistra, M. & J.J.T.I. Boetsen. 1989. Pesticide contamination of groundwater in Western Europe. Agriculture, Ecosystems and Environment 26: 369-389.

Leonard, R.A. 1990. Movement of pesticides into surface waters. In Pesticides in the Soil Environment: Processes, Impacts, and Modeling. SSSA Book Series 2 (Ed H.H. Cheng). pp 303-351. Published by Soil Science Society of America, Inc. Madison, USA.

Mattheissen, P., C. Allchin, R.J. Williams, S.C. Bird & D. Brooke. 1992. Translocation of some herbicides between soil and water in a small catchment. Journal of the Institution of Water and Environmental Management. 6: 496-504.

Mudd, P.J., R.J. Hance & S.J.L. Wright. 1983. The persistence and metabolism of isoproturon in soil. Weed Research 23: 239-246.

Pilgrim, D.H., Huff, D.D & Steele, T.D., 1978. A field evaluation of subsurface and surface runoff, 11. Runoff processes . Journal of Hydrology., 38: 319-341.

Pothuluri, J.V., T.B. Moorman, D.C. Obenhuber & R.D. Wauchope. 1990. Aerobic and anaerobic degradation of alachlor in samples from a surface to groundwater profile. Journal of Environmental Quality 19: 525-530.

Priebe, D.L., & A.M. Blackmer. 1989. Preferential movement of oxygen-18-labelled urea through macropores through a nicollet soil. Journal of Environmental Quality 18: 66-72.

Putz, T.H., W. Mittelstaedt, & F. Fuhr. 1992. Comparison of the time course of temperature, water content and organic carbon in top soil and subsoil in lysimeters with the field. In Lysimeter Studies of Pesticides in the Soil, BCPC Mono No. 53 (Ed R.J. Hance and F. Fuhr) pp 163-172. Published by British Crop Protection Council.

Radulovich, R., P. Sollins, P. Baveye, & E. Solorzano. 1992. Bypass water flow through unsaturated microaggregated tropical soils. Soil Science Society of America Journal 56: 721-726.

Robinson, M., & Beven, K.J., 1983. The effect of mole drainage on the hydrological response of a swelling clay soil. Journal of Hydrology 64:205-223

Robinson, M., Mulqueen, J., & Burke, W., 1987. On flows from a clay soil-Seasonal changes and the effect of mole drainage. Journal of Hydrology 91:339-350.

Sims, G.K., J.D. Wolt, & R.G. Lehmann. 1992. Bioavailability of sorbed pesticides and other xenobiotic molecules. In Proceedings of the International Symposium on Environmental Aspects of Pesticide Microbiology in Sigtuna, Sweden pp159-164.

Soulas, G. 1982. Mathematical model for microbial degradation of pesticides in the soil. Soil Biology and Biochemistry 14: 107-115.

Starr, J.L. & D.E. Glotfelty. 1990. Atrazine and bromide movement through a silt loam soil. Journal of Environmental Quality 19: 552-558.

Stehouwer, R.C., W.A. Dick, & S.J. Traina. 1993. Characteristics of earthworm burrow lining affecting atrazine sorption. Journal of Environmental Quality 22: 181-185.

Taylor, A.W. & W.F. Spencer. 1990. Volatilization and vapor transport processes. In Pesticides in the Soil Environment: Processes, Impacts, and Modeling. SSSA Book Series 2 (Ed H.H. Cheng). pp 213-270. Published by Soil Science Society of America, Inc. Madison, USA.

Trojan, M.D. & D.R. Linden. 1992. Microrelief and rainfall effects on water and solute movement in earthworm burrows. Soil Science Society of America Journal 56: 727-733.

Walker, A. 1991. Review: Influence of soil and weather factors on the persistence of soil applied herbicides. Applied Plant Science 5: 94-98.

Walker, A. & P.A. Brown. 1983. Spatial variability in herbicide degradation rates and residues in soil. Crop Protection 2: 17-25.

Walker, A., R.J. Hance, J.G. Allen, G.G. Brigs, Y.L. Chen, J.D. Gaynor, E.J. Hogue, A. Malquori, K. Moody, J.R. Moyer, W. Pestemer, A. Rahman, A.E. Smith, J.C. Streibig, N.T.L. Torstensson, L.S. Widyanto, & R. Zandvoort. 1983. EWRS Herbicide-soil working group: Collaborative experiment on simazine persistence in soil. Weed Research 23: 373-383.

Weber, J.B. & H.D. Coble. 1968. Microbial decomposition of diquat adsorbed on montmorillonite and kaolinite clays. Journal of Agricultural Food Chemistry 16: 475-478.

White, R.E., S.R. Wellings, & J.P. Bell. 1983. Seasonal Variations in Nitrate Leaching in Structured Clay Soils under Mixed Land Use, Agricultural Management, 7: 391-410.

White, R.E., J.S. Dyson, Z. Gerstl, & B. Yaron. 1986. Leaching of herbicide through undisturbed cores of a structured clay soil. Soil Science Society of America Journal 50: 277-283.

Williams, R.J., & P.C.R. Völkner. 1993. Total Impact Assessment of Pollution in River Basins - Pesticide Impact Modelling, NRA Draft Final Report, R&D 119/9/W.

Williams, R.J., D.N. Brook, P.J. Glendinning, P. Matthiessen, M.J. Mills, & A. Turnbull. 1991. Movement and modelling of pesticide residues at Rosemaund farm. In Brighton Crop Protection Conference, Weeds, vol. 2 pp 507-514. Published by British Crop Protection Council.

Williamson, A.R. & A. Carter. 1991. Field studies to determine the potential risk of contamination of ground and surface waters by an autumn and spring applied herbicide in oilseed rape and fodder maize. In Brighton Crop Protection Conference, Weeds, vol. 2 pp 477-484. Published by British Crop Protection Council.

Annex A Pesticide transport literature review

A 1 HYDROLOGICAL PROCESSES IN CRACKING CLAY SOILS

One of the challenges to environmental scientists is still to determine by what routes the escaping '1 %' is lost from clay soils. Pesticide may be transported in solution, co-transported with other organics, or bound to sediment particles (Ghodrati and Jury, 1992) depending on the sorption coefficient of the pesticide, and type of indigenous organic compounds (Leonard, 1990).

Four different types of water movement in clay soils can be identified:

A 1.1 Infiltration into the matrix.

Occurrence:
Predominant in dry spring and summer periods, when rainwater fills micropores in the soil matrix from which water has been lost by evaporation and crop uptake. Once the infiltration capacity has been satisfied, preferential flow will occur. The hydraulic conductivity of the saturated matrix is seen as extremely low. It has also been noted that cracked dry clay soils have an initially reduced hydraulic conductivity, exhibiting almost hydrophobic characteristics which will also promote preferential flow during intense rainfall.

A 1.2 Vertical bypass flow

Occurrence:
When the infiltration capacity of the matrix is exceeded or when rainfall intensity exceeds the matrix infiltration acceptance rate (White *et al.*, 1986; Radulovich *et al.*, 1992)

Transport routes
Cracks induced by soil shrinkage from evaporation or those induced by agricultural activity such as mole draining (Harris *et al.*, 1984). Biopores which include worm burrows and root holes.

Research
As vertical macropores appear to represent the principal route whereby pesticides can enter the subsurface drainage system or groundwater, they have received considerable attention. Prior to macropores transporting water, surface ponding of rainwater must occur (it is plausible that localised perched water tables may feed macropores below the soil surface). In these situations the rainwater that has not been accepted by the matrix runs over the surface, looking for an escape. This ponded mobile water is believed to interact with the top cm or so of the soil surface, the so called mixing zone (Ahuja and Lehman, 1983), whose thickness will vary with the surface structure of the soil. This mixing zone is of great significance with respect to clay soils, as the great majority of the pesticide remains in the top soil surface, sorbed onto soil particles or in the soil solution. Therefore the rainwater prior to moving into macropores will be running through the 'pesticide rich' part of the soil. The principal reason for the pesticide remaining in the top few cm of the soil surface is due to adsorption reactions with organic matter. This is in contrast to other solutes such as halides

(Fermanich and Daniel, 1991).

In late spring and summer shrinkage cracks are the principal macropore component, Kneale and White (1984) estimated 10-20% of rainfall in dry periods bypassed the top 9 cm via this route. The amount of water leached via shrinkage cracks decreases with time during prolonged rainfall events as the clay soil begins to swell, and the cracks close (White *et al.*, 1986). Pesticide contamination of water courses in these conditions, however, may not be serious as with a low water table drain flow is rarely initiated. Deep penetration of pesticides into the soil matrix may present a longer term problem, due to low degradation and sorption potentials at depth (Pothuluri *et al.*, 1990). The pesticides may persist and become mobilised when the water table rises in the winter.

In the wetter conditions of the autumn and winter, vertical worm burrows represent the principle macropores available to rainwater. Vertical worm burrows are formed by detritivores, the worm population that feeds or collects organic matter at the soil surface which is then ingested within the confines of the burrow (Lee, 1985). The most well known of these worms is *Lumbricus terrestris*. The number of these organisms is much reduced in fields under arable cultivation compared with pastures. Studies have shown that only a small number of the available worm burrows actually transport water during a preferential flow event. Trojan and Linden (1992) correlated volumes of water transported to the topographical aspect of the worm openings, with worm burrow openings on ridges transporting less water than those in depressions. Worm casts or the worms themselves may block the openings (Ela *et al* 1992) and of course very few of the worm burrows are continuous in terms of reaching groundwater depth or intersecting field drains. In addition, worm burrows may not transport rainwater throughout a rain event due to the formation of surface seals or plugs by sediment (Bouma and Anderson, 1977; Ela *et al*, 1992). At the beginning of a rain event rainwater may initially only run down the walls of a worm burrow rather than filling the whole pore (Radulovich *et al.*, 1992) and run at comparatively low flow velocities (Bevan and German, 1982). This may give opportunities for readsorption of the pesticide on burrow walls which have a higher TOC than the surrounding soil matrix, particularly with increasing depth (Stehouwer *et al.*, 1993). Edwards (1991) suggested this may be why less pesticide leached out of worm burrows compared with artificial macropores in his experiments. It can be assumed that once the burrow is completely full of water and the water is being transported at higher velocities (up to 6 cm s^{-1}, Bevan and German, 1982) the opportunities for significant adsorption are much reduced.

Contamination significance

In the critical autumn and early winter period in which winter cereals are sown and herbicides applied, vertical bypass flow, particularly via worm burrows, is seen to represent the principal loss route. Water moving via lateral interflow may enter vertical macropores and then be transported to the field drainage system. Another possibility is that worm burrows which open at footslope areas which have received additional deposits of pesticide after overland flow can transport above average concentrations of pesticide in subsequent rainfall events.

A 1.3 Lateral bypass flow or interflow

Occurrence

This will only occur in saturated conditions in fields containing a gradient and a subsurface boundary layer of a lower hydraulic conductivity than the upper horizon.

Transport routes
This type of water movement may utilise structural cracks or biopores, predominantly laterally aligned worm burrows and in certain circumstances possibly along buried straw stalks.

Research
Of the three preferential flow routes lateral interflow seems to have received the least attention. It is difficult to study outside the field environment and methods to study it within the field are faced with the difficulty of assessing whether an interceptor trench may act as a sink, and so create artificial interflow. A likely transport route would be along horizontal worm burrows formed by sub-surface foraging (geophagus) worms (Lee, 1985). Harris *et al.* (1984) related a plough pan to a perched water table and lateral interflow at Brimstone. Results from Brimstone suggested that whilst lateral interflow accounted for 15% of the rainfall, only insignificant amounts of the pesticides under study were involved.

Contamination significance
The significance of lateral interflow in terms of pesticide contamination may be :

- In feeding vertical macropores below the soil surface which connect to the field drainage system.
- In conducting pesticide down the slope to the riparian zone, and from there into drainage ditches.
- In conducting pesticide down the slope to an area of the field with a more conductive soil type, where it percolates down to groundwater.

A 1.4 Overland flow or surface runoff

Occurrence
This will be the same as for vertical bypass flow. Overland flow may be seen as a two-stage process involving small short-range movement, and large-scale overland flow or sheet flow. The short-range overland flow is drained away by macropores and when this capacity is exceeded the short range overland flow movements coalesce to form sheet flow.

Transport routes
This occurs over the soil surface and within the top soil to a 1-2cm depth mixing zone. When not drained away by macropores, rivulets form in natural depressions or wheel tracks left by agricultural machinery, allowing rapid transport over long distances.

Research
Harris *et al.* (1984) estimated that 4-11% of rainfall at Brimstone over the winter could be accounted for by overland flow. Ahuja and Lehman (1983) simulated overland flow in the laboratory using soil boxes and a 4° slope. Water moving laterally during overland flow was observed to interact with solutes in the top 2 cm (mixing zone).

It is believed that pesticide extraction from the soil surface into the moving overland flow water is related to diffusion and turbulent transport of dissolved pesticide in soil pores and desorption from soil particles, as well as the dislodgement and suspending of soil particles containing sorbed pesticide (Leonard, 1990). Much of this pesticide extraction is related to the impact and turbulence created by raindrops. Observations in the field (Buttle, 1990) indicate that high concentrations of pesticides are carried in overland flow, and that the concentration carried reduces with time as the compounds are degraded in the topsoil. At the same time, however, it is interesting to note an increase in soil residues with time in the footslope area compared with up slope as pesticide is carried and then deposited downhill. It was estimated by Buttle (1990) that 0.6-0.9% of the pesticide losses from the field site had been by overland flow. Baker and Laflan (1979) observed greater transport of pesticides in overland flow in plots containing tractor wheel tracks. It was suggested that the wheel tracks by compacting the soil, reduced penetration of surface-applied pesticides into the soil immediately over them. The wheel tracks were also thought to act as a conduit for the surrounding area during heavy rainfall events.

Contamination significance

The importance of overland flow in terms of transporting pesticides directly to field drainage ditches is unlikely to be great as few agricultural fields slope directly into ditches. Translocating pesticides into footslope areas (Buttle, 1990) may have significance in representing a field 'hot spot' from which subsequent vertical bypass flow may transport high concentrations to nearby drainage ditches.

A 2 HYDROCHEMICAL AND BIOLOGICAL PROCESSES

A 2.1 Degradation

The major factor influencing the concentration of pesticide available for transport is degradation. The fate of the vast majority of all herbicides applied to the field is degradation, and depending on the compound and environmental conditions a pesticide may persist for days or months in the top soil. This may result from direct chemical transformation, such as by hydrolysis catalysed by organic matter (Hance, 1987). But almost always soil microorganisms are involved in degrading the compound.

The pesticides may be directly metabolised and the microorganism derive energy from them, presumably because the compounds resemble its natural substrates and so stimulate an appropriate enzyme system to degrade them. An alternative is co-metabolism, in which the microorganism derives no energy benefit. In these situations an enzyme whose production has been stimulated by the presence of another substrate can coincidental catalyse the partial breakdown of the pesticide (Soulas, 1982).

A large number of soil properties can influence biodegradation. Organic matter is of particular importance, as it is often the main factor controlling pesticide adsorption. As degradation of most organic compounds occurs within the bacterial cell, uptake must occur from solution, therefore sorbed species must be desorbed. Where pesticides have a slow desorption kinetics relative to their degradation rate, the degradation rate will be reduced to that of the desorption rate. This was noted with simazine degradation and organic matter content (Walker *et al.*, 1983). It must be noted, however, that microbial activity is often highest in soils with a high organic matter content.

Pesticide adsorption to clay particles has also been observed to reduce degradation rates such as with metamitron (Allen and Walker, 1987) diquat (Weber and Cable, 1968), isoproturon (Blair *et al.*, 1990), and simazine (Walker *et al.*, 1983). Expanding lattice clays have been identified by Sims *et al.* (1992) as having a particular importance in reducing biodegradation.

Another factor to be considered is soil pH, both for its effect on the microbial population and on adsorption where this influences the electronic charge of the compound (Graham-Bryce, 1981). The other main variables that influence degradation are temperature and soil moisture. There is often a 2 to 2.5-fold increase in degradation rate if temperature is increased by 10°C, and a 1.5 to 2-fold increase in rate of loss if soil moisture content is increased by a factor of 2 (Walker, 1991).

The microbial community of the top soil often gives good replication when degradation rates are measured, suggesting a widespread distribution of microbial competence to degrade the compound. Variation in residue concentrations found in the top soil are more likely to be due to errors in spraying than variation in degradation potential (Walker and Brown, 1983). However, the ability to degrade pesticides becomes much more variable with depth (Dictor *et al.*, 1992) leading to generally lower subsurface degradation rates (Pothuluri *et al.*, 1990). A number of suggestions have been put forward to explain this trend, such as lower microbial populations, low nutrient status and a lack of competence to degrade the compound (Pothuluri *et al.*, 1990), all of which may be involved. Little work has been done on the potential for anaerobic degradation of pesticides. This pathway for pesticide degradation may be insignificant in the largely aerobic topsoil, but may be more important in subsurface environments which have low oxygen partial pressures (Pothuluri *et al.*, 1990).

A 2.2 Sorption characteristics

The extent and nature of the sorption and desorption characteristics of a pesticide are influenced by the chemical nature of the compound, and the nature of the surrounding soil particles. Soil particles with a high clay content can present an enormous surface area potentially available for binding such as 100 $m^2 g^{-1}$ (Graham-Bryce, 1981). Broadly speaking, sorption reactions can be divided into hydrophillic and hydrophobic interactions. Hydrophillic reactions are seen as generally more reversible than hydrophobic ones. Hydrophillic interactions with soil surfaces include:

- Hydrogen bonding (sharing a H atom between two electronegative elements).
- Ion exchange (pesticides which act as organic bases will adsorb to cation exchange sites, and those which act as organic acids will adsorb to anion exchange sites, such as alumina or magnetite).
- Covalent or ionic bonds (can occur with reactive groups in organic matter).
- Coordination reactions (ligand exchange, which has been suggested for triazines binding to the transition metals of humic acids)
- Van der Waals forces

Hydrophobic associations or entropy generations can best be described as hydrophobic molecules melting into organic matter. The hydrophobicity of molecules depends on pH, i.e. a pesticide remaining un-charged for example, acting as a weak base would undergo a hydrophobic association reaction with an organic adsorbent in alkaline conditions, but not in neutral or acid conditions. The hydrophobicity of a molecule can be estimated from the octanol/water partition coefficient.

It is worth noting that pesticides can bind to mobile organic fractions such as humic acids. Humics have surfactant properties ie they have hydrophillic and hydrophobic ends and therefore can solubilise hydrophobic pesticides (Graham-Bryce, 1981).

The adsorption potential of a soil is often found to closely correlate with its organic matter content. The organic fraction of the soil is often associated with a high CEC and therefore represents a potential for cation exchange reactions with basic pesticides, and in addition it can undergo hydrophobic associations. The exact nature of all the adsorption interactions that occur with a pesticide in a particular soil are rarely studied, however an apparent change in the adsorption equilibrium with time, leading to greater adsorption, has been noted with certain pesticides (White *et al.*, 1986). This suggests a reduction in the proportion of pesticide immediately available for transport with time. Sorption reactions are time-dependent and rarely take place in situations resembling the typical batch experiments undertaken in the laboratory. Therefore in the disequilibrium conditions of pesticide transport down a macropore for instance, sorption may be much reduced (Kookana *et al.*, 1992) from that which may be estimated in the laboratory. It has also been noted that strongly sorbed pesticides are likely to persist for longer as biodegradation is reduced (Sims *et al.*, 1992; Allen and Walker, 1987).

It would appear that clay soils with a high TOC have the greatest potential for pesticide sorption (Kookana *et al.*, 1992). It must be noted that soils of this type, which retain pesticides in the top few cm, are also maintaining the pesticide in the position where it is most likely to be involved in transport by bypass flow mechanisms.

A 2.3 Volatilization processes

The amount of pesticide available for transport in the water phase can be depleted by volatilization. This process represents a phase change into vapour from the liquid or solid state, which is then followed by vapour dispersion into the atmosphere. The principal features controlling volatilization are (i) vapour pressure of the pesticide (ii) distribution of residues and (iii) the moisture status of the soil.

The vapour pressure of many herbicides used today is very low, such as atrazine, 0.09 mPa (25°C), and isoproturon, 0.0033 mPa (20°C), in which volatilization would be expected to be low. Compounds with a higher vapour pressure such as trifluralin (10.5 mPa at 20°C) have been shown to lose as much as 32% to the atmosphere two days after application (Taylor and Spencer, 1990). In practice the majority of the pesticide is not immediately available for volatilization, being adsorbed to soil surfaces or dissolved in water deep within soil micropores. Therefore, like other pesticide loss mechanisms, volatilization is influenced by soil water content, soil texture and organic matter content. Most rapid losses are likely to occur with residues on the surfaces of bare moist soils (Taylor and Spencer, 1990). Losses from plant surfaces may also be rapid, although residues under the canopy may be in some degree protected by the sheltering action of the leaf cover.

A 3 METHODS OF STUDYING PESTICIDE TRANSPORT

A wide variety of different techniques have been used to study pesticide transport in the past 20 years, from analysis of pesticides in water courses draining catchments of hundreds of hectares to the leachate emanating from re-packed soil columns measuring 10 x 20 cm. Each method can provide information on pesticide transport and the mechanisms involved. However, the drawbacks and disadvantages of the different methods must be taken into account.

A 3.1 Catchment studies

Pesticide concentrations have been measured in water courses which drain catchments at Swavesy in Cambridgeshire (Harris *et al.*, 1991) and Rosemaund in Herefordshire (Williams *et al.*, 1991). Flow in ditches and streams is measured by v-notch weirs from which a series of water samples is collected automatically, triggered by the flow. Flow, pesticide concentration and rainfall can then be compared. Assessing the relationship between the three is difficult particularly as this is influenced by different pesticide properties. Harris *et al* (1991) reported levels of 1-3 ppb of isoproturon in metered ditches and a maximum level of 13 ppb isoproturon was reported by Williams et al (1991) after a storm event. Williams *et al* (1991) estimated a total of 0.8% of the applied isoproturon escaped from the field to nearby water courses. A difficulty with these studies is partitioning the water balance, such as how much of the rainfall is conducted to the drains as deep percolation is difficult to assess.

Whilst figures generated by these studies are important from the point of view of assessing hazards and modelling, they tell us little about the actual mechanisms involved.

A 3.2 Field plot studies

To get closer to the events that lead to stream contamination it is necessary to work in the field itself. The most methodical approach to studying water movement and pathways within a field has been done at Brimstone on a heavy clay (Denchworth series) soil (Cannell *et al.* (1984). Large 0.3 ha plots have been isolated with polythene down to a depth of 1.3 m and are equipped with trenches, pipes and ditches to study overland flow, lateral interflow and drainflow. However, interpretation is complicated by the difficulty in estimating deep percolation and deep lateral interflow. Isoproturon concentrations in drains from these plots showed up to 50 ppb during rainfall events, and were observed to occur before the formation of a water table in the subsoil. Macropore flow was implicated in the estimated 1% loss of isoproturon from the plots (Harris *et al.*, 1992).

Overland flow has been studied in field sites using isolated, bounded field plots (Buttle, 1990; Baker and Laflan, 1979). These studies have shown the relatively high concentrations of pesticides mobilised during overland flow events (293 ppb metalchlor, Buttle, 1990; 6000 ppb alachlor, Baker and Laflan, 1979) which are found both in solution and adsorbed onto sediment. Because of the variability in microtopography, it is difficult to quantify for a given area how much pesticide is moved in this way; for example wheel tracks left by machinery have a disproportionate influence (Baker and Laflan, 1979).

Suction or porous pot samplers are often used in the field as a way of measuring penetration of pesticides below the soil surface in the soil pore water. They enable estimations to be made of pesticide soil water concentrations below the surface in a non-destructive way (Williamson and Carter, 1991). However, care must be used in the interpretation of results. Suction in the sampling system generates a potential gradient in the suction sampler. The radius of the 'recharge area' may extend to 50 cm or more in all directions. Therefore they may suck water up from groundwater below or via macropores from the soil surface above (Grossmann and Udluft, 1991). As with core sampling mentioned below, low pesticide concentrations found in the soil pore water at 25 or 50 cm may be misleading; macropores may be conducting high concentrations of pesticides to greater depths, yet remain undetected by these methods.

Many field experiments involve coring or sectioning parts of the field after applications of herbicide and a conservative tracer and irrigation, or rainfall, has taken place. This allows an accurate assessment to be made of the amount and proportion of pesticide/tracer that penetrates into the soil. However, even with a seemingly well defined plot mass balances are often difficult to achieve (Ghodrati and Jury, 1992). The simplest type of experiment involves continuous ponding of water on the soil after application of the pesticide/tracer (Starr and Glotfelty, 1990). However, this seems a rather unrealistic treatment and may induce certain macropores to flow which would not otherwise do so (Trojan and Linden, 1992). Soil coring has shown that under normal rainfall conditions, pesticide concentrations remain at their highest level at the soil surface (often correlated with organic matter) and reduce with depth (Blair *et al.*, 1990). The problems for sampling produced by preferential flow even in sandy soils are well described by Ghodrati and Jury (1990) where the distribution of an acid dye showed some areas with staining down to 90 cm and others less than 40 cm after irrigation.

An alternative approach was provided by Edwards *et al.* (1989), in which wormholes were connected to sampling bottles situated in an underground gallery. On average 29% of the wormholes transported water during rainfall events, but accounted for 1-6% of the rainfall water. Unfortunately not all soils are amenable to digging galleries, although this type of study underlines the potential influence of macropores in pesticide transport.

A 3.3 Lysimeters

An intermediate between the field and the laboratory is provided by the large lysimeter. Crops can be grown and cultivations mimicked, weather regimes can be altered, whilst ^{14}C-labelled pesticides can be used and a mass balance of the compound assessed. The introduction of legislation in Germany which includes lysimeter studies in pesticide registration has increased the number of lysimeter studies now being carried out. Despite being a good representation of the field and a useful research tool, the lysimeter does not completely mimic field conditions. By necessity all lysimeters or undisturbed soil columns are cut off from the parent soil below. This will cause the truncation of macropores, which may then transport water which would not otherwise have happened. In addition, leaching is only considered in the vertical phase and not lateral movement which occurs in sloped fields is ignored. Below 1 m water is lost to the crops as it becomes leachate whereas in the field roots can extend below this depth (Hellpointner *et al.*, 1992). Before water leaches from the bottom of a lysimeter or any soil column the base must first become saturated, a situation which only occurs in the field if a water table is present at the same depth. An alternative is to apply suction to the bottom of the column so that the soil water potential remains the same throughout the profile (Isensee and Sadeghi, 1992). Putz *et al.* (1992) compared the water content of lysimeters with the parent soil from which they have been taken using a neutron probe. The field was found to have a higher water content throughout the year than the parent soil. These drawbacks do not prevent the lysimeter's use as a research tool but they do make the rationale behind its use in pesticide registration more difficult to justify.

A 3.4 Undisturbed soil columns or mini-lysimeters

Smaller undisturbed soil columns provide a more flexible tool for researchers, allowing a wide variety of different treatments or irrigation regimes to be studied, whilst retaining the original soil structure. However, their smaller size can lead to a wide difference between replicates, reflecting the natural inhomogeneity of the soil (Priebe and Blackmer, 1989; Hance and Fuhr, 1992). Their smaller size brings additional problems to that of the larger lysimeter. Whilst soil columns taken from the soil are routinely described as 'undisturbed', researchers are often coy as to the exact details of their extraction from the soil. Often a 10 or 20 cm diameter tube is hammered directly into the soil (albeit at field capacity) prior to extraction. In many soils particularly those with a high clay content, the pressures developed by this process can lead to compaction, additional fractioning and an upward heave of the soil in the centre of the core. A somewhat safer method involves the digging out and exposing of a soil island, enabling the tube to be carefully slid down over the top with minimum force (Cameron *et al.*, 1990). In addition they have all the disadvantages of the larger lysimeter with the so called edge effect being a particularly difficult problem. When water is applied to soil columns/lysimeters the route of least resistance is downward along the wall of the retaining vessel. This is particularly true of soils with a low hydraulic conductivity. Because of the large size of most lysimeters (0.5 - 1.0 m in diameter) this is not so important, but the smaller the diameter of the column, the more important this effect becomes. An effective solution proposed by Cameron *et al.* (1990) is to insulate the soil from the retaining wall with vaseline, applied in the field in liquid form after being heated. Isensee and Sadeghi (1992) used epoxy cement as an alternative method of sealing the soil column.

Notwithstanding these problems, undisturbed soil columns have allowed researchers to get closer to some of the fundamental processes which take place in the field itself. White *et al.* (1986) demonstrated a reduction in leaching volumes with time, as fractures were compressed in a swelling clay soil, whilst Radulovich *et al.* (1992) described two phases of macropore flow using undisturbed soil cores.

A 3.5 Re-packed soil systems

As mentioned above, the natural soil inhomogeneity leads to many problems in interpreting results from soil column work in which a number of different treatments have been used. In an effort to obtain a better understanding of the fundamental mechanisms involved in pesticide transport, particularly with respect to macropore flow, many researchers have used re-packed soil columns in an effort to simplify the system and reduce variables. In these systems the parent soil is sieved and mixed prior to careful re-packing to a bulk density similar to the original soil. To these systems Trojan and Linden (1992) and Ela *et al.*, (1992) added live worms to create natural macropores. A further simplification is to add artificial macropores. With this technique the differences in leaching between a conservative tracer and a pesticide could be observed (Czapar *et al.*, 1992) and related to movement into the matrix with respect to the macropore. Guo *et al.* (1993) and Dao (1991) studied the influence of manure and straw respectively on pesticide leaching in re-packed columns. Ahuja and Lehman (1983) used an imaginative technique of re-packed soil in boxes maintained at a 4% slope, to study the mixing zone associated with overland flow.

A 3.6 Summary of advantages and limitations of different study methods

1. Catchment studies

For:	Studying undisturbed natural system Provides important data for modellers and legislators.
Against:	Gives few clues about processes happening in the field.

2. Field studies

For:	At the site of the action, can observe the different types of runoff as they occur and study the antecedent conditions which promote them.
Against:	Climate cannot be altered. Wide variability in soil types may occur within the field, leading to different drainage characteristics Installation of equipment may alter field conditions. Mass balance of rainwater or pesticide fate rarely achieved.

3. Lysimeter studies

For:	Minimum disturbance to soil physical, chemical and microbiological characteristics. Allow mass balance to be calculated. Climate conditions can be altered and crops grown to simulate different field conditions.
Against:	Water content and drainage conditions may not mimic the field. Expensive and time-consuming. Does not include lateral flow component.

4. Undisturbed soil columns

For:	More flexible, easier to control parameters than with large lysimeters. Can study macropore processes in greater detail.
Against:	Drainage can be even less realistic than with large lysimeters, particularly with respect to the edge effect. Variability between replicate soil columns.

5. Re-packed soil columns

For:	Researcher has total control over the system.
Against:	Situation created may be totally unrealistic.

Despite more than 20 years of research, many aspects of water movement in soils and solute transport are poorly understood.

For example:
In particular very little data is available on what actually happens in the field in terms of bulk water movement during rainstorms and the amounts of pesticide associated with the different flow pathways.

Whilst macropores have often been highlighted to be of key importance in pesticide contamination of surface water courses and groundwater, many aspects of their function are not yet fully understood, for example:

- How pesticide is released from soil particles during rainfall events, is it removed from the solid phase, and how is this influenced by rainfall intensity?

- The movement of water through a topsoil mixing zone prior to entry into a macropore.
- The difference in behaviour between the different types of macropore.
- The interaction of water and solutes with the surrounding soil matrix
- The relationship between neighbouring continuous and discontinuous macropores.

Against this background each of the different methods described above have something to offer the researcher provided their drawbacks and limitations are appreciated.

A 4 ISOPROTURON LOSSES FROM AGRICULTURAL LAND

Williams *et al.* (1991) and Harris *et al.* (1991) have measured isoproturon in streams draining defined catchments from clayey soils. At Rosemaund (Bromyard series) a peak concentration of 13 ppb was detected in an instrumented stream following a rainstorm event. It was estimated that 0.8% of the applied isoproturon escaped from the field into the surrounding water courses (Williams *et al.*, 1991). At Swavesy (Denchworth series) Harris *et al.* (1991) detected levels of 1-3 ppb in ditches draining the catchment. Levels of 0.25 to 0.75 ppb isoproturon were detected in the river Granta from January to May draining a Chalk catchment (Clark and Gomme, 1992).

Levels of 10-50 ppb isoproturon have been detected in the drainage from the 0.2 ha mole field plots at Brimstone after a 2.5 kg/ha application in winter seasons (Harris, 1991; Harris *et al.*, 1992). Up to 100 ppb isoproturon concentrations have been detected in lateral interflow in similar experiments (Harris *et al.*, 1993). In contrast to winter applications, concentrations as high as 550 ppb have been detected in drainwater after spring applications (Harris *et al.*, 1993) although in smaller volumes of water. Total reported losses of isoproturon to drainwater over drainage seasons at Brimstone have been assessed as $< 1\%$. It would appear that throughout most of the drainage seasons the water table was below the depth of the mole drains. Therefore water must have entered them from above via cracks, with hydrographs showing peaky responses to rainfall. The peak and total water involved in drainflow was related primarily to the soil moisture status. A reduction in drainflow peaks in response to rainfall was noted over a number of years as the mole drains deteriorated (Harris, 1991).

Degradation experiments under simulated field conditions give isoproturon a DT_{50} of 30 days (Blair *et al.*, 1990) and a greater persistence in soils with a high clay content has been noted. Mudd *et al.* (1983) reported a DT_{50} of 40 days in field experiments with a sandy loam soil but noted that a small remaining proportion of isoproturon ($< 4\%$) persisted beyond 203 days. This suggested that a proportion of isoproturon was protected in some way from degradation, possibly due to irreversible adsorption to an organic fraction. In addition Harris (1991) noted isoproturon in drain water (at a low concentration) emanating from plots which had not had a pesticide application, so the pesticide may have been a legacy of a previous year's application.

Annex B Staff list

A large number of IH staff have contributed significantly to this project, these include:

Project Supervision:	Dr P. Whitehead, Dr C. Batchelor
Project Coordination:	Dr A. Johnson
Soil Hydrology:	J. Bell, A. Haria, D. Robinson,
Soil Chemistry and Microbiology:	Dr A. Johnson, V. Cruxton
Hydrology and Modelling:	R. Williams, C. Volkner, A. O'Donohue
Laboratory Analysis:	C. Smith, L. Bhardwaj, M. Neal, H. Jeffrey
Instrumentation:	M. Turner, Dr T. Dean
Worshops:	A. Warwick, G. Walley, J. White
Transport and Site Services:	J. Fraser, I. Standbridge, R. Drewett

Annex C Glossary of terms

Suction samplers	Also known as suction cups or suction candles. Consist of plastic tube with ceramic bulb at the end. Installed in the soil at different depths and water extracted by applying suction.
Overland flow	Also known as surface runoff. Term used to describe water moving over the soil surface, both for limited distances (a few cm) and during sheet flow, when water may transport solutes over many tens or hundreds of metres.
Lateral interflow	Term used to describe lateral movement down the slope within the soil, ie below the surface.

Natural
Environment
Research
Council