Session 2
Field and Lysimeter Studies

Chairman   Dr T R ROBERTS

Session Organiser   S W BAILEY

A CRITICAL EVALUATION OF FIELD MONITORING TECHNIQUES USED TO DESCRIBE THE LEACHING AND RUN-OFF BEHAVIOUR OF PESTICIDES

A. D. CARTER, P. FOGG
Soil Survey and Land Research Centre, Cranfield University, Shardlow Hall, Shardlow, Derby, DE72 2GN, UK.

ABSTRACT

UK and European regulatory authorities require field studies to characterise the leaching and run-off behaviour of some pesticides but guidelines for such studies are not available. The agroclimatic characteristics of sites vary considerably and those selected for monitoring studies should be representative of defined, realistic scenarios, eg average, worst or extreme conditions, in order that environmental risks can be properly evaluated and placed in their true context. Various techniques are available to determine the leaching or run-off behaviour of pesticides in the field. The construction, installation and monitoring strategies will influence the monitoring data obtained. An example of results from a field monitoring programme is used to describe effective monitoring techniques for defining field leaching and run-off. Interpretation of data is aided and placed in context by reference to statistical parameters derived from long term rainfall data.

INTRODUCTION

Field studies to monitor the fate of applied agrochemicals are often required to meet regulatory concerns over the behaviour of a particular chemical/ formulation with regard to its potential impact on the environment. Studies may also be carried out to develop a better understanding of specific processes which determine fate. Pesticide fate in the soil environment depends upon the integrated effects of the processes of sorption, leaching, transformation, degradation, volatilization, erosion and uptake by plants. In order to be able to monitor accurately the fate of any particular pesticide it is essential to have a clear understanding of these controlling factors and how both the soils and climate, the agricultural practices and even the monitoring methods will influence the type and quality of data generated.

SITE SELECTION

In order that a comprehensive environmental risk assessment can be derived from the field study, sites should be established in locations which typically would be used for growing the target crop or where the target pest occurs. The diversity of situations is however extremely large and it would be impractical to carry out field experiments in such a range of risk situations. Several regulatory authorities have therefore stipulated that worst or even extreme case monitoring scenarios should be adopted for field study site selection. The difficulty with this concept is how to interprete and extrapolate study data, which has been

generated from such a restricted situation, to produce a national or even European risk assessment. The BBA guidelines (BBA, 1990) effectively specify an extreme case scenario for lysimeter leaching studies, whereby a sandy soil of low organic carbon content (<1.5%) is required with an annual precipitation of 800mm. For a Western European study this scenario may be too extreme and not necessarily representative, indicated by the fact that this soil/agroclimatic combination represents only 1-2% of arable land in the UK (Fogg *et al.*, 1994). A herbicide used on winter wheat in the UK could, in contrast, be used on approximately 30% of arable land. Drafts of Annexes II and III of the EC Harmonisation Directive 91/414 do not yet detail or stipulate any requirements or scenarios for the location of field studies for leaching or run-off. The use of realistic worst case and realistic average (typical) scenarios have been promoted with regard to UK environmental fate modelling requirements by Craven (1994) and Brown and Hollis (1994). It would be more meaningful if fate and behaviour studies, which are established to satisfy regulatory authority requirements, were carried out in situations which represent the main usage area but with soils and agroclimatic conditions representing a realistic or reasonable worst case scenario. The choice of site will vary acccording to active ingredient and intended use and the conceived potential environmental problem. Its location will be determined by factors such as the suitability of land for the production of the crop, the distribution of the target pest and the climatic range.

The potential areas where a product might be used can be identified by crop suitability assessments. These depend on factors such as soil water availability, accumulated temperature, trafficability of land, relief, average yields and in some cases the market area. Climatic data evaluated would include average annual rainfall total and the maximum potential soil moisture deficit (PSMD), the average field capacity return date, excess winter rainfall, the average monthly rainfall and the average potential monthly soil moisture deficit relative to the intended application times of the pesticide. As an example, the range of average annual rainfall for arable England and Wales is approximately 500mm to 4000mm. Just over a quarter of arable land receives between 600-700mm, whilst 12% of land receives between 1000-1250mm (Bradley, pers. comm.). These rainfall ranges could be considered to represent average and realistic worst cases respectively for leaching/run-off studies.

Within the UK, soil types have been grouped into 29 hydrological classes according to their main pathways and rates of water movement. The system is known as HOST - Hydrology of Soil Types, (Boorman and Hollis, 1990). The percentage of land occupied by each hydrological group has been estimated and each soil series allocated a HOST class. For example, two relevant groups of soils are those with a predominant downward movement to underlying aquifers and those which show rapid lateral flow to surface waters. Selection can be further refined by considering ranges of properties such as organic carbon content, hydraulic conductivity and depth to water table, within the HOST classes using the SEISMIC database (Hollis *et al.*, 1993). Final site selection will require that specific local requirements are met, eg for run-off studies, slope, susceptibility to surface capping, proximity of surface water sources, width and vegetation intensity of headland areas and farming practise. Average slopes for arable agriculture in regional areas of England and Wales are between 1 and 4%, however steeper slopes of between 8 and 14% or greater are cultivated.

Each field site should be subject to a detailed survey (Hodgson, 1974) to characterise the soil, its surface and ground water hydrology, topography and site variability and the soils

should be classified, (Clayden and Hollis, 1984; FAO-UNESCO, 1988). International standards for many aspects of characterising soil quality, sampling or monitoring have recently become available or are in preparation and will provide internationally agreed methodologies for future studies. (ISO TC/190 Soil Quality, available from NNI, Netherlands). Details of previous cropping history, agrochemical applications for at least the previous 5 years and drainage plans should be obtained from the land owner.

MONITORING AND SAMPLING

Environmental fate studies are both costly and time consuming and it is therefore important to have a targeted sampling strategy in order to keep the amount of time spent collecting and analysing samples to a minimum. Soil dissipation studies typically adopt logarithmic sampling, with sampling intensity greater immediately after application. However leaching and run-off processes which transport pesticides are initiated by rainfall and have most impact on water contamination when they occur shortly after application. The continuing impact depends on rainfall characteristics and the persistence and aqueous availability of the pesticide. Sampling to characterise leaching and run-off can be rainfall / SMD trigger-driven, (Williamson and Carter, 1991) and should continue at the discretion of the investigator following interpretation of previous data.

Leaching

Previous methods used for tracing pesticide movement in soils have relied mainly on core sampling, followed by laboratory extraction techniques. The type of sampling equipment and the number of cores required was investigated by Holzwarth *et al.*, (1994), who concluded that variability in concentration is independent of type of corer if the core diameter is >4.5cm and no more than 10 cores (if taken at random) are necessary. Soil analyses from core data will provide essential data on the depth of leaching of the majority of the pesticide. However there are circumstances whereby pesticide can leach from soil profiles with by-passing of the main body of the soil and core data would not necessarily provide evidence of such movement. Detection limits for pesticides in soil samples need to be sufficiently sensitive if they are to be related to the EC maximum admissible concentration for pesticides, ie 0.1µg/l. To achieve this low level of detection large volumes of soil sample can be required and the analytical methodology becomes time consuming and susceptible to contamination. Clark *et al.*, (1990) identified that a major difficulty in studying pesticide movement in the unsaturated zone was the need to obtain large volumes of water for analyses. Extraction of water from the unsaturated zone has been carried out using techniques such as centrifugation and pressure techniques, but these techniques are site destructive and require large volumes of material. To overcome these problems and to enable an earlier insight into the mobility of a pesticide in the field, ceramic cup soil water suction samplers can be used (Eadsforth, 1991).

The suction sampler or tension lysimeter comprises a hollow tube with a porous ceramic cup at the lower end and an arrangement of valves at the upper. The suction sampler can be manufactured to various lengths (depending upon the requirements of the study) and constructed of materials which are likely to cause the least risk of contamination and adsorption. The main components used in the 'inert' suction sampler are fabricated from

stainless steel and PTFE, with the ceramic cup being fitted to the stainless steel tube by means of a threaded collar to facilitate replacement. For studies on nitrate movement and for pesticides with a low Koc (<300) costs can be greatly reduced by using less expensive polymeric materials such as ABS (acrylonitrile butadiene styrene) or PVC (polyvinyl chloride) in the construction of the samplers.

Many researchers have questioned the validity of the porous ceramic cups that have been used as semi-permeable membranes to separate soil and water since their introduction in the early 1900's. Trials have compared the performance of porous ceramics against other materials such as PTFE, cellulose fibres and fritted glass, (Beier and Hansen, 1992; Beier *et al.*, 1992; McGuire *et al.*, 1992; Silkworth and Grigal, 1981). It has been observed that the preparation of the sampling membrane is all-important, since the ceramic cups themselves have been found to contribute excessive amounts of calcium, sodium and potassium to solutions drawn through them, yet adsorb significant amounts of phosphorous (Grover and Lamborn, 1970; Hansen and Harris, 1975). It is not known what the effect of these inorganic molecules might have on pesticides in solution, whilst it is possible that the microbial population of the ceramic pot may cause increased degradation (Lewis *et al.*, 1992). McGuire *et al.*, (1992), working with trace metals, concluded that there were advantages to be gained from using PTFE, fritted-glass or stainless steel even though these material tended to have a more restrictive operational range in relation to the soil water status. The main problem was the influence of adsorption-desorption that was observed with ceramic pots, which could result in sampling error particularly when analysing at the microgram per litre concentration level. Despite these observations suction samplers have been shown to be invaluable tools in pesticide leaching studies, particularly for those pesticide application rates which are exceptionally low, e.g. 8g/ha.

Suction samplers can operate in freely draining or slowly permeable soils even if the water table is above the sampling depth. Sampling from a saturated zone may have a diluting impact on pore water and water table monitoring is essential to aid interpretation. In a soil known to have by-pass flow systems, Hollis and Carter (1990) describe a soil whereby subsequent results showed a bi-modal distribution of pesticide concentrations, which was attributed to sampling water from the soil matrix and from by-pass flow. Earl and Carter (1991) describe the installation procedure using silica flour as a bedding material and bentonite as a sealant. The silica flour ensures contact between the pores within the sampler pot and the surrounding soil matrix. It has been suggested by Lewis *et al.*, (1992) that the silica may in fact impede solute transport, as work carried out comparing bromide concentrations in a soil column with those from the suction samplers indicated different concentration levels. Smith *et al.*, (1990) reported concentrations three to five times lower in the suction samplers. This difference may be attributable to a dilution effect caused by different water status in the silica flour compared to the surrounding soil or sorption by the ceramic cup.

The remainder of the hole is backfilled using a granular bentonite clay up to the base of the top soil, to eliminate any preferential water movement down the sides of the sampler. Top soil can then be used to fill the remainder of the hole. Backfilling with bentonite is an essential procedure, since preferential flow has been shown to occur even within repacked sandy soil material (Williamson and Carter, 1993).

Since the collection of water samples using suction samplers actually depletes soil water, care must be taken to obtain water only when there are known periods of flux or after recharge (Earl and Carter, 1991). Water samples are collected by applying a negative pressure of 0.3 - 0.7 bar to the suction sampler. This causes water within the silica flour, previously in equilibrium with the surrounding soil water and originating from the adjacent soil, to move through the ceramic cup and into the sampler. The sampler should always be evacuated of any water that may have flowed into the cup due to gravity before the vacuum is applied as this standing water may contain unrepresentative concentrations. The rate at which the water moves into the sampler depends on the soil moisture status and the hydraulic gradient. Two hours is typically sufficient, after which the sample can be drawn into a collection vessel, again constructed of an inert material which is unlikely to adsorb the test material.

Cochran et al., (1970) stated that the collection of vastly different volumes of soil water and associated solute concentrations can be due to the heterogeneity of the soil structure, large differences in soil water retention and hydraulic properties. If the applied suction of 0.3 - 0.7 bar is greater than the tension by which the soil solution is held, an artificial hydraulic gradient is established which may result in over-estimates of the solute flux (Perret, 1993). Provided pore water pressures remain at or near field capacity and the sampling time is minimised, the resulting soil water should be representative of that which drains rapidly through the soil profile. The use of a longer extraction time and a lower suction (0.1bar) has been suggested by some authors eg Severson and Grigal (1976), who stated that for a true sample, suction should be applied that is equivalent to the pressure at which the soil solution itself is held. An increase in sampling time was also found similarly to increase the accuracy of sampling. Perrin-Ganier et al., (1994) investigated sample volume and cup size and confirmed the variation of pesticide content in water samples when the cup size was smaller than 50 ml capacity. The presence of soluble organic matter or suspended clay did not influence the system compared to sampling a filtered solution of pesticide.

Targeted sampling is essential since it is most appropriate to sample mobile soil pore water or that draining against gravity. Collection of pore water samples when the soil profile moisture status is not sufficiently wet to sustain significant leaching conditions will significantly affect the hydrological status of the soil around the sampler and may produce data which implies leaching is worse than is actually occurring. Sampling should be carried out when the soil moisture deficit is <40mm (Eadsforth et al., 1991) and an information service like MORECS (Meteorological Office Rainfall Evaporation Calculation System) might be used to trigger sampling. In order to identify potential leaching conditions and soil water/pesticide fluxes the profile soil water content needs to be established. Carter (1991) identified several methods for the in situ measurement of profile water content and soil pore water pressures without the need for destructive sampling. When using instrumentation to identify possible flux conditions it should be remembered that soil is heterogeneous and hydrology can vary considerably for even a closely defined soil type. It is therefore essential to replicate the measurements taken. An area of approximately 0.04 ha, representative of the study field or plot area, is normally used by the authors. The experimental area is usually equipped with three sets of instruments, installed in nests to enable the entire soil profile to be monitored and subsequently sampled, eg Williamson and Carter (1991; 1993). The plot area is enlarged or replicated to accommodate soil dissipation and accumulation studies as required, though this may depend on resources available.

Following the application of the test material in a leaching study, the site should be monitored on both a routine scheduled pattern (Fichter, 1992) as well as in response to rainfall trigger events (Carter, 1991; Earl and Carter, 1991), which are typically represented as rainfall events ≥10mm over a 24 hour period or ≥15mm over a 48 hour period. Continuous rainfall events are sampled according to the length of time after treatment of the site and the quantity of rainfall received. Real time weather data can be obtained from either on-site instrumentation or the local meteorological station, from which a wide range of descriptive statistics can usually be obtained. Rainfall events can be put into context by comparison to statistical averages for the area being studied. For example, a 25.8mm rainfall event over a 24 hour period in the West Midlands is considered statistically to occur twice a year, with an event approaching 52mm having a 10 year return interval. Data on rainfall intensity and duration on an hourly basis can be advantageous for determining the sequence of events which give rise to the initiation of leaching or run-off events.

Run-off

Surface run-off or overland flow occurs intermittently and its occurrence or location in a field situation is often difficult to predict. It is not practical to monitor all potential locations and Williamson and Carter (1993) illustrate a design which has proved to be practical and provided data from sites which were *a priori* determined as likely to produce run-off, ie realistic worst case situations. Similar designs have been adopted by Real *et al.*, (1993) and Kördel and Klöppel (1993). Run-off traps have been designed which permit pesticide partitioning between the solid and liquid phases to be followed under dynamic conditions. The run-off traps are typically placed across the slope of the field and avoid field headlands and tramlines, unless worst/extreme case scenarios are being monitored. The enclosed area behind the run-off trap enables calculation of pesticide losses due to run-off, whilst some designs are attached to flow monitors to enable timing of events to be monitored. Wauchope (1987) has experimented with a range of systems for monitoring run-off, but they are mainly developed for use under semi-controlled conditions. In the context of monitoring field run-off they could perhaps be considered equivalent to a lysimeter being used to characterise field leaching.

Overland flow rarely occurs in the UK when field conditions are drier than field capacity since water infiltrates the soil surface. Pore water pressures can therefore be used to aid the assessment of the likely risk of run-off within the field. Nests of tensiometers can be installed along the slope profile and set up to record when rainfall events occur. Such work was carried out by Turner (1994), in which the effect on pore water pressures over time and depth in response to rainfall events were observed. In a sandy textured soil, water was seen to infiltrate the profile in response to rainfall, with sequential wetting up of the profile as the rainfall input moved through the soil column. Tensiometer data for a contrasting clay soil illustrated clearly the response to rainfall of a finer textured soil. The top 5cm rapidly reached saturation with the water infiltrating the profile down to 25cm. Positive pore water pressures were recorded indicating a perched water table, presumably over a plough layer or other slowly permeable layer, because deeper tensiometers were still recording negative pressures. Under these conditions overland flow typically could occur. Correct interpretation of data obtained from such run-off traps is crucial. Sediment or solute losses only represent the area for which they have been collected from and do not represent the entire experimental area. If a

correction is not made for these other areas, data can be used to indicate extreme worst case scenarios for an entire field.

EXAMPLES OF DATA

Figure 1 illustrates data on pore water pressures monitored using tensiometers in a clay loam soil.

FIGURE 1. Mean pore water pressures in a clay loam soil.
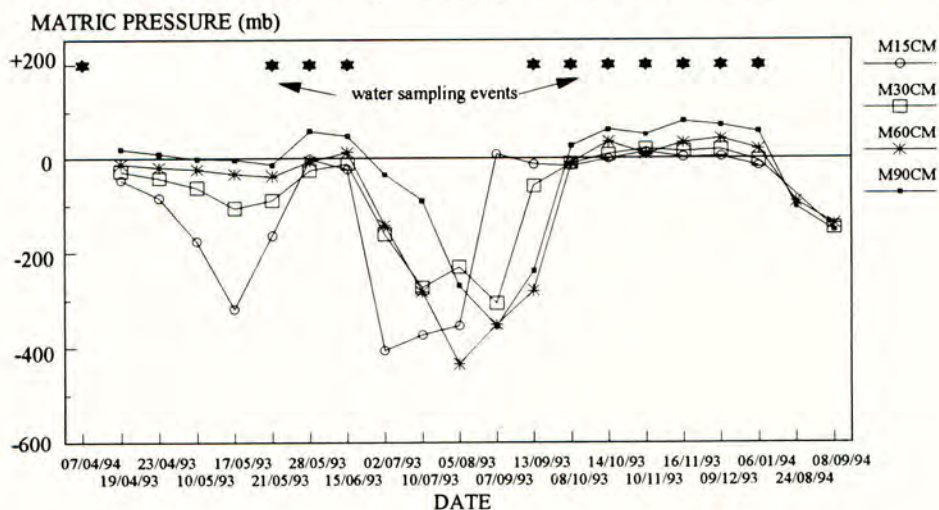
The experimental site was established in April to enable the antecendent conditions to be monitored and for pre-spray (control) samples to be obtained. This procedure is not always possible due to cultivation and application constraints. A delayed herbicide application was made on 10/05/93 following a particularly wet spring. Application was made when ground condition permitted agricultural machinery to travel. Following application the profile drained, with the top soil pore water pressures showing a typical response to the effects of evapotranspiration. Significant rainfall almost immediately after application caused a late spring return to field capacity with a predominant downward flux of soil water being identified by tensiometer and neutron probe data. Soil water leachate sampling from ceramic pot suction samplers, (installed at 25, 40 and 80cm depths with three replicates at each depth), was targeted at this point. Subsequent analysis of water samples both from the suction samplers and drain outflows showed there to be concentrations of up to 200µg/l measured at all sampling depths. In contrast, analyses of soil dissipation in cores from day 0 up to 180 days after treatment suggested that no pesticide had leached beyond 10cm depth. No run-off was observed initially due to the advanced growth stage of the crop, which intercepted the rainfall and infiltration took place. A summer deficit period then developed and the top soil began to dry. Pore water pressures did not however reach typical summer values due to the late return

to field capacity. The site was cultivated after harvest and drilled with a following crop. Mid-September saw an early autumn return to field capacity with water sampling again being targeted at this point. Measured pesticide concentrations indicated a second flush of pesticide, with a maximum of 25µg/l measured in soil water from 80cm depth. Concentrations gradually declined in the soil water throughout the profile but were still detectable 8 months after application. The entire profile was at or close to saturation from early October through to December with a water table detected at 20cm depth. Surface run-off within the field occurred on three occasions as the bare, cultivated soil, high incident rainfall and proximity of the water table were conducive to run-off from the predetermined sites. Concentrations of pesticide were low (maximum concentration 17µg/l) because the topsoil had been cultivated since application and residues were now distributed throughout the topsoil. By this time the aqueous availability of the pesticide was also low in comparison to the spring period following application.

The site characterisation, hydrological monitoring and sampling strategy enabled a comprehensive assessment of the fate of the pesticide in this soil type. Data was used to validate model predictions of fate and subsequently to provide a means of determining fate in a range of soil types. Data were used by the sponsor to identify leaching and run-off of the pesticide under agroclimatic conditions typical for the use of the product and the target crop. Rainfall events which generated leaching or run-off were classified according their statistical frequency to indicate whether conditions were average, worst or extreme case scenarios.

CONCLUSION

Field data on soil properties and water regime are essential when interpreting analytical data produced during a fate and behaviour study. Field studies are now being requested by regulatory authorities as alternative second and third level studies, following results from lysimeter and laboratory studies, in order to assess the impact on water quality under normal use conditions. A targeted sampling regime is essential, because the analytical costs can be 29% greater than for a comparable lysimeter study, due to the additional number of samples generated and the more costly analytical procedures for unlabelled material (Fogg et al., 1994). The site specific data generated can provide the essential validation data for subsequent modelling studies. Predicted data will allow extrapolation to a range of use scenarios, with the possible result that extensive monitoring need not be carried out in alternative areas of use.

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MONITORING OF PESTICIDES IN SUBSURFACE AND SURFACE WATER WITHIN AN AGRICULTURAL CATCHMENT IN SOUTHERN SWEDEN

J. KREUGER

Swedish University of Agricultural Sciences, Div. Water Quality Management, Dept. Soil Sciences, P.O. Box 7072, S-750 07 Uppsala, Sweden

ABSTRACT

A catchment in the southernmost part of Sweden was selected for intensive monitoring of pesticide occurrence in surface water. Information on farm management practices within this area was collected annually and most of approximately 40 pesticides used were included in the analytical procedures. Results showed large fluctuations in pesticide concentrations from day to day, with the highest concentrations occurring at the time of spraying, or later in the season associated with storm flow events. During the first three years of investigation a total of twenty-five different pesticides were detected in surface water leaving the catchment. Many of the pesticides were found over several months and some were found before the spraying season started. Transport calculations show that between 0.01-0.9% of an applied pesticide was transported in surface water leaving the catchment area.

INTRODUCTION

Monitoring programmes throughout the Nordic countries during the past eight years have detected 41 different pesticides (including 28 herbicides, 7 insecticides and 6 fungicides) occurring in surface waters in Denmark, Finland, Norway and Sweden, (Lundbergh *et al.*, 1994). For adequate exposure assessment, as a part of risk evaluation, good quality data is needed on pesticide exposure patterns and characteristics. The ecological effects of pesticides on flora and fauna in surface waters are dependent on both peak concentrations and the duration of exposure. The objective in many of the above monitoring studies has been to determine pesticide concentrations in surface waters on single occasions. This is inadequate for assessing the ecological risks posed by pesticides in surface waters. As a basis for exposure assessment and regulatory pollution control measurements, improved monitoring strategies are desirable. There is also a great need to increase our knowledge of transport pathways within a watershed, including processes (spills, runoff, leaching, drift, etc.) influencing stream water quality, to produce better guidance on minimising pesticide loss to water.

The overall objective of this study was to monitor the occurrence, temporal distribution and mass transport of pesticides to stream water from an intensively cultivated agricultural catchment.

MATERIAL AND METHODS

Catchment description

The Vemmenhög catchment is situated in the far south of Sweden, on the south-western plain of Skåne (Scania county), with undulating topography and glacial till-derived soils rich in chalk, crystalline rock and shale. The clay content of the till varies between 10-18%. The total thickness of the Quaternary deposits is 60-120 metres (Daniel, 1992). The catchment has an area of 8.55 km^2 consisting of 95% arable land, predominantly sandy loam in texture. Tile drainage systems are frequent within the area, with drainage water having a pH-value in

the range of 7.5-8.0. In the upper part of the catchment stream water is channelled through a large culvert. Water samples taken at the outlet of the culvert (site UT10) provide a measure of concentrations in drainage and runoff leaving fields and include losses from areas where pesticides are handled. At the discharge from the catchment (site LU12) the water has flowed 1.1 km from the culvert outlet. Samples taken at this site provide a measure of exposure not only to runoff and leaching, but also to drift, sedimentation, degradation and possible filling and washing of spraying equipment directly in the stream.

Agricultural practice in the watershed is comprised of a 4-year rotation with winter rape, winter wheat, sugar beet and spring barley on about 80 % of the area and with spring wheat, peas, oats, grass leys, winter barley, rye and spring rape on the remaining area. The total amount of pesticide applied within the catchment each year has been on average 1500 kg AI, with 80% applied during spring/early summer and 20% in the autumn. The pesticide usage during spring/early summer is dominated by herbicide applications (85%), but with the remainder made up of fungicides (12%), insecticides (2%) and growth regulators (1%). Autumn application is dominated by herbicides (99%). About 40 different AI´s are used annually, but with only 10 of these accounting for 85% of total weight applied; 80-90% of pesticides used (by weight) were included in the analyses.

Measurements

Water outflow from the catchment area was continuously recorded by a water level gauge situated 200 m down stream from sampling location LU12. In April 1991 a Campbell datalogger was installed at sampling location LU12 to record water flow, using a submerged probe. Culvert flow rates at UT10 were measured using a 90-degree V-notch weir and an ISCO model 3210 ultrasonic sensor, starting in April 1993. Rainfall was recorded by two gauges within the catchment and at an official meteorological station located 6 km to the north-east.

Water samples were collected May-September, starting in 1990, using programmable automatic samplers (ISCO models 2700, 2700R and 3700FR), except at site UT10 where manual grab sampling during May-June was used during the first two years (1990-1991). With the automatic samplers, time paced samples were taken at daily or weekly intervals, each sample being a composite of sub-samples taken at 10-minute or houly intervals respectively. Between October 1992 and April 1993 additional sampling was carried out at UT10 to study pesticide transport during the winter period. To inhibit microbial degradation of the pesticides dichloromethane was added to the sample bottle in advance, plus distilled water to prevent evaporation losses of the dichloromethane. After completion of the sampling programme the samples were delivered to the laboratory within 48 hours and extracted within 24 hours of delivery.

Information on pesticide usage on a field scale (types of pesticide, amounts and application dates) and handling was collected annually from the 35 farmers operating within the area. Only one farm (2% of the area) did not participate. Non-farming residents within the catchment area were also interviewed about possible pesticide usage.

Analytical methods

Unfiltered water samples were analysed by two different procedures, the phenoxy acid method and the multiresidue method. In the former, phenoxy acids and related compounds were hydrolysed with alkali for one hour at 100°C. After acidification the acids were extracted with dichloromethane. Extractive alkylation with pentafluorobensylbromide and gas chromatography were conducted, as described by Åkerblom et al., (1990). Confirmation was by gas chromatography and mass spectrometry (GC-MS), with a limit of detection in the range of 0.05-0.1 µg/l. Pesticides analysed by this method were bentazone, clopyralid, 2,4-D, dichlorprop, fluroxypyr, flamprop-M, ioxynil, MCPA and mecoprop.

With the multiresidue method semi-polar and non-polar pesticides were extracted with dichloromethane. Hydrophobic gel permeation clean-up and capillary column gas chromatography with selective detectors (GC-NP and GC-EC) were conducted according to Åkerblom *et al.*, (1990) and Andersson and Ohlin, (1986). Confirmation was by GC-MS, with a limit of detection in the range of 0.1-0.5 µg/l.

Quality assurance

The possible loss of unstable compounds during the collection and transport procedure was evaluated in two separate studies, using 14 pesticides representing different intrinsic properties. In the first study spiked surface water samples were run through the ISCO model 2700R automatic water sampler in the field, testing the stability during the collection procedure (i.e. passage through the tubes of the sampling equipment) and during storage in the sampler (Kreuger, 1992). In the second study pesticide stability was tested under different storage conditions, (storage time, storage temperature and following dichloromethane addition), (Kreuger, 1994). The general conclusion of these studies was that the sampling and storage procedures used were adequate, with recoveries within the normal variance of the analytical procedures.

RESULTS AND DISCUSSION

Precipitation and discharge of water from the area showed great fluctuations between years, with high flow during the cold and rainy spring and early summer of 1991 and extremely low flow in 1992 when no precipitation fell for two months. 1990 was closer to the average, but with thunderstorms in June and July giving sudden high flow events.

In 1990 samples were collected daily during the first month of the investigation, (Figure 1). Results showed large fluctuations in pesticide concentration between days. The highest concentrations occurred during spraying in May without any large increase in discharge, indicating inputs from pesticide handling, (spills). Increases in concentration also occurred later in the season associated with storm flow events, indicating contributions from runoff and preferential flow. Surface runoff rarely occurs in this area due to the permeability of the soils, except in extreme situations with long periods of intense rainfall. In other investigations, subsurface flow through macropores has been shown to be a possible mechanism during storm flow, (Wilson *et al.*, 1990). Richard and Steenhuis, (1988),

FIGURE 1. Water flow and total pesticide concentration in discharge from the catchment in 1990.
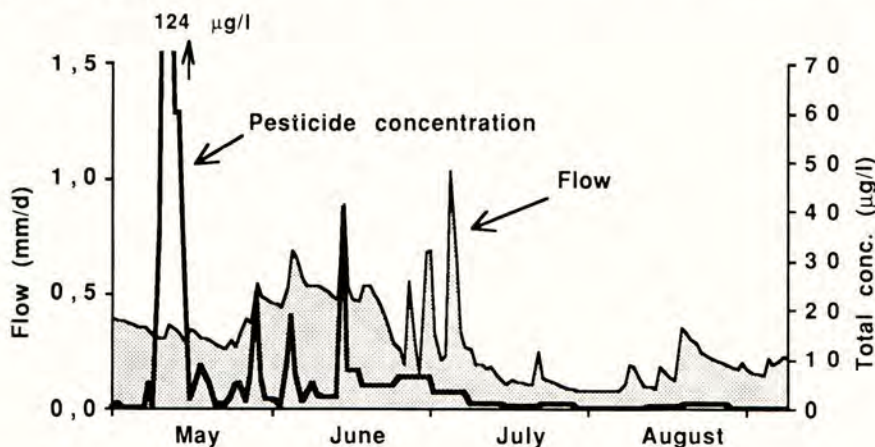
demonstrated the importance of macropores on the concentration of a solute in tile drains, with a travel time of the solute to the tile drains of 3 to 4 hours.

In order to study storm flow in more detail, samples were taken during an intense rainfall event on 15 June 1990. The event started at noon and within less than two hours 16 mm of precipitation had fallen. The first sample was taken as a grab sample at 14.30 when water flow was at its peak. This was followed by three composite samples collected at hourly intervals by the automatic water sampler, with 5 minute increments between the sub-samples, during the descending part of the hydrograph. Finally the automatic sampler collected a composite sample over the following 60 hours. To support the pesticide data, grab samples for analysis of nutrients and other constituents were also collected during the same period.

The results showed a very rapid increase and decrease in pesticide concentrations during the storm flow event (Figure 2). Peak concentrations for several of the pesticides were found in the second sample taken during the early stage of the descending hydrograph, 2.5-3.5 hours after the start of the rain event. A slightly different profile was shown by the phenoxy acids MCPA and dichlorprop with peak concentrations later in the hydrograph. The pesticide findings correlated well with the concentrations found for the nutrients potassium, nitrogen and phosphorus, showing maximum concentrations at the same time as most pesticides. In contrast, the reverse situation was found for other constituents, like sulphur, calcium, magnesium, sodium and bicarbonate, all of which showed a marked decrease in concentration during peak flow. A different response profile to the storm flow event was shown by bentazone and metazachlor, both of which did not show any change in concentration during peak flow, (bentazone 0.03-0.04 µg/l and metazachlor 0.1 µg/l). Both pesticides showed increased concentrations, however, in the last sample representing the end of the hydrograph and early base flow.

These findings indicate that pesticides and nutrients with peak concentrations coinciding with peak flow are easily translocated during a storm event with little interaction with the soil matrix and are either dissolved in the soil solution or bound to soil particles. Other constituents, e.g. calcium, are not readily transported and show a dilution effect. The slow response to storm flow for both bentazone and metazachlor could indicate that they were present in the soil solution in deeper soil layers and therefore not readily available during the initial stage of the subsurface flow process. These two chemicals have also been shown to persist in stream water for long periods at low concentrations and between seasons. Atrazine and terbuthylazine are only used in this area for occasional weed control on farmyards (1-3 farms per year per substance). The quick response of these two compounds during storm flow also demonstrates the influence of runoff from non-crop application.

A total of twenty-five pesticides were detected in stream water leaving the catchment area (LU12) throughout the sampling season (May-September) during the first three years of investigation. Many of the pesticides were found in water (at varying concentrations) over several months. MCPA, dichlorprop and metamitron were detected in the highest concentrations (40 µg/l, 20 µg/l and 45 µg/l respectively). Bentazone was the most frequently detected pesticide, followed by dichlorprop, terbuthylazine, MCPA, mecoprop and metazachlor. The results indicate an annual cycle of pesticides entering the stream water during the period of application, followed by a series of flushing events during storm flow periods. In 1992 the sampling period was extended into winter and continued until April 1993. Small amounts of pesticides (<2µg/l total concentration) were detected throughout the winter season. Pesticides were found at higher concentrations and with a longer duration in culvert water (UT10) than in water from the open part of the stream (LU12), perhaps illustrating that drift did not contribute to pesticide levels in the stream. Pesticides in the open part of the stream would also be subject to degradation, sedimentation and dilution by ground water inflow during base flow conditions.

FIGURE 2. Water flow and concentrations of nutrients (mg/l), suspended solids (mg/l) and pesticides (µg/l) at catchment outlet (LU12) during a storm flow event in mid-June 1990.

June

June
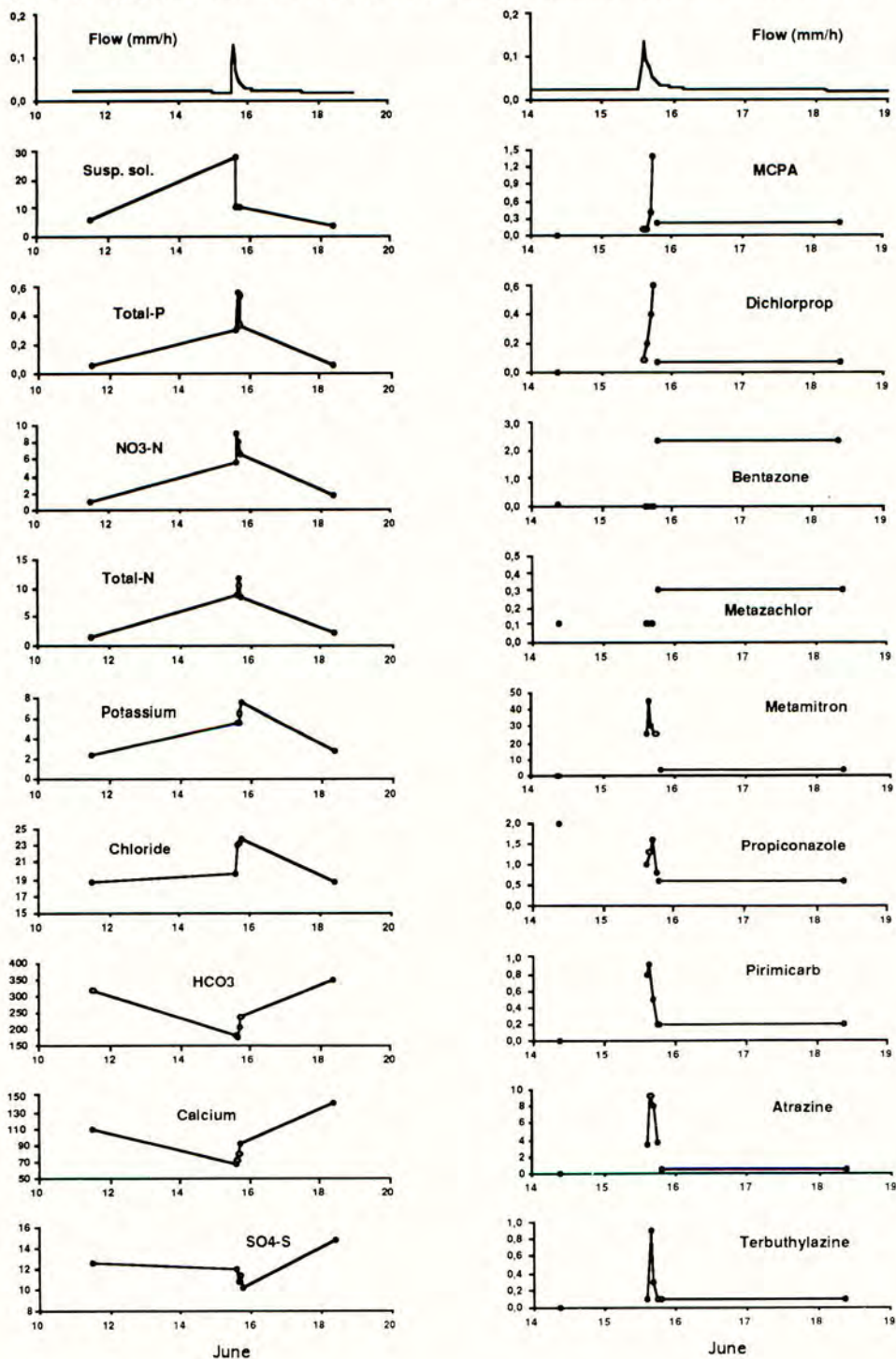
Suspended sediment samples and sediment cores were also collected to study the distribution of pesticides between the different matrices. Results showed that pesticides detected in the sediments mainly consisted of insecticides and fungicides. DDT was only found in the sediment cores (0-10 cm) and not in the suspended sediment samples. The fungicide `Tilt Top´ (fenpropimorph 75% and propiconazole 25%) is extensively used in the area. The less water soluble fenpropimorph was found at lower concentrations in water samples than propiconazole, but at higher concentrations in sediment samples. These findings illustrate the importance of accounting for pesticide distribution between the different matrices when setting up monitoring programmes.

Transport calculations show that between 0.01-0.9% of the different pesticides applied within the area were transported in the surface water leaving the watershed, with the non-crop, farmyard applied pesticides atrazine and terbuthylazine being transported in the largest quantities. This correlates well with estimations made in a study by Gomme et al., (1991) who found that about 0.1% of the pesticides applied left the catchment via the river. The amount of atrazine transported from the same area was one order of magnitude higher than other pesticides.

ACKNOWLEDGEMENTS

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AN ASSESSMENT OF THE BEHAVIOUR OF SELECTED PESTICIDES AT ADAS ROSEMAUND

A. Turnbull, R. Harrison
Institute of Public and Environmental Health, University of Birmingham, Edgbaston, Birmingham B15 2TT

A. Di Guardo, D. Mackay
Institute for Environmental Studies, University of Toronto, Toronto, Ontario M5S 1A4, Canada

D. Calamari
Institute of Agricultural Entomology, University of Milan, Via Celoria 2, 20133 Milano, Italy

ABSTRACT

Three pesticides applied to fields within an isolated, surface water dominated catchment at ADAS Rosemaund have been measured in runoff during rain events. The levels detected have been compared to a fugacity-based mathematical model which predicts mean runoff concentrations leaving the catchment. The experimental measurements clearly indicate the value and the limitations of using predictive models in the real environment.

INTRODUCTION

The movement of pesticides to surface waters has particular significance for sensitive aquatic ecosystems and for human drinking water supplies. Potentially, high concentrations can reach surface waters near agricultural land under normal agricultural practice. High levels during isolated runoff events may suppress species diversity in some situations. Contamination of drinking water supplies above European Union limits have also been reported (Lees and McVeigh, 1988). Understanding of the fate and behaviour of applied pesticides continues to attract considerable research, within both government and the agrochemical industry.

The potential for transport from agricultural fields to surface waters will depend on the physical and chemical properties of individual compounds. In this study, trifluralin, deltamethrin and simazine, reflecting commonly applied and widely different compounds, have been measured in surface waters at ADAS Rosemaund after autumn applications. The measured concentrations have been compared to levels predicted by the SoilFug mathematical model, (Di Guardo et al., 1994a).

EXPERIMENTAL METHODOLOGY

ADAS Rosemaund, situated in the west of England, was particularly suitable for this research as the farm boundaries contain the majority of a small catchment of the upper river

Lugg river basin. The silty clay soils are subject to considerable cracking during dry summer weather and rainfall is known to move rapidly to surface waters via macropores which extend to the full depth of the field drainage system, (Carter, 1991). With an impermeable geology of silt and mudstones, the site represents a reasonable worst case scenario for the movement of agrochemicals to surface waters. Application of the compounds under investigation in this paper took place during the 1992-93 cropping season and were applied to fields within the upper 33.7 hectares of the catchment. A single stream flows from the area with individual field drains, representing smaller portions of the catchment, feeding this stream. Pesticide concentrations were measured on a number of occasions in the stream and at a field drain outfall, by a series of 24 samples taken automatically at 30 minute intervals. Sample collection was triggered by rising runoff flow induced by rainfall. The site and experimental design have been described in more detail elsewhere, (Williams *et al.*, 1994). Application details for the selected compounds and some of their relevant physical and chemical properties are listed in Table 1.

TABLE 1. Details of applied compounds.

	Date of application	Application area (ha)	Application rate (g/ha)	Solubility (mg/l)	Vapour pressure (Pa)	K_{oc}	Log K_{ow}	Half life (days)
trifluralin	9/11/92	5	1104	0.5 [1]	0.0147 [1]	8000 [2]	5.07 [1]	60 [2]
deltamethrin	15/12/92	5	5	0.002 [1]	0.002 [1]	110700 [5]	5.43 [1]	30 [3]
simazine	15/12/92	4	1150	5 [2]	8.1×10^{-7} [2]	130 [2]	1.9 [4]	60 [2]

(1) Worthing & Hance, 1991 (2) Wauchope *et al.*, 1992 (3) Anon., 1982
(4) Suntio *et al.*, 1988 (5) calculated from Karickhoff, 1981

Analysis was carried out at the University of Birmingham using liquid extraction of unfiltered one litre water samples into hexane. The instruments used were Hewlett Packard gas chromatographs linked to either an electron capture detector or a bench-top mass selective detector.

Rainfall and stream flow rate at both sites were electronically recorded on an hourly basis throughout the period. The resultant plot of stream flow rate leaving the top 33.7 hectares, Figure 1, reveals the sharp hydrograph peaks resulting from rainfall.

FIGURE 1. Runoff hydrograph from top catchment at Rosemaund during 1992-93.
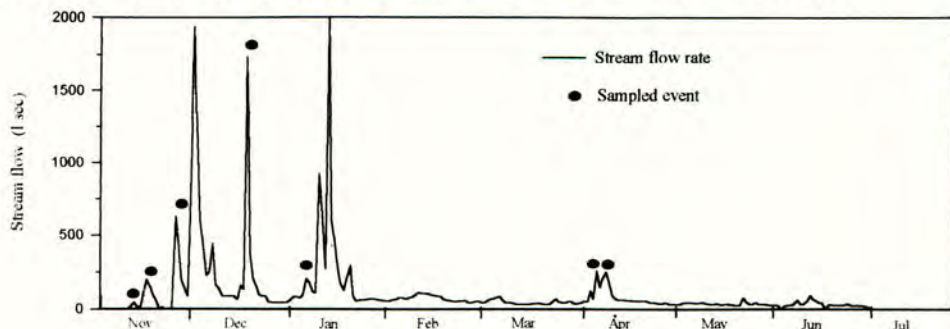
Sampled runoff events are marked in Figure 1, although the final two events were measured only at the field drain site, flowing from 5.96 hectares of the upper catchment. An estimated 2 hectares of this area received application of the compounds.

RESULTS

Some mean concentrations for each compound are given in Table 2, in which samples below the detection limit have been included in the calculations as zero.

TABLE 2.   Mean concentrations in the stream or field drain during runoff events (ng/l)

	11/11/92	15/11/92	26/11/92	16/12/92[†]	18/12/92	5/1/92	7/4/93*	9/4/93*
trifluralin	520	207	67	180	177	51	62	48
deltamethrin	1.3	0.3	3.2	80	163	1.8	3.7	0.8
simazine	0	2.3	13	900	448	1660	7.6	39

† estimated from single manual sample during hydrograph peak

* sampled at field drain site

Trifluralin

Trifluralin was detected in both the stream and the field drain through until April 1993, when levels were still occasionally above 100 ng/l. Concentrations peaked at around 1000 ng/l in the stream on 11th November and also 18th December, with levels at the field drain outfall reaching 3000 ng/l on 11th November. A typical plot of stream concentration with rainfall and stream flow for the mid-December period is illustrated in Figure 2. Initial rainfall on the 16th December produced a small hydrograph, when a single measurement for trifluralin was made during peak flow. The first series of samples, collected on 17 December after the first hydrograph peak, show much lower levels compared to the series of samples collected during the second large runoff event of the 18th December. The autosampler had been started manually on 17 December, due to failure during peak flow the day before.

FIGURE 2.   Trifluralin in stream flow during December 1992.

89
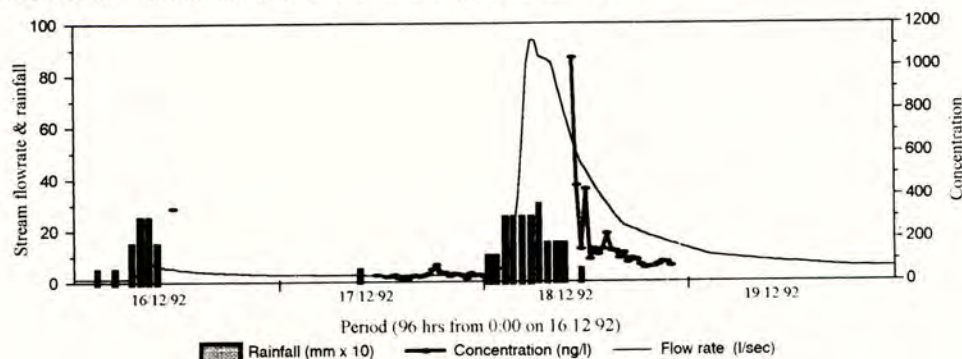
Deltamethrin

This compound was applied at the low rate of 5 g/ha and was the least volatile and least soluble pesticide considered. Because of this, it was not expected that significant quantities would be detected in the stream. However, concentrations of 250 and 850 ng/l were detected in the stream and field drain respectively shortly after application. It is suspected that soil conditions on 16th December were such that surface particulates with adsorbed deltamethrin were carried rapidly by rainfall through macropores into the field drains and through to the stream. Liquid extraction of whole water samples was, therefore, essential to detect deltamethrin in these samples. Within a few hours, levels had decreased to the low ng/l. Two days later a further 20 mm of rainfall again produced high concentrations in the stream, this time approaching a maximum of 2000 ng/l although again, levels declined rapidly and never exceeded 20 ng/l for the rest of the experiment. The occurrence of low levels prior to application would reflect the relatively frequent use of deltamethrin at ADAS Rosemaund.

Simazine

Simazine was applied at the same time as deltamethrin and was found in the stream at levels up to 1500 ng/l during the hydrograph peak of mid December, one day after application. The highest concentrations, however, were observed in early January at over 6000 ng/l and levels continued to exceed 100 ng/l during April 1994. As with deltamethrin, low levels of simazine were present in the drainage prior to application.

MODELLING

The SoilFug model, (Di Guardo *et al.*, 1994a) has been employed to predict the concentration of these pesticides in surface water. SoilFug is an unsteady-state fugacity model that performs the calculation for specific periods of time (i.e. the rain events). It has been previously applied to calculate the predicted concentrations of ten pesticides at ADAS Rosemaund, generally giving results within an order of magnitude of the measured results, (Di Guardo *et al.*, 1994b). The environmental scenario adopted for the simulation is the same as in the above mentioned article: the selected soil depth was 0.5 m; the air and water volume fractions in soil at field capacity were 0.09 and 0.385 respectively. The organic carbon volume fraction was 0.0136. Ten rain events were selected for the trifluralin simulation (from 11/11/92 to 9/4/93), but only five for simazine and deltamethrin, because the pesticides were applied at a later date (15/12/92). The predicted and the correspondent measured concentrations in surface water are reported in Table 3.

DISCUSSION

The simulation results are close to the measured concentrations for trifluralin, differing by a factor of 2 to 3, as indicated in Figure 3. The aim of the SoilFug model is to predict average concentrations during an event to within an order of magnitude of the measured results. The model overestimated in the case of simazine, by slightly more than an order of magnitude. The Koc values in Table 3 were used for trifluralin and simazine, but the value

given was calculated from the Kow according to Karikchoff (1981), in the case of deltamethrin, as no measured Koc was available at the time.

TABLE 3. Comparison of measured and modelled concentrations in runoff (ng/l)

Rain event	date	Trifluralin		Deltamethrin		Simazine	
		Measured	Calculated	Measured	Calculated	Measured	Calculated
1	11/11/92	520	252	-	-	-	-
2	14-15/11/92	207	239	-	-	-	-
3	25-26/11/92	67	208	-	-	-	-
4	1-3/12/92	-	199	-	-	-	-
5	6/12/92	-	189	-	-	-	-
6	16/12/92	180*	167	80*	8.2×10^{-2}	900*	11000
7	18/12/92	177	164	163	7.9×10^{-2}	448	10700
8	4-6/1/93	51	132	1.5	5.1×10^{-2}	1660	8600
9	10-15/1/93	-	114	-	3.8×10^{-2}	-	7160
10	6-9/4/93	15	45	-	5.3×10^{-3}	22	2690

* estimated mean concentration of event from single sample

Predictions for deltamethrin show a very different behaviour. In this case the predicted concentrations are 2 to 4 orders of magnitude different from the measured results. Due to its low solubility, deltamethrin would not be expected to leach to any significant extent and this discrepancy may partly be due to the partition coefficient in soil being much less than the one deduced from the Kow, which will require further investigation. However, bypass flow through macropores, as discussed earlier, could also partially explain these results. Preliminary calculations for two additional compounds applied at Rosemaund, fenpropimorph and chlorpyrifos (not reported here), provide estimated concentrations within a factor of 2 of measured levels.

FIGURE 3   Measured and predicted trifluralin levels in Rosemaund runoff.
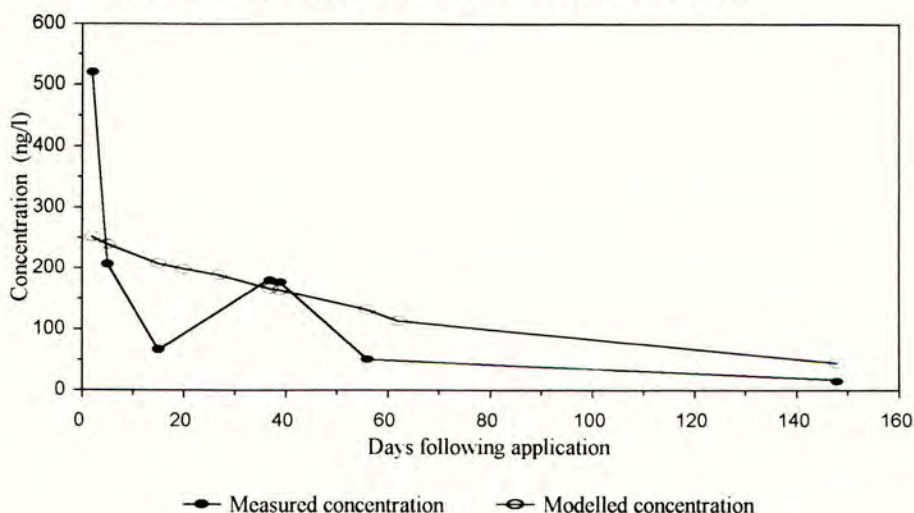
The SoilFug model can, therefore, adequately predict (within an order of magnitude) worst case runoff concentrations of certain groups of compounds. However, experimental data clearly reflect the more complex influences which limit the range of compounds for which the model works. Further development will attempt to identify improvements in the scope of the model.

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EFFECTS OF PREFERENTIAL FLOW UPON THE MOVEMENT OF PESTICIDES AND A CONSERVATIVE TRACER FROM A HEAVY CLAY SOIL

C.D. BROWN, D.A. ROSE, J.K. SYERS

Department of Agricultural and Environmental Sciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU

R.A. HODGKINSON

ADAS, Anstey Hall, Trumpington, Cambridge, CB2 2LF

ABSTRACT

A field experiment investigated losses of pesticides to surface waters from a clay loam soil in which preferential flow can be a dominant process. A bromide tracer was applied to the site to compare the movement of a non-sorbed solute with that of various pesticides. Losses of pesticides to surface waters via drainflow or surface-layer flow were greatest when interaction between moving soil water and the bulk soil was minimised by preferential or surface lateral flow. Preferential flow also affected the transport of bromide, but later in the season was observed to decrease concentrations of bromide in flow by decreasing interaction between solute residues and water. The breakthrough curve for bromide suggested that matrix flow is also significant for solute transport in this heavy clay soil.

INTRODUCTION

A field experiment was conducted at Cockle Park, Northumberland, on a clay loam soil cropped with winter wheat, to investigate the effects of drainage and timing of application upon losses of pesticides to surface waters, (Brown et al., 1995). During the first season of study (1989/90), several pesticides were applied at normal agricultural rates and their loss in surface-layer flow and drainflow monitored. In accordance with findings from other studies (Kladivko et al., 1991; Harris et al., 1993), pesticides with a wide range of physico-chemical properties were found in both types of flow shortly after application, indicating that preferential flow through macropores was an important process both for soil hydrology and for solute movement. In order to further investigate the influence of preferential flow upon water and solute movement in this soil, a bromide tracer was applied to the site in autumn 1990/91 and its fate was compared to that of four contrasting pesticides applied over the same period. This paper will compare mechanisms of transport through soil for a range of solutes retained by the soil to differing degrees.

MATERIALS AND METHODS

Field work was conducted on North Field at Cockle Park farm, approximately 30 km north of Newcastle upon Tyne. A detailed description of the site and the experimental

methodology has been given by Brown *et al.* (1995). The soil is a clay loam (26% sand, 40% silt and 34% clay at 500 mm depth) pelostagnogley of the Dunkeswick series, derived from glacial till. The soil has a sharp transition between the finely-structured, permeable topsoil and the massively prismatic, only slowly-permeable subsoil and requires artificial drainage to allow consistent arable cultivation. The characteristics of any drainage system installed will have a major effect upon site hydrology and solute transport. The site slopes gently at about 2% and there is also considerable potential for lateral movement of water and associated solutes either over the soil surface or through the top layers of the soil.

Three hydrologically isolated plots, each of 0.25 ha, were monitored during the study. Two were mole-drained (moles installed 2 m apart at a depth of 550 mm) and used to investigate the effect of timing of application upon pesticide fate. The third was an undrained control, to allow the effect of drainage upon pesticide fate to be studied. Only the undrained control (plot A) and one of the mole-drained plots (plot B), both receiving pesticide inputs in autumn, will be considered in this paper. The plots were instrumented to allow drainflow and surface-layer flow (collected to a depth of 300 mm) to be monitored at 10-minute intervals. A winter wheat crop (var. Mercia) was sown in the autumn of 1990 and a range of pesticides plus the bromide tracer were applied to the site. Subsamples of flow were collected automatically according to changes in rate of flow and were analysed for residues of pesticides and bromide. Bromide was determined colorimetrically as described by Greenberg *et al.* (1985).

TABLE 1. Summary of applications and properties for pesticides and bromide.

Property	Bromide	Isoproturon	Mecoprop	Trifluralin
Application rate (kg Al/ha)	67.2	2.50	2.40	0.96
Application date	04/12/90	13/11/90	13/11/90	13/11/90
Topsoil K_d (ml/g)	-0.04	0.81	0.31[†]	199
Topsoil retardation factor	0.91	3.02	1.77	499
Subsoil K_d (ml/g)	-0.11	0.18	0.05[†]	29.3
Subsoil retardation factor	0.65	1.61	1.18	98.6
Half-life in soil (d)[‡]	-	30	10	60

[†] K_d calculated from: $\log K_d = 0.52 \log K_{ow} + 0.62 + \log (\%OM/100)$

[‡] Representative value derived from the literature

Table 1 summarises the applications of pesticide and bromide made to the site during the 1990/91 season as well as selected properties of the solutes. Isoproturon, mecoprop and trifluralin were applied as a tank mix of commercially formulated material in mid-November 1990 and bromide was applied as a spray around three weeks later by dissolving 50 kg KBr in 200 l water. In order to characterise sorption/exclusion of pesticides and bromide to this soil, batch-suspension studies were carried out as described by Brown *et al.* (1995) on topsoil (5-12 cm depth) and subsoil (40-50 cm depth) samples from the site. K_d values derived by fitting linear sorption isotherms are given in Table 1. In addition, retardation factors (R_f) were calculated according to the equation:

$$R_f = 1 + (\rho_b . K_d / \theta_v)$$

where ρ_b is soil bulk density (g/cm^3) and θ_v is the volumetric water content of the soil (cm^3/cm^3) for which representative winter values for the Dunkeswick soil were used. Solutes which are retained by the soil (i.e. positive values of K_d, $R_f > 1$) will move at a retarded velocity V_1 compared to the velocity of the soil solution, V according to the relationship, $V_1 = V/R_f$. Conversely, solutes which are excluded by the soil (i.e. negative values of K_d, $R_f < 1$) are predicted to be transported at a greater effective velocity than expected in the absence of exclusion.

RESULTS AND DISCUSSION

Results given in Table 1 indicated that bromide was excluded by the Dunkeswick soil, with the effect particularly apparent in the clay-rich subsoil. By contrast, the pesticides were retained by the soil to varying degrees with sorption following the ranking mecoprop < isoproturon < trifluralin. Bromide was an excellent tracer for water movement at the site (see Figure 1). Maximum concentrations of bromide observed in water leaving the site were similar for all types of flow (36.4 mg/l in mole drainflow from plot B and 34.9 and 26.4 mg/l in surface-layer flow from plots A and B, respectively).

FIGURE 1. Total losses of water and bromide in surface-layer flow (SLF) and drainflow (DF) from plots A and B during the 1990/91 season.
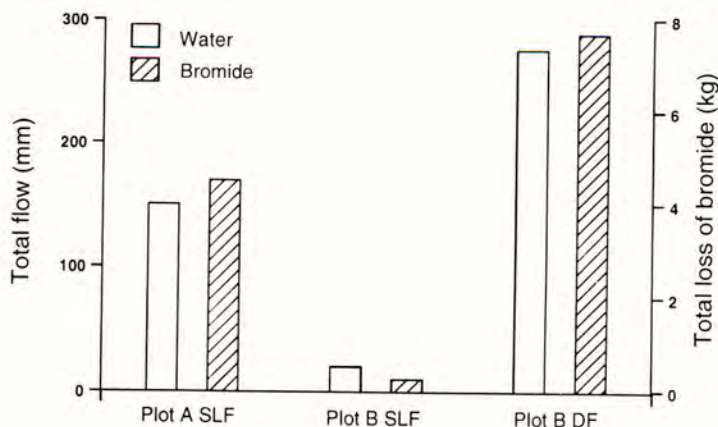
The pattern of maximum concentrations of pesticides in flow was very different from that of bromide. Maxima for pesticides in surface-layer flow observed during autumn/winter were around 10 times larger than those observed in drainflow, because of greater interaction of surface-layer flow with pesticide residues concentrated in the top layers of the soil (e.g., for isoproturon, maxima were 4.2 µg/l in drainflow from plot B and 39.2 and 35.3 µg/l in surface-layer flow from plots A and B, respectively). These much higher concentrations in surface-layer flow meant that total losses of pesticide from the undrained control were larger than those from the mole-drained plot because there was more surface-layer flow from the former.

Thus effective drainage may be proposed as a management practice for such soils to decrease total amounts of pesticides moving to surface waters. An ideal system for pesticides would decrease surface-layer flow as much as possible, whilst maximising the contact between the soil and water moving down to the drains. Results for bromide indicate that best management practices for non-sorbed solutes such as nitrate may be somewhat different.

Water flow in heavy clay soils similar to the one at Cockle Park can be conceptually divided into preferential flow, that which effectively bypasses the main soil body and matrix flow where interaction between soil and soil water is much greater. Clearly, however, there is a continuous spectrum between the two types of flow and no clear dividing line exists. The relative importance of preferential and matrix flow to solute transport differed according to the degree of sorption of the solute to soil. Thus, for trifluralin, which is predicted to travel through topsoil with a velocity approximately 500 times slower than the soil water (Table 1), it can be stated that all pesticide observed in flow from drains at 550 mm depth (maximum concentration 0.06 µg/l) over the relatively short period of monitoring has been transported by preferential flow. For less strongly sorbed solutes, the division between flow is less clear, but Figures 2-4 show drainflow and associated concentrations of isoproturon and bromide throughout the winter of 1990/91. Concentrations of isoproturon in drainflow were very peaky and have been shown to be generally high at the start of each new flow event and then to decrease over the course of the event (Brown *et al.*, 1995). This pattern of residues in drainflow has been observed by Kladivko *et al.* (1991) and others and is characteristic of non-equilibrium sorption and/or two-region water flow. Isoproturon concentrations during periods between storm events are relatively small, suggesting that larger concentrations have resulted mainly from preferential flow transporting small pulses of pesticide from surface layers to drain depth with relatively little interaction with the soil and thus possibility for sorption.

Transport of bromide through this soil was also influenced by preferential flow and resulted in concentrations observed in the first drainflow collected after application. In addition, a number of peaks in concentrations of bromide in drainflow were observed during December and January at the time of drainage events, with peaks in concentration lagging slightly behind those in flow. It is again hypothesised that these concentrations resulted largely from rapid preferential movement of residues from the soil surface to drain depth. However, sorption of bromide is not a limiting factor for leaching (although velocity of soil water movement is) and matrix flow has an overall greater potential for transport of non-sorbed solutes to depth as interaction between water and soil - and thus with associated solute - is maximised. The breakthrough curve for bromide shows a number of transient peaks followed by a plateau around the end of January. We suggest that this plateau reflects the slower movement to depth of a band of bromide as a result of classical matrix flow. Once applied bromide has largely moved out of the surface horizons, matrix flow becomes the dominant process for transport of this ion but with a dilution effect observed during periods of more intense flow in March when preferential flow is assumed to be occurring.

It is likely that reductions in losses of pesticides to surface waters could be achieved by management practices such as topsoil cultivations aimed at decreasing preferential flow. Again, the effects of such treatments upon the movement of other solutes through soil could conflict. The data presented suggest that, after an initial rapid breakthrough of non-sorbed solute, increased amounts of preferential flow may act to decrease concentrations of solute at depth by decreasing the interaction between moving soil water and the soil matrix.

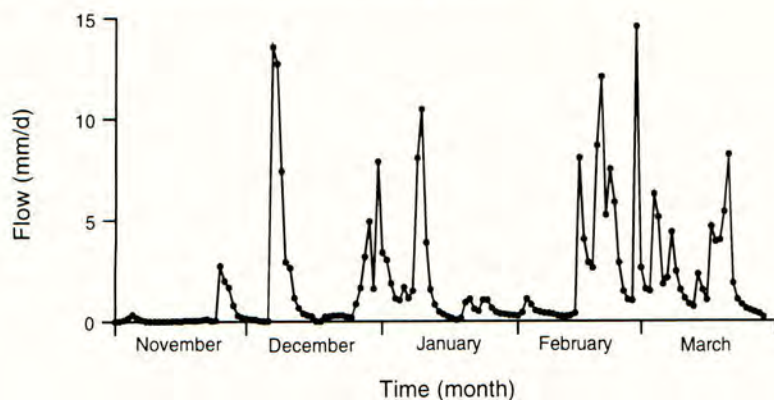FIGURE 2. Drainflow from plot B during winter 1990/91.

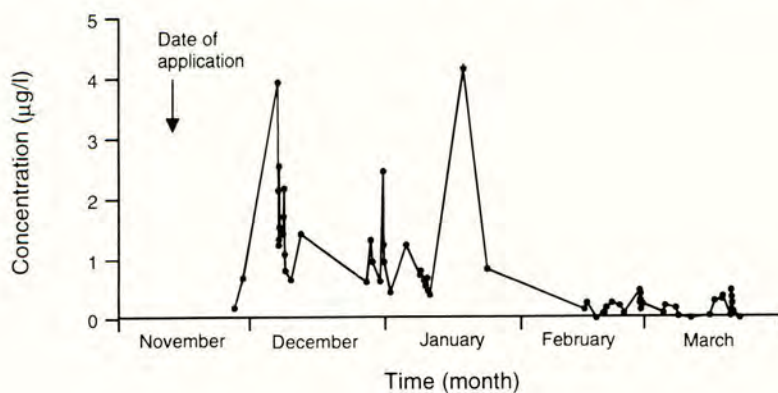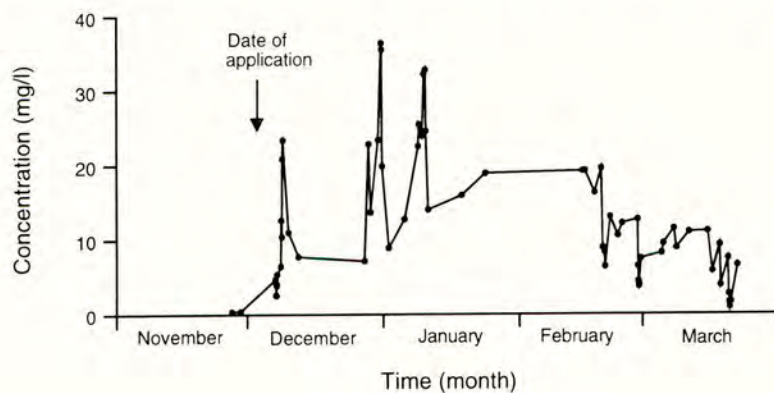FIGURE 3. Isoproturon concentrations in drainflow (plot B, winter 1990/91).

FIGURE 4. Bromide concentrations in drainflow (plot B, winter 1990/91).

The different transport processes resulted in different patterns of leaching and these are summarised for the winter of 1990/91 in Figure 5 which shows normalised cumulative loss to drains of water, bromide, isproturon and mecoprop. Around 40 and 90% of the total losses of isoproturon and mecoprop, respectively, occurred in the first large event after application, whereas the loss of water and bromide from the site was more evenly spread throughout the season. Because of the influence of degradation and the importance of preferential flow to movement of pesticides, the weather shortly after application is critical to the environmental fate of pesticides, but is of little significance to non-sorbed solutes.

FIGURE 5. Cumulative loss as a percentage of the total for water, bromide, isoproturon and mecoprop in drainflow from plot B.
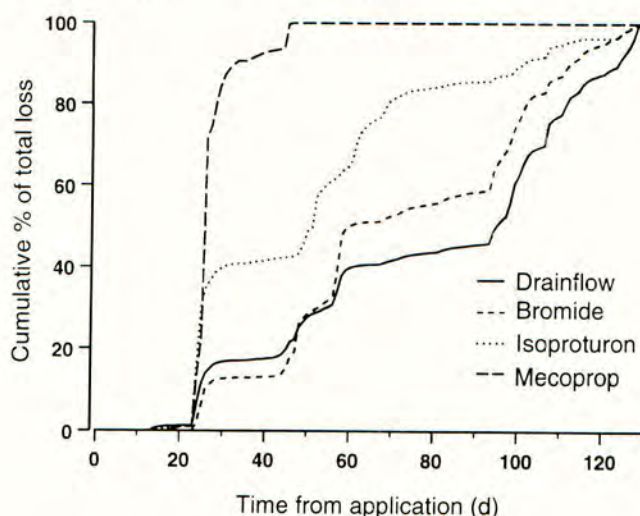
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HERBICIDE TRANSPORT IN DIFFERENTLY STRUCTURED SOIL HORIZONS UNDER CONSTANT AND TRANSIENT FLOW CONDITIONS

S. MEYER-WINDEL, B. LENNARTZ

Institute for Water Management and Landscape Ecology, University of Kiel, Olshausenstr. 40, D-24118 Kiel

ABSTRACT

The transport of two phenylurea and two triazine herbicides through undisturbed columns of the A- and B-horizons of a sandy soil was studied under unsaturated steady state and transient flow conditions. In both horizons classical transport behaviour was observed for all applied chemicals under steady state flow. No change in transport behaviour of bromide and reactive chemicals was detected under transient flow conditions in the single-grained B-horizon, whereas in the crumb structured A-horizon preferential flow occured under the discontinuous watering regime. In this case adsorption strength of the herbicides did not affect their breakthrough time but was reflected in the slope and maximum height of the breakthrough curves.

INTRODUCTION

Herbicide transport in soils is mainly associated with water movement, modified by sorption and transformation processes. Laboratory experiments investigating transport behaviour of chemicals are frequently performed under steady state flow conditions, whereas field soils are subjected to a wide variety of flow regimes. Recent field and laboratory studies have demonstrated the preferential transport of chemicals in aggregated loamy soils with visible cracks or macropores. In these experiments preferential flow phenomena were limited to either near-saturated steady state flow (Seyfried and Rao, 1987; O'Dell et al., 1992; Jardine et al., 1993) or to transient water flux (Germann et al., 1984; Shipitalo et al., 1990). The objective of this study was to investigate herbicide transport under both steady state and transient flow conditions in a sandy soil, without macropores.

MATERIALS AND METHODS

Soil columns (two per horizon) were taken from the A- and B-horizons of a sandy soil in Northern Germany. Spruce trees were planted on the field three years previously and no tillage had been performed subsequently. The A-horizon (loamy sand) had developed a stable crumb structure whereas the structure of the subsoil (B-horizon, sand) was single grained. Selected properties of the soil are given in Table 1. Chemicals used were the two phenylurea herbicides chlorotoluron and isoproturon and the two triazine herbicides atrazine and terbuthylazine, which are frequently used in maize, cereal or tree production. The herbicides

were analysed by UV-VIS HPLC with online solid-phase extraction. Bromide (KBr) was used as a non-reactive tracer and concentrations were measured by ion chromatography.

TABLE 1. Selected properties of the horizons under study.

Horizon	Depth (cm)	Structure	Bulk density (g/cm^3)	Sand (%)	Silt (%)	Clay (%)	Texture	Org. Matter (%)	pH (CaCl$_2$)
A	0-25	crumb	1.45	71.0	19.0	9.2	LS	0.8	6.1
B	25-60	single grain	1.49	91.6	4.4	3.9	S	0.1	5.9

Adsorption experiments

Batch adsorption studies were performed as an initial assessment of herbicide mobility in the two horizons to help in design of the column experiments. The studies were conducted according to OECD Guideline 106 in a concentration range of 0.02-6.2 mg/l and 0.02-26 mg/l for terbuthylazine and the other three herbicides respectively. Linear (K_d) and Freundlich (K_{Fr};1/n) adsorption coefficients were calculated from the measured data (Table2).

TABLE 2. Linear (K_d) and non-linear (K_{Fr}) adsorption coefficients determined from batch equilibrium experiments.

Herbicide	A-horizon					B-horizon				
	K_{Fr}	1/n	r^2	K_d	r^2	K_{Fr}	1/n	r^2	K_d	r^2
Atrazine	1.0	1.04	0.98	0.82	0.98	0.44	1.13	0.96	0.65	0.99
Terbuthylazine	4.39	1.09	0.98	4.21	0.87	1.08	0.98	0.99	1.24	0.98
Isoproturon	1.41	0.93	0.99	1.47	0.98	0.22	0.57	0.92	0.08	0.96
Chlorotoluron	2.90	0.82	0.99	2.02	0.99	0.54	0.79	0.96	0.38	0.99

Column experiments

In order to collect undisturbed columns a pit was dug isolating a pedestal of soil with a diameter slightly greater than that of the column (14.7 cm). A PVC pipe (15 cm and 30 cm length for the A- and B-horizons respectively) lined with a PTFE film was forced over the pedestal. The filled pipe was cut or broken from the pedestal and the soil was levelled at the end of the pipe. The laboratory apparatus described by Rambow and Lennartz (1993) was used for the displacement experiments. This apparatus allows the simulation of a broad range of conditions of rainfall and soil water tension. Prior to mounting on the apparatus tensiometers were inserted in the columns at depths of 2.5 and 12.5 cm, (A-horizon) and 2.5, 10, 20 and 25 cm, (B-horizon).

Two displacement experiments were conducted with each column. Prior to the first experiment, unsaturated steady state flow conditions were established at flow rates and water contents of 0.6 cm/d and 30% by volume for the A-horizon and 0.8 cm/d and 20 % for the B-horizon. Bromide at 3.3 kg/ha, 1.1 kg/ha atrazine and 1.4 kg/ha chlorotoluron in 0.3 mm of water were applied to the soil surface and displaced using rainwater at the established steady

state flow conditions. The second experiment was performed under transient flow conditions. Initial water contents adjusted prior to the start of these experiments were similar to those established under steady state conditions for the respective columns. Once a week a 30 mm rainfall event over 3 hours was applied to the columns. A- and B-horizon columns received a total over 4 weeks of 120 mm. The B-horizon received two further events of 60 and 45 mm (rainfall intensity 10 mm/hour) over the next two weeks to make a total of 225 mm over six weeks. The first 30 mm rain event was given half an hour following the application of 3.1 kg/ha bromide, 1 kg/ha isoproturon and 0.9 kg/ha terbuthylazine.

RESULTS

Experiment 1 (steady state flow)

Classical transport behaviour of all applied chemicals was observed under steady state flow conditions for both the A- and B-horizon columns. Bromide breakthrough curves (BTC's) were rather symmetrical but shifted slightly to the left of 1 porevolume of effluent. Due to sorption processes herbicide concentration curves were asymmetrical and shifted to the right with respect to the bromide BTC's (Figures 1a and 2a). Rather similar results are reported by several authors working on transport of chemicals in undisturbed soils under unsaturated steady state flow, including Seyfried and Rao (1987) and Jardine *et al.* (1993). No chlorotoluron was found in the A-horizon leachate during the study period (600 mm rain, 100 d). This may be attributed to stronger adsorption and/or to an accelerated decay process of chlorotoluron. In contrast to the A-horizon, adsorption coefficients for atrazine and chlorotoluron were nearly the same in the B-horizon (Table 2). Nevertheless the total chlorotoluron leached from the B-horizon during the experiment was only half that for atrazine, indicating increased decomposition of the phenylurea herbicide.

Experiment 2 (transient flow)

B-horizon

Concentration curves from the B-horizon under discontinuous leaching are shown in Figure 2b. Bromide appeared in the leachate after 18 mm drainage. Compared with bromide, isoproturon and terbuthylazine were shifted to the right indicating retardation of the herbicides. The first appearance and concentration maximum for the bromide BTC were equal for steady state flow at a rate of 0.3 mm/h and for transient flow at a rate of 10 mm/h (Figures 2a and 2b). Although major differences in the flow regime were created by the experimental conditions, flow through the same cross-sectional area of the soil dominated the transport process in the single-grained subsoil. Contact time and surface area were sufficient to obtain almost equal adsorption conditions under both steady state and transient water flow.

A-horizon

Breakthrough curves for the A-horizon are given in Figure 1b. All applied chemicals were detected in the first 1 mm of leachate, which was obtained 31 minutes after the onset of water application. Hence, the velocity of the applied solutes and water (application rate
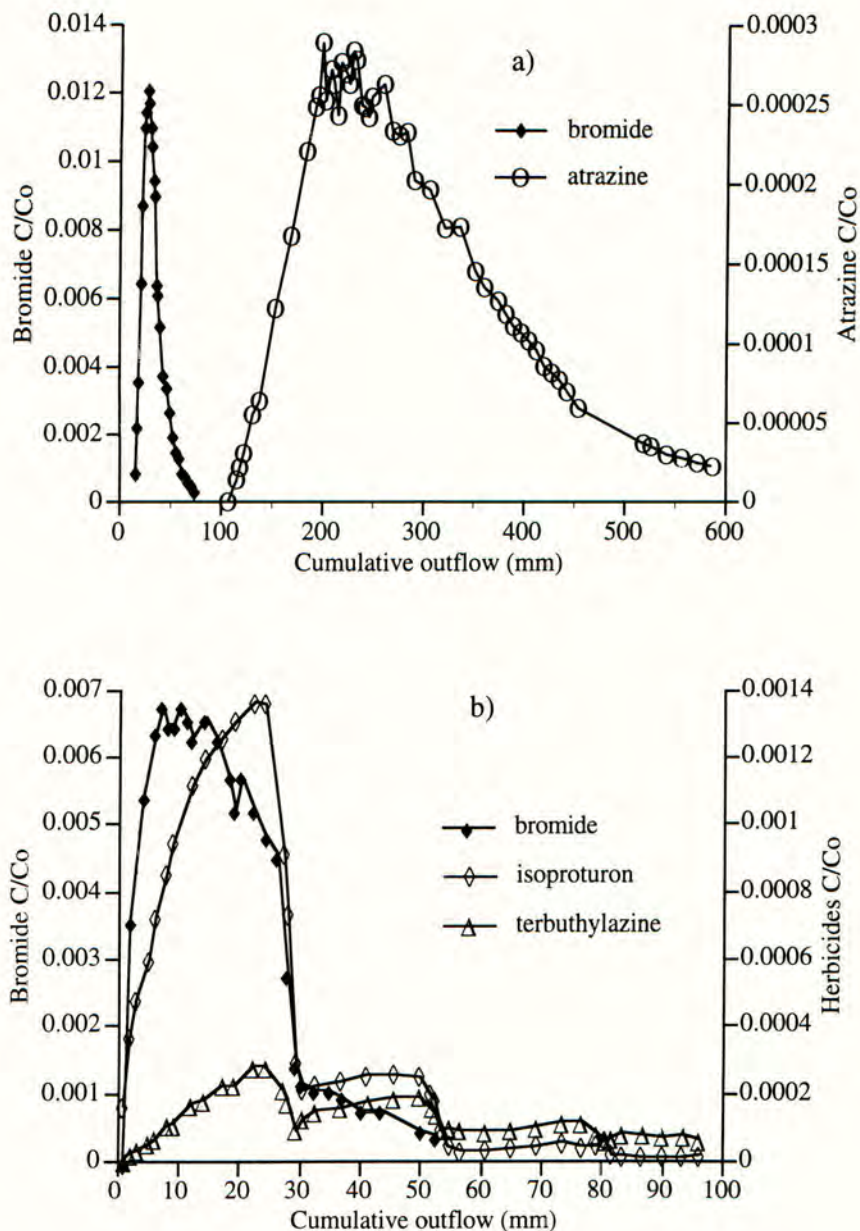
FIGURE 1. Bromide and herbicide breakthrough curves from the A-horizon:
a) bromide and atrazine leaching under steady state conditions; b) bromide,
isoproturon and terbuthylazine leaching under discontinuous watering regime
(initial water content 30 % by volume). Relative concentration C/Co, with C =
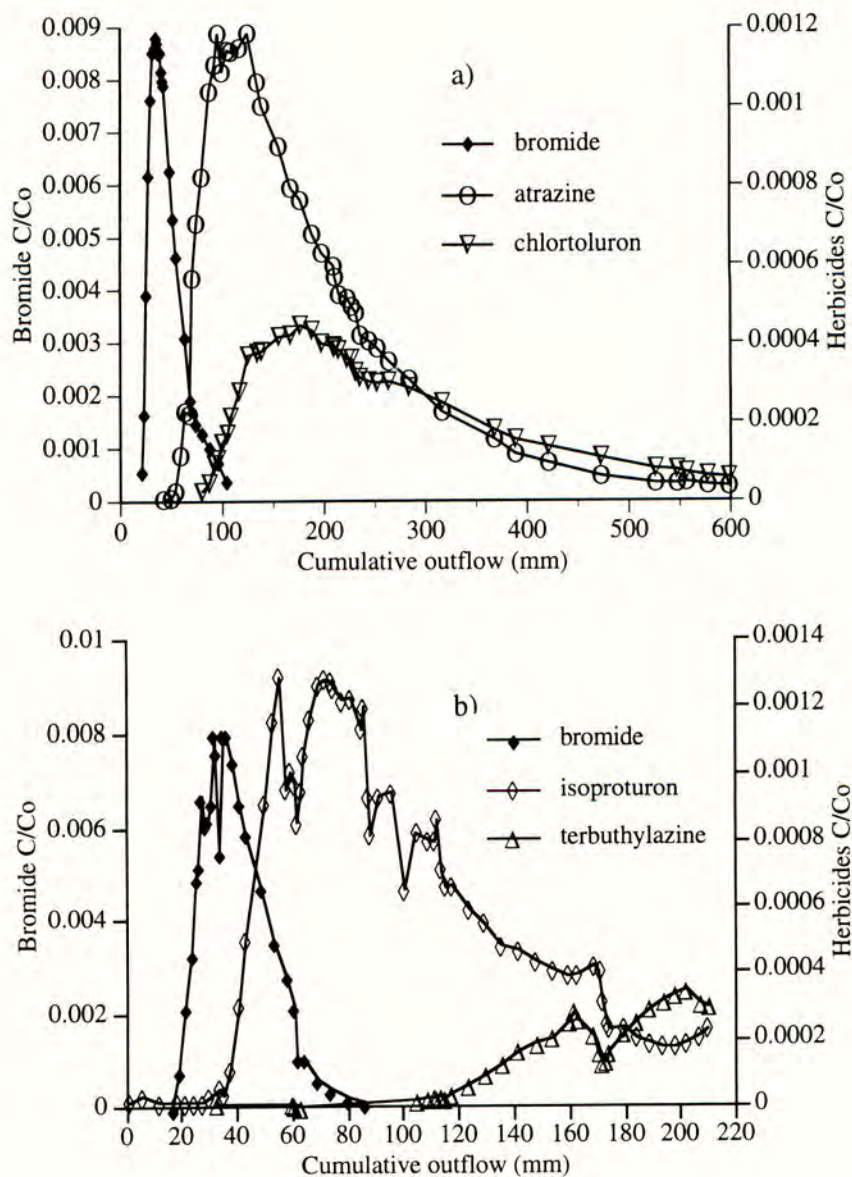effluent concentration and Co = input concentration.

FIGURE 2. Bromide and herbicide breakthrough curves from the B-horizon:
a) bromide, atrazine and chlorotoluron leaching under steady state flow
conditions; b) bromide, isoproturon and terbuthylazine leaching under
discontinuous watering regime (initial water content 17 % by volume). Relative
concentration C/Co, with C = effluent concentration and Co = input
concentration.

10mm/hour) was about 5 mm/minute. Bromide and herbicide concentration curves were similarly shaped. These findings are indicative of preferential flow conditions (O'Dell *et al.*, 1992; Jury and Flühler, 1992). Adsorption strength determined by batch equilibrium experiments did not influence the travel time of the herbicides as indicated by the simultaneous breakthrough of both herbicides. Nevertheless larger adsorption coefficients (terbuthylazine > isoproturon > bromide) were reflected by the decreasing concentration maxima and slopes of the BTC's (Figure 1b). The total herbicide loss in 100 mm leachate was 12 % of the applied isoproturon, whereas no atrazine, which shows a similar sorption behaviour to isoproturon (Table 2) was found in the first 100 mm drainage under steady state (matrix) flow conditions.

CONCLUSIONS

Transport behaviour under transient flow conditions was greatly influenced by soil structure of the sandy soil horizons. The weakly sorbing B-horizon may buffer the herbicide loss from the A-horizon, which is stronger sorbing but under certain conditions subject to preferential flow.

ACKNOWLEDGEMENTS

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ISOPROTURON AND ANION TRANSPORT BY PREFERENTIAL FLOW THROUGH
A DRAINED CLAY SOIL

A.C. Johnson, A.H. Haria, V.L. Cruxton, C.H. Batchelor, R.J. Williams

Institute of Hydrology, Wallingford, Oxfordshire, OX10 8BB

K. Heppell, T. Burt

Department of Geography, University of Oxford, Mansfield Rd, Oxford, OX1 3TB

ABSTRACT

A study of preferential flow and pesticide transport was made in a sloping field
with mole drains. The field was used for winter wheat cultivation, on Denchworth
series soil. A plot of 600 m^2 was isolated hydrologically from the rest of the field.
Included in the plot were a large number of logging instruments monitoring
hydrological processes. Data from the first storm event after pesticide application
showed that drainflow and lateral interflow only began once a temporary perched
water table developed within the A horizon, and reached to within 6 cm of the soil
surface. The B horizon soil matrix in which the drains were located remained
unsaturated whilst the drains were flowing. Peak isoproturon concentration was
closely related to peak drain flow, although conversely chloride and sulphate
concentrations were then at their lowest. The highest isoproturon concentration
(290 μg/l) was found in the drain water, with maximum concentrations of 230 μg/l
in overland flow and 210 μg/l in lateral subsurface flow. Of the pesticide lost, the
greatest load of isoproturon was carried by the drains (73%) rather than by lateral
subsurface flow (24%), with only a small proportion in overland flow (3%). For
this event, 10% of the rainfall was measured leaving the plot and carried 0.23%
of the pesticide originally applied to the field.

INTRODUCTION

The phenomenon of preferential or by-pass flow of water in structured soils to which
pesticides have been applied has been associated with high concentrations of pesticides
reaching adjoining water courses (Johnson et al., 1994). Whilst the overall amount of
pesticide lost from the field by this manner may be small (no more than 1%, Matthiessen et
al., 1992) the result is a series of episodes, possibly not lasting for more than a day
(Williams et al., 1991) in which stream concentrations may far exceed the EC drinking water
limit of 0.1 μg/l. Soils which best exhibit preferential water flow behaviour in England and
Wales have a high clay content. Due to the very small pore diameter of the soil matrix,
water can only move through the matrix at a very slow rate. In winter the topsoil, under
normal rainfall conditions, soon becomes water-logged. The natural macropores, both cracks
and worm burrows, are of crucial importance in conducting water that cannot be accepted
by the soil matrix. This water may be conducted by macropores laterally through the topsoil
and subsequently down to the drainage system. Therefore, even following the best
agricultural practice on these soils, pesticides may contaminate the surrounding water

courses.

An experimental site was set up at Wytham in Oxfordshire on a field in a winter cereal rotation. The soil belonged to the Denchworth series, which has a high clay content and in which mole drainage is necessary to supplement the field drains (back-filled with aggregate). The soil had a clearly defined Ap horizon reaching to 26 cm, with a heavier Bg horizon below. The aims of the field experiment were to ascertain the features of preferential flow, including how, when and where it occurs, to quantify the water movement and the pesticide load in the different preferential pathways and to establish their relative importance.

MATERIALS AND METHODS

After the previous winter wheat crop was harvested a 600 m^2 plot was isolated from the rest of the field. The boundaries of the plot consited either of ditches and sheeting buried vertically to prevent water entry or exit, or water collecting constructions. These included a field drain at 80 cm, fed by mole drains (which traversed the plot at a depth of 50 cm), a gulley at 30 cm depth, containing aggregate and backfilled with soil to collect lateral subsurface flow and a shallow gulley to 5 cm depth, on the soil surface to collect overland flow. The field drain was prevented from collecting water from outside the plot by the installation of a ditch and by-pass drain 1.5 m away and parallel to it. The water collected by these devices was fed into pipes which led to flow measuring stations. For field drain flow and lateral subsurface flow measurements were made by V-notch weirs with transducers and overland flow with a tipping bucket device. Water samples were taken automatically by autosamplers taking 24 x 1 litre samples at 30 min intervals. This was triggered by flows in excess of 0.054 l/s for the field drain and 0.023 l/s for lateral subsurface flow. An additional autosampler was placed in the stream adjacent to the field. Isoproturon was applied to the field in March 1994. Water samples collected by the autosamplers were analysed for the presence of the pesticide and anions by HPLC.

Hydrological instruments included pressure transducer tensiometers (PTT's) to measure soil water potential, capacitance probes to measure water content and piezometers to measure fluctuations in water table height.

RESULTS AND DISCUSSION

The first rain event to trigger sampling of drain flow occured 19 days after the application of isoproturon. The hydrograph is shown in Figure 1. The principle features are the peaked drain and lateral subsurface flow, which are characteristic of preferential water flow, the main flow of water out of the plot lasting not more than 4 h. Typical logged tensiometer data are shown in Figure 2. An increase in soil water potential at 10 cm, reflecting an increase in water content in response to rainfall, can be observed. The profile at 30 cm and below is shown to remain unsaturated throughout the rainfall event. Significant water movement out of the plot occured when a head of water developed in the Ap horizon, perched at about 6 cm or less; this was also observed with shallow piezometers.
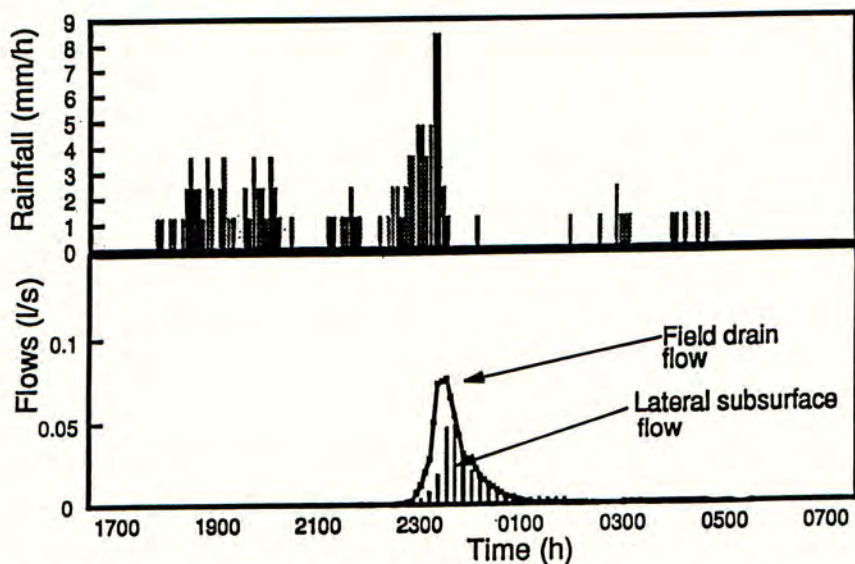
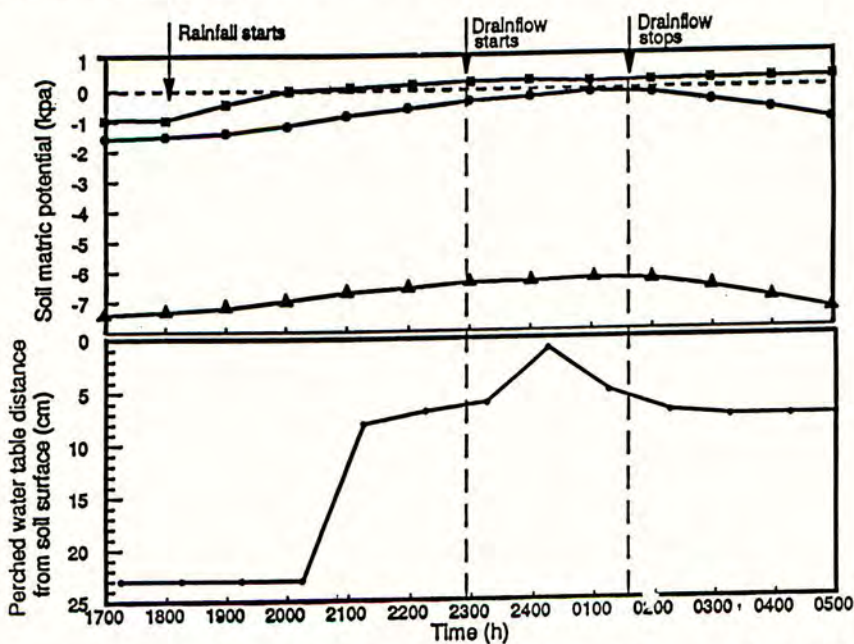FIGURE 1. Response of field drain and lateral subsurface flow to rainfall.

FIGURE 2. Comparison of changes in soil matric potential measured by the 10 cm PTT (-■-), 30 cm PTT (-●-) and 50 cm PTT (-▲-) and perched water table with the initiation of rainfall and drainflow.

The amounts of water flowing out of the plot and solute loss from the plot were calculated. Slightly less than 1 mm of the 10 mm that fell on the plot could be detected as leaving the plot. This was distributed between the field drain (63%), lateral subsurface flow (34%), and overland flow (3%). The highest recorded concentration (290 μg/l), and the majority of the pesticide transported (73%) was from the field drain. Lateral subsurface flow carried 24 % and overland flow 3 % of the pesticide lost from the plot in this event. The maximum concentration of isoproturon in overland flow was 230 μg/l and 210 μg/l for lateral subsurface water (Figure 3). The majority of the solutes measured (data not shown) were carried in proportion to the volumes of water, with the exception of isoproturon. A smaller proportion of isoproturon was carried in relation to the volume of water in the collected subsurface flow water than in overland or field drain water.

The lower concentration of isoproturon in the lateral subsurface water may be related to readsorption. To reach the collector, at the end of the plot, this water needed to move up to 30 m *through* the soil, whereas to reach the drainage system this may only mean travelling vertically for 0.5 m. The loss of isoproturon from all measured flow routes from this event amounted to 0.57% of that believed to be present in the soil surface at the time (estimated from isoproturon analysis of a soil surface sample taken one day previously). This compares with 0.23% of that sprayed onto the plot 19 days previously.

An additional calculation for aqueous available isoproturon can be made using a Kd of 2.5 for isoproturon in Wytham topsoil (Walker, personal communication). Assuming an equilibrium exists between the aqueous and sorbed phases of isoproturon the calculation is made as described by Johnson, (1995). To complete the calculation, information on the antecedent water content, the total amount of pesticide available and Kd are used to predict the aqueous available pesticide concentration. As we know how much of the water left the plot, we can predict how much of the aqueous phase pesticide would have left the plot also. The observed loss of pesticide amounted to 52 % of the predicted loss of aqueous available pesticide. The over-estimation of loss by the calculation may be due to: (i) the Kd being an underestimate; (ii) readsorption of pesticide within the soil; (iii) not all the aqueous phase pesticide being available to the new rainwater; or (iv) the new rainwater not mixing efficiently with the soil water containing the pesticide.

The inverse relationship between the conservative anions chloride and sulphate and isoproturon, which was observed in the previous season (Johnson *et al.*, 1994), can be seen in the field drain chemograph (Figure 4). Isoproturon is believed to be found largely in the topmost level of the soil, whilst chloride and sulphate are believed to be more evenly distributed through the soil profile. When the dominant component of drainage is water from the soil surface, which has largely by-passed the soil matrix, the isoproturon concentration will be at its highest. The highest concentrations of chloride and sulphate, (Table 1), can be observed in water collected from the suction samplers one day previous to the storm event and lowest in the rainwater. Thus, the soil water has high chloride and sulphate concentrations compared to rainwater. At the peak of drain flow the drain water chloride and sulphate concentrations are at their lowest, suggesting a predominance of new rainwater which has had the minimum opportunity to mix with the soil water. At the end of the event when drain flow is much reduced the chloride and anion concentrations are increasing (in contrast to isoproturon). This may reflect a greater proportion of the "old" soil water reaching the drains, and/or the slower water movement through the profile allowing salts to diffuse into the water and hence raise the salt concentration.

TABLE 1. Comparison on day 19 of chloride and sulphate concentrations (mg/l) of the field drain at peak flow (FD peak) and at the end of the event (FD end), in overland flow (OF), (average), in lateral subsurface flow (LSF), (average), rainwater (RW) and in a 25 cm-deep suction sampler on day 18 (SS).

Sample	FD peak	FD end	OF	LSF	RW	SS
chloride	4.5	8.0	4.5	4.5	2.7	8.0
sulphate	11.0	17.0	12.0	12.0	4.5	50.0
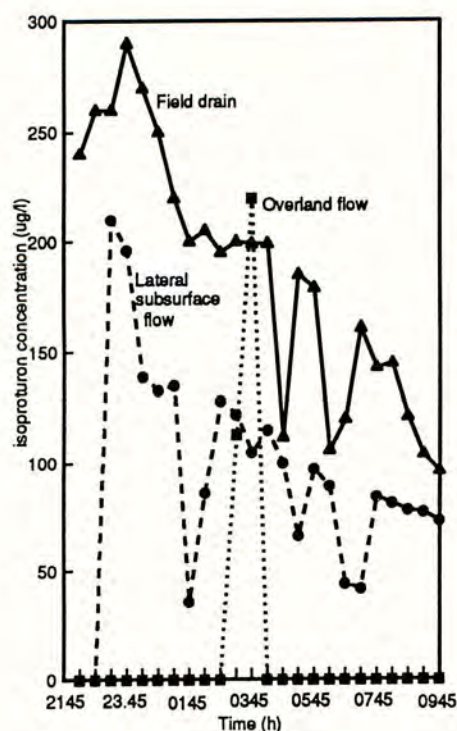
FIGURE 3. Comparison of isoproturon concentrations in drainflow, lateral subsurface flow and overland flow.
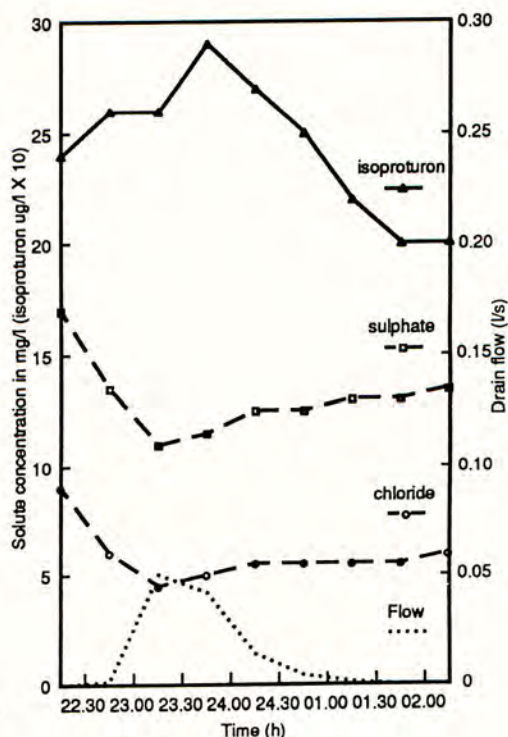
FIGURE 4. Comparison of drainflow with isoproturon, sulphate and chloride concentration in drain water.

As might be expected the overland flow water samples contained a low chloride and sulphate concentration (Table 1). This is believed to be largely rainwater moving over the soil surface, as opposed to through it. The chloride and sulphate concentrations in the lateral subsurface water appeared to be virtually identical to those in overland flow water. Thus, the anion data suggest that the water moving horizontally through the soil, by-passing the soil matrix in the subsurface layer and that moving vertically to the drains had the same rainwater origin.

Measurements were also made of the isoproturon concentration in the stream which received the drainwater from the field drains. The stream water comprised both agricultural drainwater and also water draining from the nearby Wytham Wood (which would dilute the pesticide-contaminated drainwater). Measurements were made by an autosampler triggered by floatswitch attached to a weir in the stream. For the rain event described above a maximum concentration of 25 μg/l was recorded.

Summary

1) The rapid start and stop of drain flow and lateral subsurface flow indicated preferential flow.
2) Evidence from PTTs and piezometers indicated that the development of a perched water table in the surface layer, reaching 6 cm from the soil surface, was an essential precursor to both drain flow and lateral subsurface flow.
3) The drainage system was most important in carrying water out of the plot (63%), followed by lateral subsurface flow (34%), and overland flow (3%).
4) The drainage system was most important in terms of carrying pesticide away from the plot (73%), followed by lateral subsurface flow (24%) and overland flow (3%).
5) Calculations on the loss of isoproturon from the plot suggest that 0.23 % of the pesticide initially applied, 0.57% of the actual total present on the day and 52 % of the estimated aqueous phase was carried in the outflow.
6) Pesticide concentrations broadly followed the rise and fall of drain flow. Chloride and sulphate concentrations were inversely related to drain flow.

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THE OCCURRENCE OF HERBICIDES IN AND THE MODELLING OF THEIR TRANSPORT TO THE CHALK AQUIFER BENEATH ARABLE LAND IN SOUTHERN ENGLAND

P. J. Chilton, M. E. Stuart, D. C. Gooddy

British Geological Survey, Wallingford, Oxon, OX10 8BB

R. J. Williams, A. R. Williamson

Institute of Hydrology, Wallingford, Oxon, OX10 8BB

ABSTRACT

The paper summarises the preliminary results of studies of the behaviour of the pesticides atrazine and isoproturon in the Chalk. Analytical methods applicable to both solid aquifer material and groundwater have been developed. Sampling in the unsaturated zone of the Chalk at five sites in southern England has indicated very low concentrations of isoproturon and atrazine in both solid Chalk and porewater samples. Regular sampling of groundwater from the uppermost part of the saturated zone has also indicated consistently low concentrations of pesticide residues reaching the water table.

Mathematical models can be used to assess the likely leaching of pesticides to groundwaters, as they offer a convenient alternative to costly drilling programmes. LEACHMP, an established unsaturated zone pesticide leaching model, has been tested against the observed atrazine concentrations. The model predictions were of a similar order to the observed values but did not reflect in detail the shapes of the profiles.

INTRODUCTION

Most groundwater systems are characterised by relatively slow rates of groundwater flow and pollutant transport. The average response time of deep water supply boreholes to surface inputs of pollutants can be of the order of decades. This slow response means that the analysis of pesticides from deep boreholes is a poor indicator of quality deterioration in the groundwater system as a whole. To appraise the current situation adequately and to justify any required controls, data are needed on the three-dimensional subsurface distribution of pesticide compounds beneath aquifer recharge areas and especially in the unsaturated zone. The present paper describes the preliminary results of studies to determine the distribution of selected pesticides in the subsurface.

The risk of groundwater pollution arising from pesticide usage in agriculture depends on the relationship between the persistence of the compounds and the mechanism and rate of movement through the unsaturated and saturated zones of aquifers. Preliminary estimates can be made of the possible transport of pesticides from soils into groundwater systems, based on the physico-chemical properties of the pesticides themselves and on knowledge of groundwater flow and aquifer properties (Foster *et al.*, 1991). Soil half-lives for compounds

in widespread use range from days to years, but for the most mobile pesticides are normally less than 100 days. Pesticides that are strongly sorbed onto organic matter or clay particles are likely to be retained in the soil rather than leaching to groundwater. Those compounds leached into the unsaturated zone enter an environment which contains a lower content of clay and organic matter and has a greatly reduced indigenous microbial population. The attenuation processes which affect pesticides are likely, therefore, to be much less active beneath the soil zone and the mobility and persistence of pesticide compounds should be many times greater in the unsaturated zone than in a typical agricultural soil.

Fundamental questions about the movement of pesticides through aquifers remain to be answered. Movement through an unconsolidated, granular aquifer or the matrix of a consolidated rock aquifer would allow time for attenuation processes to occur, albeit more slowly than in the soil. In fissured aquifers, such as the major aquifers of the UK, preferential flow, effectively by-passing the rock matrix, could greatly reduce the opportunity for attenuation to occur and permit rapid movement of relatively high concentrations of pesticides directly to the water table and thence to wells or boreholes. Preferential flow is, however, difficult to prove or quantify, especially under conditions of natural rainfall.

APPROACH

Field Sampling

Fieldwork has been carried out at five sites (AWC, ASM, CP, WON, LEC) on the Chalk of southern England, which had good cropping and pesticide application records, where the herbicides atrazine or isoproturon were being regularly used and where the water table was predicted to be relatively shallow. At least two shallow boreholes were drilled to the water table at each site using a dry percussion method.

Examining the vertical distribution of solutes in the unsaturated zone of the major UK aquifers by high-speed centrifuge extraction of porewater from the core material has been a highly effective approach to groundwater quality studies. For proper quantification of pesticide concentrations in water relative to the EC MAC of 0.1 $\mu g/l$, a target detection limit of 0.01 $\mu g/l$ is generally sought, although in practice this has proved difficult to achieve in this and other similar studies, (Clark *et al.*, 1991). Larger sample volumes than those used for inorganic analysis are required, to allow the necessary extraction and pre-concentration procedures. In the current study, in which allowance was made for removal of material from the edge of the core to avoid sample contamination, centrifuging most of the rest of the Chalk from 100 or 150 mm diameter cores provided minimum sample volumes of 250 ml, which proved adequate. Samples for isoproturon were analyzed by a commercial laboratory and for atrazine by the BGS laboratory. The solid core material was also analyzed for pesticides using direct solvent extraction with dichloromethane or methanol. The methods developed for the study are described elsewhere (Chilton *et al.*, 1993).

Saturated zone samples were also taken from observation boreholes reaching just below the water table using a small submersible pump. The objective of this sampling was to observe pesticide concentrations in the uppermost part of the aquifer immediately below the site of application. In this way, the concentration of the target pesticide in the most recent

recharge might be observed and the sampling schedule could be modified to take account of time of application and of major rainfall and recharge events.

Modelling

The established unsaturated zone pesticide leaching model LEACHMP (Hutson and Wagenet, 1992) was tested against the observed data. The water movement component of the model was calibrated using data from a previous soil hydrology study (Wellings, 1984) carried out at ADAS Bridgets in Hampshire, close to the pesticide field sites. Meteorological data for the pesticide simulation period (1987-1993) were also obtained from ADAS Bridgets. The model was applied to the ASM site using the application data for isoproturon and atrazine that had been collected during the study. The model profile was set up for a depth of 5 m (average water table depth) and the free draining profile option used.

Within LEACHMP and most leaching models of similar type, the depth of leaching predicted depends critically on the half-life and partition coefficient of the modelled pesticide. Laboratory measurements of the half-life of isoproturon were made on material from a range of depths through the profile. The values allocated to the various depths are given in Table 1, the large increase in half-life in the unsaturated Chalk (> 60 cm) compared to the topsoil supporting the general principles outlined in the introduction. This is probably due to the lack of bacteria able to degrade this pesticide in the Chalk. Values for the half-life of atrazine were estimated as double those for isoproturon. Partition coefficients are commonly given normalized for organic carbon content, OC, of the soil (Koc) and are assumed to be constant for all soils. In this study a value of 130 ml/g was used for the Koc (A. Walker pers. comm.). The partition coefficient will vary with depth, generally decreasing as the organic carbon content of the soil decreases. The values of OC used in the modelling at different depths are also given in Table 1. The values for the topsoil were measured while the values for the Chalk were estimated to reflect the low adsorption expected in this material.

TABLE 1. Values of half life and organic carbon content used in the model at different depths through the unsaturated zone.

Model depth (cm)	Half life (days)		Organic carbon (%)
	Isoproturon	Atrazine	
0-20	35	70	5.4
20-40	35	70	1.4
40-60	70	140	1.0
60-80	990	1990	0.5
80-220	990	1990	0.1
220-500	4200	8400	0.1

RESULTS AND DISCUSSION

Pesticide measurements

At site AWC, isoproturon had been used each autumn for the preceding four years on a rotation of wheat and barley. Most samples of both core and porewater from the

unsaturated zone were below the limit of detection (<0.5 μg/l) for isoproturon. At site ASM, maize and winter wheat had been rotated, with isoproturon application to the wheat and atrazine to the maize. Atrazine was detected in all of the extracted porewater samples and all but one of the solid chalk samples although it had not been applied for two years, (Figure 1 and Table 2). Pesticide residues were consistently detected at low concentrations at both of these sites at the water table (Figure 2).

At site CP, which had been in maize cultivation continuously for four years, atrazine concentrations were high in the soil but declined rapidly with depth, falling below the limit of detection at 4 m. No saturated zone samples were taken at this site as the water table was much deeper than expected. At the two remaining sites where isoproturon had been applied 15 and 38 months before drilling, almost all samples were below the limit of detection, both for porewaters and saturated zone samples.

Modelling

The results from the modelling exercise were compared with two sets of data, the atrazine porewater profile

FIGURE 1. Observed atrazine pore water concentration profiles from below site ASM. Modelled values using LEACHMP are shown for comparison.

obtained in April 1992 (Figure 1) and the time series of atrazine concentrations at the water table (Figure 2b). The modelled profile (Figure 1) generally falls between the two observed profiles from site ASM. The model underpredicts concentrations in the top soil and in the lower part of the profile. Also, the shape of the predicted profile is very different to the observed profiles, in both of which the highest atrazine concentrations were found at the surface. In contrast, the model indicates a clear peak just below 1 m depth. Modelled isoproturon values were lower than those for atrazine, reflecting its shorter half-life and its last application 12 months prior to the last atrazine application. No measurements of isoproturon concentration were made at this site.

Modelled water table concentrations were taken as the pore water concentrations predicted by the model at the water table depth. This is an approximation, since the model was run assuming a free draining profile (no water table) and no account is taken of dilution with existing groundwater flow. The model generally underestimates the atrazine concentration except for one occasion towards the end of the simulation where the water table begins to rise. As the water table rises it will start to reach the part of the profile where the model predicts the pore water concentrations to be highest. The model predicted that no isoproturon would reach the water table over the simulation period.

As stated in the introduction, it is likely that a component of transport of solutes in the Chalk is via preferential flow through fractures. Pesticides may pass more rapidly to depth
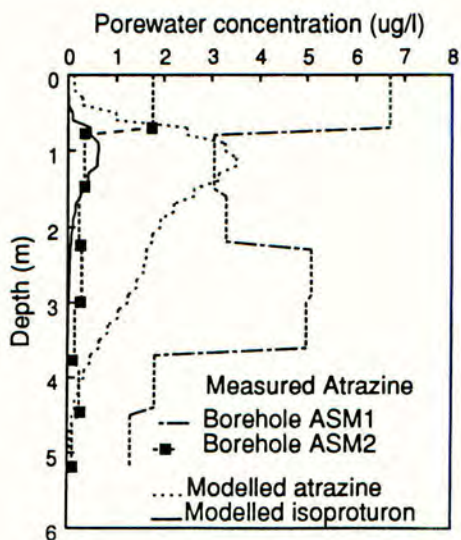
than if groundwater moved only through the matrix and a model which assumes matrix flow is unlikely to be able to reproduce the observed data. However, the model does predict atrazine concentrations at the water table, a prediction that only occurs because of the low degradation and adsoption potential of the Chalk.

TABLE 2. Atrazine profiles in the solid Chalk from two cores taken from the same field, April 1992, (μg/kg of Chalk)

ASM1		ASM2	
Depth (m)	Atrazine	Depth (m)	Atrazine
1.95-2.05	0.48	2.00-2.10	not detected
		2.62-2.71	0.24
3.00-3.20	0.31	3.43-3.48	0.21
		4.05-4.12	0.44
4.80-4.90	0.31	4.70-4.80	0.11
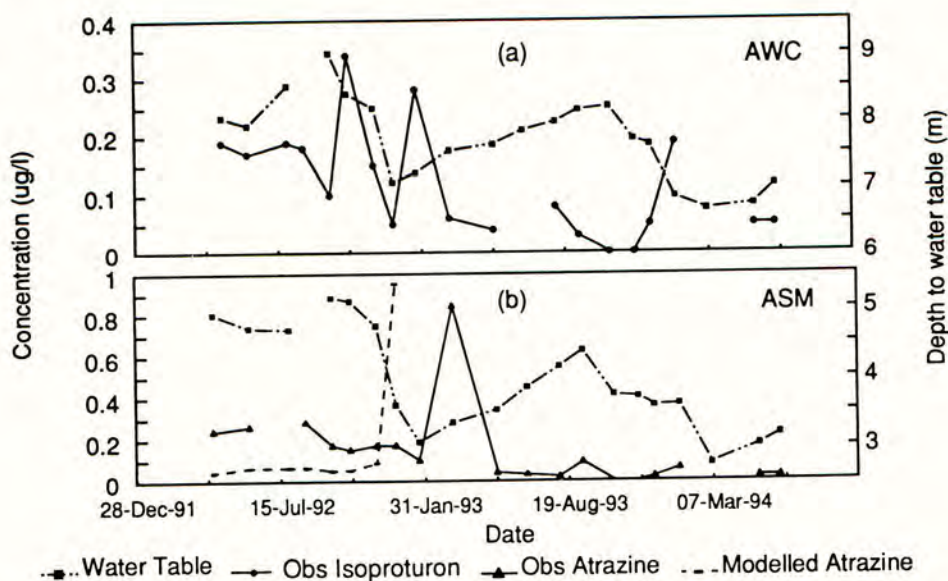
FIGURE 2. Herbicide concentrations at the water table from two sites under arable crops: (a) isoproturon at AWC; (b) atrazine at ASM. Atrazine concentrations estimated using LEACHMP are also shown for site ASM.

If preferential flow occurs it is likely to be driven by ponding of water in the profile causing a local perched water table (Haria *et al.*, 1994). It is important to know where in the profile this ponding occurs. Ponding at or near the surface is likely to maximize pesticide mass transport to depth as this is where the majority of the pesticide is located. Ponding lower in

the profile, say at the soil/Chalk boundary may result in less solute transport as here the available pesticide residues are less. Heavy rain and ponding soon after application would produce conditions particularly favourable to pesticide leaching. Work is continuing at the sites, using novel techniques to improve the capability for sampling rapid, preferential flow of recharge water and solutes to the water table.

CONCLUSIONS

Sampling in the unsaturated zone of the Chalk at five sites in southern England has observed very low concentrations of atrazine and almost negligible concentrations of isoproturon in both solid Chalk and porewater samples. Regular sampling of groundwater from the uppermost part of the saturated zone has also produced consistently low concentrations, indicating that relatively little pesticide residues are reaching the water table. Simple modelling of unsaturated zone pesticide transport has produced predicted pesticide concentrations of the same order as observed values, but has not reproduced the shapes of the observed profiles. It seems unlikely that troublesome pesticide concentrations would reach the water table in the Chalk if movement through the matrix were the only transport mechanism operating. However, it is clear that preferential flow could be an important mechanism in consolidated, fractured aquifers such as the Chalk and further work is required both to quantify this flow component and to establish its role in pesticide transport.

ACKNOWLEDGEMENTS

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A SYSTEMATIC APPROACH TO THE CHARACTERISATION OF LYSIMETER LEACHATE

A.S. TERRY, E.A. MACKENZIE, S.A. FLINT, R. ALLEN

AgrEvo UK Ltd, Environmental Sciences, Chesterford Park, Saffron Walden, Essex CB10 1XL .

ABSTRACT

The presence of radioactivity in lysimeter leachate, following application of $[^{14}C]$-labelled pesticides, at levels exceeding 0.1 µg/l is not uncommon. Often a substantial proportion (sometimes 100%) of the radioactivity in leachates is comprised of previously uncharacterised components. An approach has been adopted in which leachate samples are characterised chromatographically and the level of the pesticide and its known degradation products are determined in fractionated samples. Several methods have been used, including Sephadex LH-20 and reverse phase solid extraction. Acid/base fractionation of "humic-like" material has also been useful. The problem of handling low levels of pesticide-derived $[^{14}C]$-materials has been partly alleviated through concentration of leachate by freeze drying and by loading large volumes onto robust analytical hplc systems. The systematic and complementary fractionation approach reported here efficiently uses analytical resource and sheds some light on the nature of unknown leachate components.

INTRODUCTION

During the course of conducting a two year lysimeter study many samples are collected, typically around 40 - 50 for each lysimeter used. It has been found that, following treatment of a lysimeter with $[^{14}C]$-labelled pesticide, a large proportion of the radioactivity present in the leachate is relatively polar material containing previously unknown components, (invariably heterogeneous in nature). The overall concentration of radioactive materials is low (usually much less than 10 µg AI equivalents/l). This presents a difficult task when it comes to characterising the components of the leachate derived from the pesticide.

An approach to this task has been adopted which involves systematically applying different fractionating procedures in successive steps, each step giving more detailed information than the previous one. This enables an effective and focused use of analysis time. Examples are taken from two recent lysimeter studies, each with a different spring-applied herbicide of moderate persistence and moderate mobility.

FIRST STEP ANALYSIS - FOOTPRINTING

Samples containing less than 0.1 µg/l of AI equivalents are not ordinarily analysed. A typical distribution of radioactivity in leachate with time, during the course of a study, is shown in Figure 1.

FIGURE 1. Typical leachate profile following application of [^{14}C] pesticide in spring.
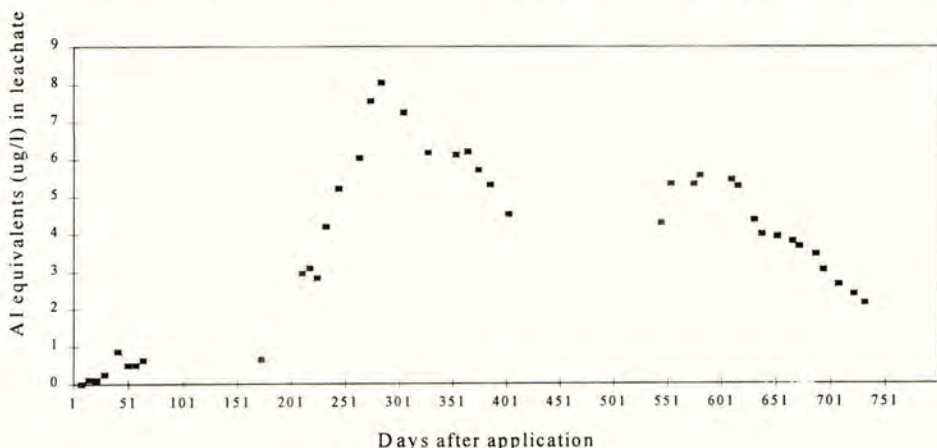
In the two studies with herbicides the radioactivity tended to appear as two peaks, one in the first winter and one in the second. The first stage in analysis was to ascertain if the distribution of radioactive components across these peaks and between different lysimeters in each study was similar or radically different. This involved choosing a representative selection of samples (spanning the two peaks) from each lysimeter and subjecting them to a footprinting procedure. Two footprinting procedures have been developed, each based upon preliminary analytical method development work on leachate samples.

The first procedure is fractionation on Sephadex LH-20 columns (size exclusion chromatography). Concentration of leachate samples using freeze drying was necessary for analysis using this method. In samples of such heterogeneity as those found in the leachates, several different fractionation mechanisms are likely to occur during chromatography on Sephadex LH-20 in addition to size exclusion (e.g. adsorption, ionic interactions), but nevertheless very useful footprints are obtained (see Figure 2). All the leachate samples footprinted from one lysimeter study gave a very similar pattern of distribution of radioactive components, but different to that obtained in the second study. This footprinting strongly suggested that further effort could be focused on samples from just one lysimeter per study and provided a crude fractionation of components for further analysis.

FIGURE 2. Typical Sephadex LH-20 profile of leachate following concentration by freeze drying.
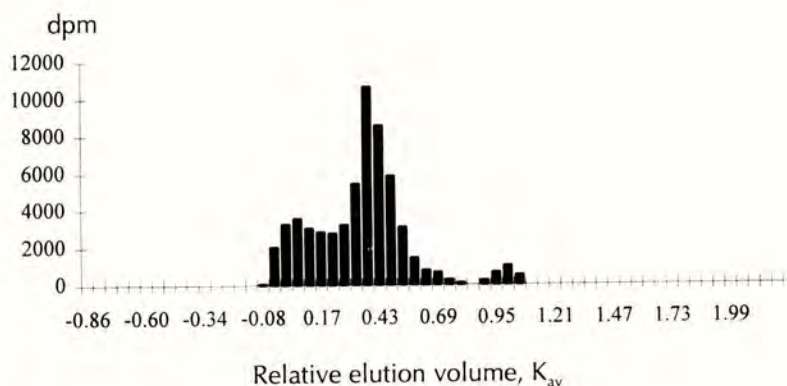
dpm, disintegrations per minute

The second footprinting method is outlined in Figure 3. This involves an initial acidification of leachate to pH 1 followed by passage through a nylon filter. Up to 45% of the radioactivity was retained on the filter and most of this released in a concentrated state (25 -fold concentration) using alkali, in a form suitable for analysis (fraction A). The acidified material not retained on the filter is further fractionated on a reverse phase (RP) solid phase extraction (spe) cartridge, yielding three fractions (C, D and E).

FIGURE 3. A typical analysis procedure for footprinting leachate.
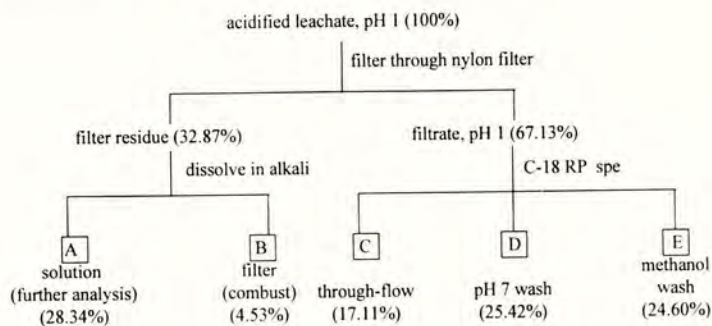
The fraction eluted with methanol is highly concentrated (25-fold) and most likely to be, or be similar to, pesticide metabolites. Again, this footprinting demonstrated that all

samples were broadly similar and provided fractionated samples for further analysis. On the basis of these results more detailed analysis was carried out on samples from just one lysimeter.

SECOND STEP FOCUSED ANALYSIS - FINGERPRINTING

High pressure liquid chromatography (hplc) with uv detection was the method found most appropriate for more detailed analytical studies of the fractions generated by the footprinting procedures. In particular, reverse phase hplc has the ability to span the large spectrum of relatively polar metabolites found in the leachate samples. The hplc systems used were adapted from those already available for the analysis of parent pesticide and known metabolites. This adaptation generally entailed making the system better able to handle the more polar components present in the leachate by modifying the gradients employed. This process invariably lengthened the run time of the starting hplc method. The systems were found to be very robust, allowing injection of large volumes of dilute material (e.g. up to 4.5 ml of fractions onto an analytical system) whilst still retaining good chromatographic results. The systems were able to detect known metabolites in addition to fingerprinting unknown components.

FIGURE 4. HPLC profile of radioactivity in leachate; matching uv absorbing profile.

(a) UV Absorbance

*standards
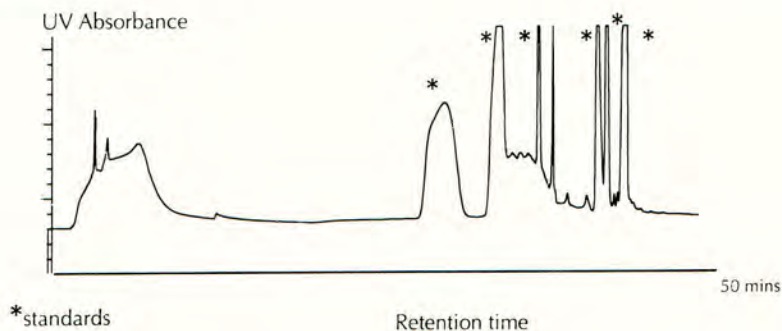
(b) Radioactive content of fractions


dpm- disintegrations per minute

Two general findings associated with the hplc investigations warrant further comment. Firstly, in all leachate analysed (including control leachate derived from a non [^{14}C]-pesticide treated lysimeter) a UV absorbing profile was evident (see Figure 4a).

This has been tentatively assigned to components generated by natural soil degradative processes (including microbial activity) and most probably fulvic and humic acids. Significantly, the hplc profile of a large proportion (up to 100%) of the radioactive components in leachate matches this UV profile (see Figure 4b). This strongly suggests that a large proportion of the radioactivity in the leachates is associated with naturally present components (natural products), either as an integral part (fully metabolised) or as covalent conjugates.

Secondly, in one study an unknown $[^{14}C]$-metabolite was detected that did not co-chromatograph with any known soil metabolite and which was not associated with UV absorbing material (see Figure 5). So, unlike a large proportion of the radioactivity present in the leachates this component is clearly not associated with natural products. Having detected this component in the representative selection of leachate samples investigated other samples were then chosen to further investigate its rate of formation and decline.

FIGURE 5. Presence of unknown $[^{14}C]$-metabolite not associated with uv absorbance.
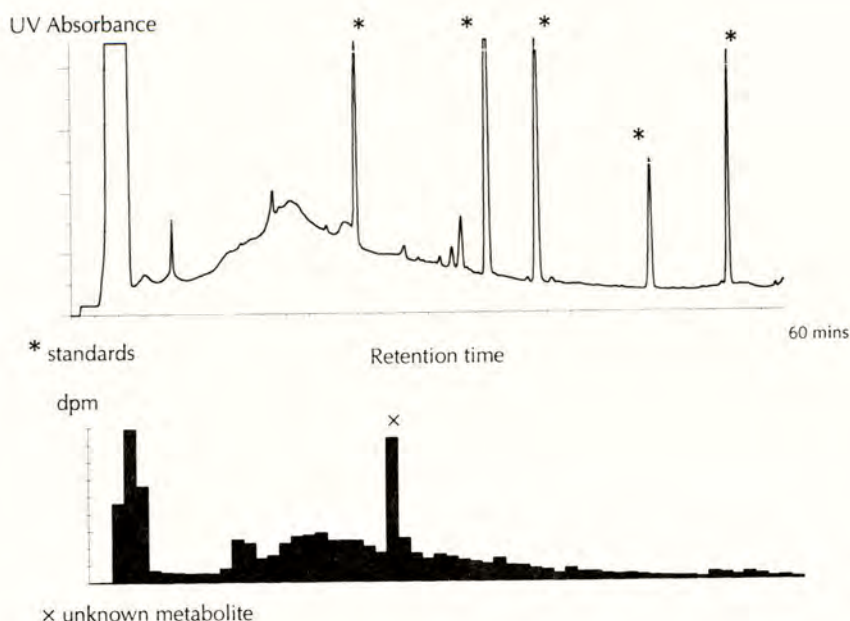
DISCUSSION

It is possible to combine the results of these diverse methods to draw conclusions about the nature of the different radioactive components present in the leachates. For example, some material that was not retained on the RP spe cartridge even at pH 1 (see Figure 3, C), was also not retained at all in an RP hplc system. However, it was retained

very strongly on strong anion exchange media. This suggests that it could consist of relatively low molecular weight components containing multiple carboxylic acid moieties.

The radioactive material deposited on nylon filters at pH 1 (A, Figure 3) has a very similar hplc fingerprint to that given by the methanol wash of the RP spe (E) after the acidified leachate has passed through it. This suggests that the components in these fractions are very similar, perhaps differing only in the number of acid groups (the nylon retained material having less).

Chromatographic characterisation of radioactivity present in leachates is difficult. Leachates invariably contain an heterogeneous collection of relatively polar material present in low concentrations. Clearly, identification of these components could be extremely difficult and our results suggest that the majority is either fully metabolised and incorporated into natural products, or covalently associated with natural products.

CONCLUSION

A systematic and layered approach to leachate analysis has been adopted, using either fractionation on Sephadex LH-20, or acid/base fractionation followed by further fractionation on RP spe cartridges, as a footprinting exercise. This is followed by more focused hplc analysis guided by the results of the footprinting. Reverse phase hplc has been shown to be a useful tool, especially when coupled to carefully chosen gradient systems, but the long run times required necessitate a prudent choice of samples to be analysed. This approach has been found to be both an efficient and effective use of analytical resources.

CELL LYSIMETER FOR STUDYING SOLUTE MOVEMENT AS INFLUENCED BY SOIL HETEROGENEITY

G. Trapp, S. Meyer-Windel, B. Lennartz

Institute of Water Management and Landscape Ecology, University of Kiel, Olshausenstr. 40, D -24118 Kiel

ABSTRACT

A cell lysimeter study with bromide and two herbicides was carried out on a sandy soil in northern Germany. Twenty five individual suction plates were installed on a 0.64 m^2 plot at 1.1 m depth.

The equipment proved suitable for investigating small scale variability of flow and transport processes in undisturbed soil profiles. A highly irregular flow and transport pattern was observed for the sandy soil. The unsaturated transient flow regime, adjusted to simulate natural rainfall, caused an early breakthrough of all applied chemicals from one of the cells, indicating pronounced preferential flow.

INTRODUCTION

In recent studies dye experiments have frequently been used to identify the spatial variation of flow paths in soils (Flury *et al.*, 1994; Germann *et al.*, 1984). The stained soil profiles are a helpful tool for an initial evaluation of the transport properties of soils. Dye experiments do not provide data on water and leached solute quantities and their distribution over a given cross-sectional area. Both the spatial distribution of leachate and its appearance with time at a certain depth are required to determine the importance of various transport processes.

Sixty-four individual wick soil-solution samplers over an area of 0.64 m^2 were installed by Poletika and Jury (1994) to obtain a better spatial and temporal resolution in transport experiments. Such samplers, however, do not permit adjustment of water tension as a lower boundary condition according to the adjacent soil matric suction. The objective of this study was to evaluate the spatial and temporal distribution of water and solute movement in quantitative and qualitative terms in a sandy soil by means of a modified wick sampler, hereafter called cell lysimeter.

MATERIALS AND METHODS

The cell lysimeter was installed in an undisturbed sandy soil in northern Germany. The soil was crumb-structured: selected properties at 4 different depths are given in Table 1.
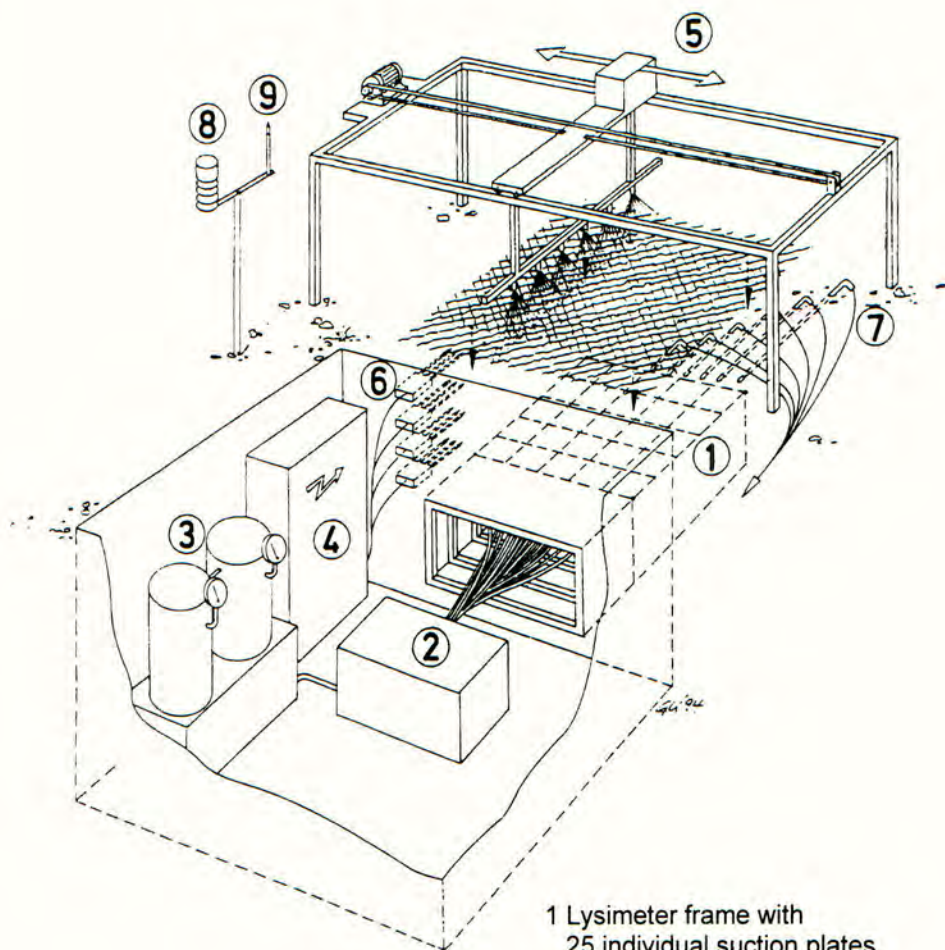
1 Lysimeter frame with
   25 individual suction plates
2 Fraction collector
3 Vacuum unit
4 Controller and logger
5 Sprinkler
6 TDR probes
7 Tensiometer
8 Humidity meter
9 Air thermometer

FIGURE 1. Installed cell lysimeter

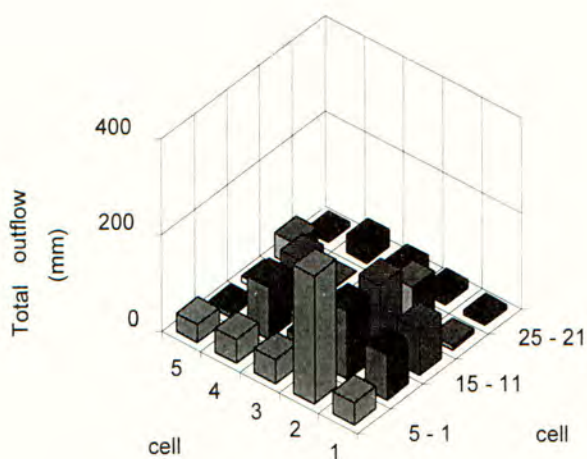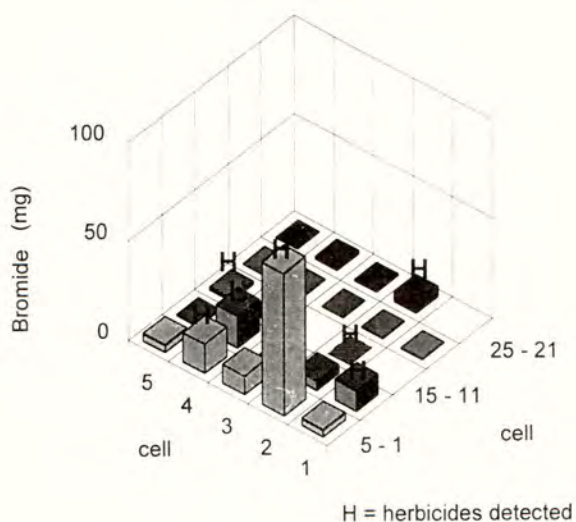FIGURE 2. Distribution of cumulative drainage after 153 mm
precipitation.

H = herbicides detected

FIGURE 3. Distribution of bromide after 153 mm precipitation.

TABLE 1.   Soil texture at four different depths, (%).

Depth	20 cm	40 cm	70 cm	110 cm
sand	72	61	92	95
silt	19	22	4	3
clay	9	17	4	2

The central unit of the lysimeter consists of a steel frame holding 25 individual suction plates (cells) which cover a total cross sectional area of 0.64 m^2 (Figure 1). The hydraulic contact between the soil and the cells of the lysimeter was secured by silt. In order to maintain unsaturated flow conditions within the soil profile a suction of 2 kPa was exerted to each suction port (Figure 1). Outflow was collected by an automated time-dependent sampling device. The cell block was installed by digging an access pit 1.6 m deep beside the experimental plot. From this pit the cell block was driven horizontally into the soil at a depth of 1.1 m beneath the lysimeter, after excavating a cavity. Hence, the soil unit under study was not affected by surrounding side walls.

Rainfall was simulated by an automated spray bar, while natural precipitation was prevented. Time domain reflectrometry (TDR) probes and tensiometers were used to register soil water content and suction at different soil depths. Terbuthylazine (1 kg/ha), isoproturon (1 kg/ha) and bromide (200 kg/ha) as an indicator of water flux were applied to the initially dry soil. The intermittent irrigation scheme shown in Figure 4c started on the following day.

RESULTS

Lysimeter

The input/output water balance demonstrated the lysimeter was functioning properly:

rainfall		+ 153 mm
drainage		- 48 mm
storage	(as registered by TDR)	- 75 mm
evaporation	(as calculated from Haude equation)	- 27 mm

However, the spatial distribution of the drainage was highly irregular, (Figure 2). About 50% of the outflow was limited to 20% of the lysimeter cross-sectional area. The outflow varied from < 2% up to 500% of the mean cell drainage (48 mm). The highest drainage amount (cell 2) was almost twice the rainfall depth, indicating horizontal influx. During the experimental period 1.1% of the applied bromide was eluted. Only partial agreement of the spatial distribution of leached bromide and water flow was observed (Figures 2 and 3). Dilution effects due to horizontal flow paths are likely to account for the differences. Herbicides were detected in the outflow of seven cells.
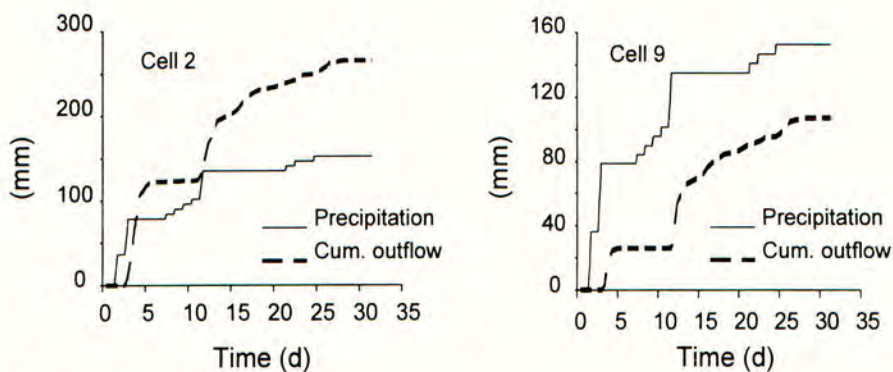
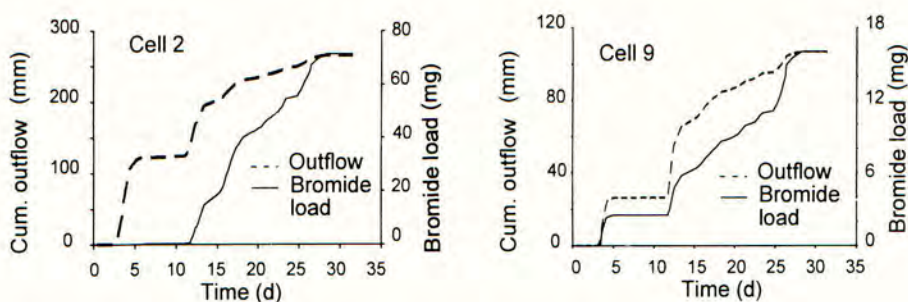FIGURE 4a. Cumulative outflow and precipitation of cells 2 and 9.

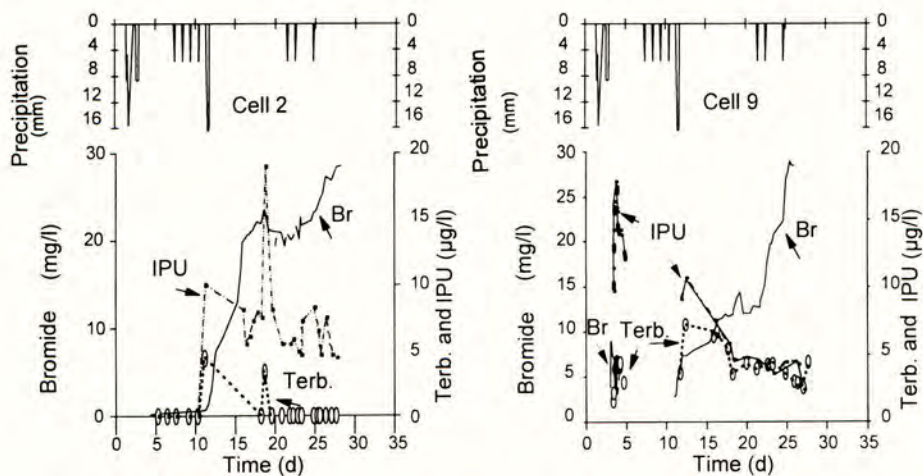FIGURE 4b. Bromide load and cumulative outflow from cells 2 and 9.

FIGURE 4c. Breakthrough curves of bromide and two herbicides of cells 2 and 9.

<u>Cell level</u>

Cells 2 and 9 can be used to demonstrate two different flow and transport patterns. A rapid breakthrough with the onset of rainfall was observed in both cells (Figure 4a). However, the total drainage differed in the cells and was 2- and 5-times higher respectively than the mean of all cells. The cumulative outflow of cell 2 exceeded precipitation by as much as 100 mm. A different pattern of bromide leaching was also detected for the two cells (Figure 4b). Bromide was found in the first effluent of cell 9 whereas in cell 2 a considerable time lag of seven days occurred between the onset of drainage and bromide appearance. The two distinct bromide load curves may point to preferential solute movement and matrix flow conditions in cells 9 and 2 respectively.

First appearance of the herbicides was not influenced by adsorption as indicated by their near-simultaneous appearance with the non-reactive tracer (Figure 4c). The pronounced preferential transport situation of cell 9 led to high concentrations of both herbicides in the first drainage event. Bromide reached an initial peak within the same outflow event. A further rise in bromide concentration may be attributed to matrix transport. In contrast to cell 9, no early bromide peak was observed in cell 2. The increase in bromide concentration in this cell corresponded to the second concentration rise of cell 9. Even though matrix flow may be considered as the dominant transport process in cell 2, the isoproturon breakthrough curve (BTC) was not clearly shifted to the right with respect to bromide. The transport behaviour of the pesticide did not support the matrix flow assumption deduced from the bromide BTC.

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A STUDY OF SUSPENDED AND COLLOIDAL MATTER IN THE LEACHATE FROM LYSIMETERS: IMPLICATIONS FOR POLLUTION AND LYSIMETER STUDIES.

F.Worrall, A.Parker, J.E.Rae

Postgraduate Research Institute for Sedimentology, The University, Whiteknights, Reading, RG6 2AB.

A.C.Johnson

Institute of Hydrology, Wallingford, Oxon., OX10 8BB.

ABSTRACT

In order to investigate transport mechanisms for pesticides in the unsaturated zone, an array of mini-lysimeters was set up at Reading University using soil from ADAS Rosemaund (Hereford and Worcester, U.K.). The leachates were collected and volume, pH, dissolved organic carbon content, suspended sediment concentration, suspended sediment composition and isoproturon concentration were determined for each sample. The results suggest that:

(i) the concentration of the suspended matter decreased over the period of sampling, but not monotonically;
(ii) the suspended matter had a distinct composition (e.g. increased organic carbon content relative to the top soil) that would increase its potential for transporting pesticides;
(iii) the dissolved organic carbon content was highest in the initial samples where it reached values of around 400 mg/l and
(iv) the concentration of isoproturon was also highest in the initial samples (up to 800 μg/l) and was below detection limits after 30 days.

The results also suggest there may be flushes of material following cultivation in the field that potentially could transport significant quantities of the applied pesticide. The suspended sediment concentration is not necessarily high during the initial period of sampling, which suggests it is of secondary importance to the dissolved organic carbon content, which is at its highest during the period of greatest isoproturon leaching.

INTRODUCTION

Bypass flow (overland or vertically through macropores) has been identified as an important mechanism for transporting pesticides to surface and groundwater (e.g. Foster et al., 1991; Williams et al., 1991). Pesticides can be transported by bypass flow either in solution or in the adsorbed state on suspended or colloidal matter. Worrall et al.,

(1993) reported results of a study of the properties of vertical bypass flow, which investigated the suspended and colloidal matter in the leachates from lysimeters. Lysimeters have subsequently been set up for another season in order to look in greater detail at the temporal occurrence of suspended and colloidal matter in the leachate and also its composition and relation to pesticide movement. The question of the source of the material in the leachate is discussed elsewhere (Worrall *et al.*, 1994).

Soil from ADAS Rosemaund (Hereford and Worcester, U.K.) was used in a series of mini-lysimeters at PRIS (Reading University) over the period December 1993 to March 1994. The soil is a typic brown earth, Bromyard series, with 16% clay, 66% silt and 18% sand.

METHODOLOGY

The mini-lysimeter design (Worrall *et al.*, 1993) was developed for its ease of construction and handling, making it possible to set up and monitor a relatively large number of lysimeters in a very short space of time. The lysimeter soil core is taken by hammering into the soil a 15x20 cm section of uPVC drainpipe, with a bevelled lower edge, until it is flush with the field surface. The core is then carefully extracted and placed on top of the collector device, which is housed in a 15x30 cm section of uPVC drainpipe and consists of a gauze stretched over a glass funnel which feeds into a 0.5l glass bottle. The two sections of pipe are then glued and taped together so as to prevent water entering through the join and left free-standing at a site on the university campus. In total, eight lysimeters were used over the entire season. To avoid the problem of shrinkage away from the walls of the lysimeter, the experiment was run only during the winter months (November 1993 to March 1994), when the soil was most likely to remain above field capacity and therefore suffer less from shrinkage.

A dose of isoproturon ("Javelin Gold") was applied to all lysimeters by hand sprayer (500 g of AI/ha) and they were left to stand under natural precipitation. The leachate was collected at regular intervals, at least once a week starting from the first week of December. The volume and pH of the leachate was recorded immediately before filtering through a 0.45 μm cellulose nitrate filter and the pH of the solution remeasured. For the purpose of this study, suspended matter was arbitrarily defined as being larger than 0.45 μm and colloidal matter as being smaller than 0.45 μm.

After filtration the leachate was sub-sampled so that both the dissolved organic carbon content (DOC) and the isoproturon concentration could be measured. The DOC was measured using an Astro 2001 carbon analyser (the DOC content is taken as a proxy measure of the colloidal-matter content of the leachate, as very few mineral particles have sizes below 0.45 μm). The isoproturon was analysed by HPLC with UV detection at 240 nm, using a mobile phase of 50% water, 31% methanol and 19% acetonitrile. No pre-concentration steps were performed on the samples and so the detection limit was relatively high - 20 μg/l

The residue from the filtration process was dried and weighed in order to calculate the concentration of suspended matter. If the size of the sample allowed, the sample was analysed for its total organic carbon content (TOC) by wet titration (Gaudette *et*

al., 1974).

Throughout the period of the experiment, the amount of rainfall and the grass minimum temperature were recorded at the long-established meteorological station on the university campus. The grass minimum temperature was recorded as a means of assessing the effect of freeze/thaw action on the release of sediment to the leachate.

RESULTS

The concentration of suspended matter decreased over the season, but not monotonically (Figure 1). All lysimeters showed the same general pattern with three observable peaks in suspended sediment levels and no correlation with the volume of the leachate. The reasons for this pattern appear to be complex. In Figures 2a, b and c the sediment concentration is compared with the rainfall and the grass minimum temperature over certain periods within the experimental season. In Figure 2 it can be seen that there is little correlation between the sediment released and either meteorological indicator. For example, in Figure 2a the heaviest rainfall events (those most likely to cause bypass flow events) occur after the peak in sediment concentration. Similarly, in Figure 2b there is little apparent correlation between freeze/thaw cycles and peaks in the sediment concentration. Towards the end of the sampling period (Figure 2c) the sediment concentration goes into decline, coming close to zero as the amount of material available to be moved decreases.
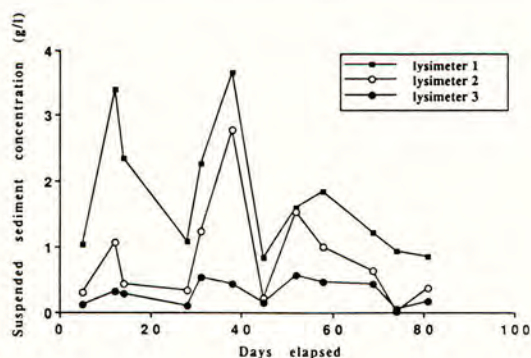

FIGURE 1. The change in the suspended sediment concentration in the leachate of three lysimeters over the period of the experiment.

The TOC of the suspended sediment in the leachate showed a significant difference (by t-test at the 95% level) from that of the top-soil (taken at 5cm below the surface). Samples were taken from different lysimeters at different times and showed no temporal trends but averaged 3.36% TOC (s.d. =1.06) whilst the top-soil had a TOC of 1.65% (s.d.=0.17).

The occurrence of DOC in the leachate of the lysimeters followed a consistent pattern, illustrated for one of the lysimeters in Figure 3. The levels of DOC dropped
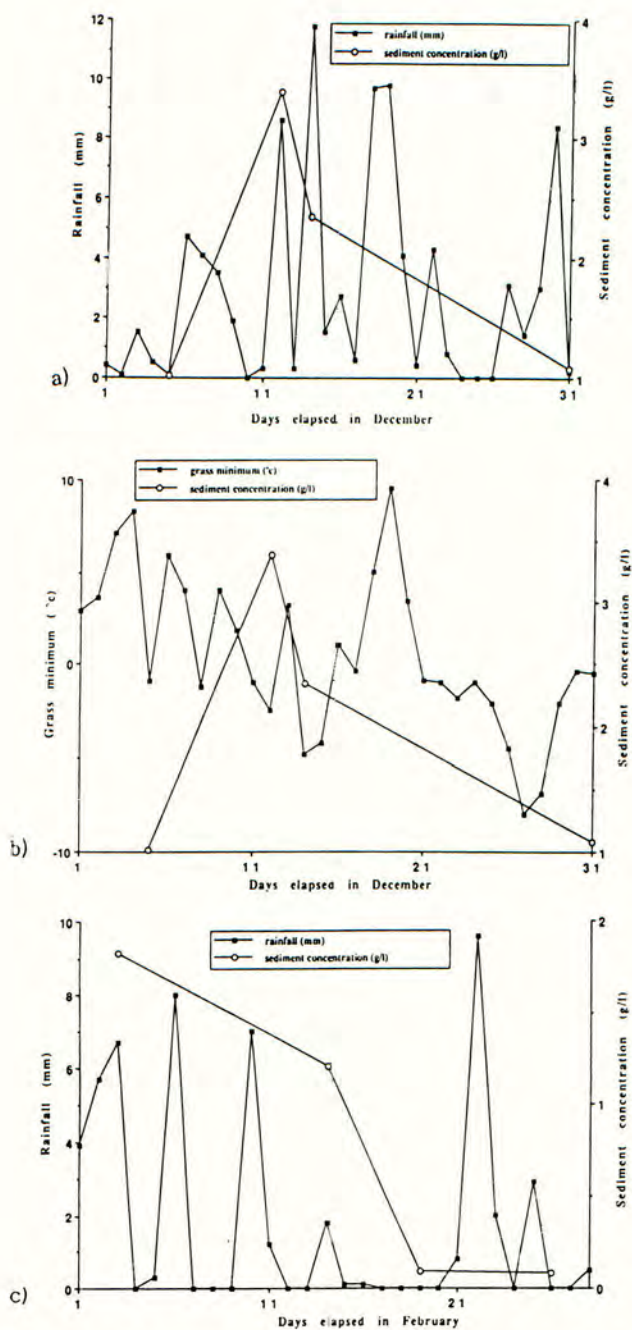
FIGURE 2. Daily plots of suspended sediment concentration in leachate from Lysimeter 1 compared with: a) rainfall for December; b) grass minimum temperature for December and c) rainfall for February.

rapidly to a background level within two samples. This initial flush shows that there is a limited amount of DOC available which is readily mobile. The background levels can be ascribed to the natural turnover of the soil's organic matter content, whilst the initial flush may result from the disturbance caused by the setting up of the lysimeter, exposing fresh material to mobile water. The implications of this initial flush are discussed below. Isoproturon appears in the leachate only in the initial samples (Figure 4) and drops below the detection limit within 30 days for all lysimeters. However, the decrease is not as sharp as that for DOC and there is no readily observable background level at this detection level.
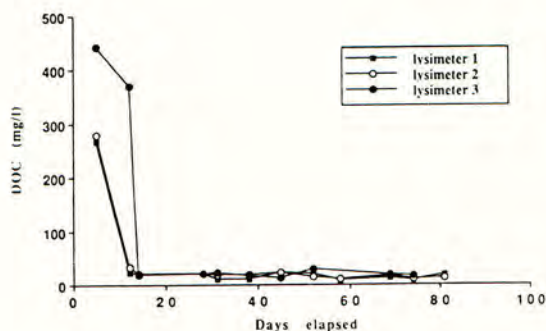

FIGURE 3. Occurrence of dissolved organic carbon (DOC) in the leachate of three lysimeters over an 82-day period.
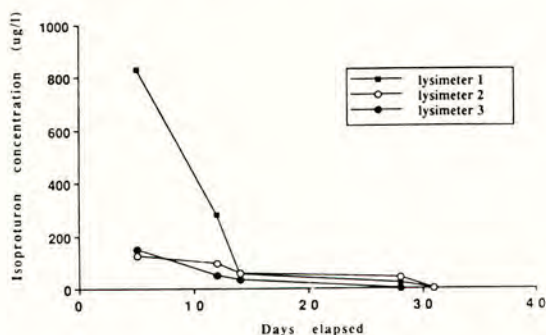

FIGURE 4. Isoproturon in the leachate of three lysimeters over a 32-day period.

DISCUSSION AND CONCLUSIONS

This study has shown that the release of suspended matter into the leachate is not easily explained, although the size of the reservoir of available material is one

controlling factor . The composition of this sediment would lend itself to adsorbing and transporting pesticide. The high TOC relative to the matrix would increase the potential to transport all types of pesticide, but especially those of a low solubility and/or a high K_{oc} (e.g. pyrethroid insecticides).

The DOC released from these lysimeters appears related to the disturbance caused by digging them. If this type of process occurs at a field-scale then flushes of DOC could be expected after mechanical disturbance such as ploughing. This colloidal carbon may be particularly important for carrying the more insoluble pesticides, which would not normally be transported in significant amounts in solution.

This study demonstrates the different behaviour of the suspended and colloidal phases, presenting the question - which is the most important for pesticide transport? The actual amount carried on these phases has not been looked at directly, but from the distribution of the phases it can be inferred that the colloidal matter is the most significant. Means and Wijayaratne (1982) suggest that partition coefficients (Kd) for colloidal matter are relatively high compared to those for soil. In the current study the greatest movement of pesticide observed coincides with DOC availability. The suspended sediment concentration is not at its highest in the initial samples.

ACKNOWLEDGEMENTS

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