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Hydrochemical Processes Controlling Pesticide Mobility in Structured and Non-structured Soils

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Introduction

Since the discovery in the early 1980s of trace levels of pesticide residues in well water in many agricultural areas of the USA, there have been numerous reports of water contamination by these compounds in most countries where intensive agriculture is practised. There has subsequently been increased research interest aimed at understanding the processes that control the penetration of pesticides into soils and the subsequent contamination of water systems. The most widespread contaminants from agriculture are soil-applied herbicides used in major crops such as cereals, and the extent of water contamination is often (but not always) associated with autumn and winter rather than spring or summer application.

A number of mathematical models are available to predict the redistribution of pesticides in the surface soil layers. Most of these models are based on conventional chromatographic transport theories, and they rarely predict significant transport to drain water or deep groundwater. It is now widely recognised that macropores in soil such as cracks, fissures, root and worm channels, provide routes for rapid flow of water through soil. In some circumstances, solutes which are normally adsorbed may pass through the macropores so quickly that they have insufficient time to diffuse into the micropore structure or to reach equilibrium in adsorption reactions. Pesticide degradation rates and adsorption are often broadly related to soil organic matter content with faster degradation and greater adsorption with higher organic content. Hence the small proportion of an applied pesticide that leaches to deeper soil horizons may eventually pollute groundwater or be carried by drains to neighbouring streams and rivers. That which stays in the deeper soil horizons may be more persistent and more readily mobile than that in the upper soil profile.

The main aims of this project were to investigate how various hydrological, physico-chemical and microbiological processes interact to determine penetration of pesticide residues into soils with and without potential for bypass movement. The objectives were (1) to gain further basic information from field and laboratory experiments on how rates and routes of water flow interact with rates of pesticide degradation and adsorption/solution reactions to determine drainage water concentrations of pesticide, and (2) to provide a comprehensive data set which can be used to evaluate and improve mathematical models of solute transport that take account of both micro and macropore processes.

Sites, soils and herbicides

The experimental sites were located at Temple Balsall, Warwickshire, and at Oxford University Farm, Wytham, Oxford. The soils selected at Temple Balsall were an non-structured sandy loam (typical of the Ollerton and Newport series) and a moderately structured clay loam (Brockhurst series), whereas that at the Wytham site was a highly structured heavy clay (Denchworth series). These soils will be referred to throughout the text as the sandy loam, clay loam and clay soils respectively. Typical analyses of soil from profile pits dug at the three sites are given in Table 1.

The non-structured sandy loam soil had a brown to dark brown sandy loam upper horizon which merged downwards into brown or reddish brown structureless subsoils of loamy sand or sand. Soils of the Ollerton and Newport series are generally very porous but ped strength is extremely weak leading to possible capping of the soil surface or occasionally bad compaction and pans at the base of the plough layer.

The moderately structured clay loam soils of the Brockhurst series are typified by fine loamy A and E horizons over reddish clay B horizons. The structure is moderately developed sub-angular blocky leading to a coarse prismatic structure in the lower subsoil. In dry periods, the surface horizons crack, often to below 50 cm thus providing the potential for preferential flow pathways. Drains are usually installed in these soils at 30-40 m spacing.

The highly structured clay soils of the Denchworth series have a dark brown clayey Apg horizon with a well-developed sub angular blocky structure overlying an olive clayey Bg horizon which has a strongly developed coarse angular block structure. The soil can be waterlogged for long periods in winter but in dry conditions at other times of year it develops deep cracks. These soils are often drained artificially with closely spaced (20 m) pipes and gravel fill supplemented by mole drains.

The main pesticides selected for study were the soil-applied herbicides alachlor and isoproturon. They are used for pre- or early post-emergence weed control in the two major UK autumn sown crops; oil-seed rape (alachlor) and winter wheat (isoproturon). Average field half-lives derived from the literature indicate that alachlor (DT50, 15 to 35 days) may be less persistent than isoproturon (DT50, 25-50 days). Both compounds are relatively weakly adsorbed by soil with average partition coefficients between organic carbon and the soil solution (Koc-values) of 170 (alachlor) and 110 (isoproturon). The vapour pressure of alachlor (2.9 mPa) indicates a slight potential for volatilisation, whereas that of isoproturon (0.0033 mPa), suggests that it is non-volatile.

Laboratory and small scale field studies

Degradation studies

The adsorptive and degradative properties of the different soils were characterised in detailed laboratory studies using standard methodologies. Incubation experiments were made with both herbicides in the sandy loam and clay loam soils, and with isoproturon only in the clay soil. All incubations were made at 15°C and with soil moisture adjusted to that equivalent to an applied pressure of 33 kPa. The results in Table 2 show a relatively rapid rate of degradation of alachlor in soil from the 0-20 cm horizon; first-order half-lives were approximately 23 days in the sandy loam soil and 12 days in the clay loam soil. Half-lives in soils from deeper in the profile were much longer showing much slower degradation in the subsoils. In the deepest sample from the clay soil (60-80 cm) the half-life was greater than 1 year. The data indicate that isoproturon was more persistent than alachlor in the different topsoil samples, and the degradation rate for both herbicides generally declined with depth. In the heavy clay soil, isoproturon degradation rates also showed marked variations between the different soil horizons, with the most rapid rate of loss in the narrow soil zone in which straw from a preceding cereal crop was located. The data showed an overall correlation between rates of loss of both compounds and soil microbial respiration (Figure 1). The results of further experiments to investigate the effects of temperature and soil moisture on degradation indicated a strong effect of temperature (average Q_{10} of 2.3), and a considerably reduced rate of loss in drier soils.

Adsorption studies

Standard slurry techniques were used to measure the adsorption distribution coefficients (K_d-values) of the two herbicides in the different soils. This involved shaking 2-mm sieved, air dry soil (5 g) with a solution of the appropriate herbicide (20 ml; 2.0 g/ml^{-1}), and measuring the concentration in solution after 24 hours. The K_d-values, defined as the amounts adsorbed by unit weight of dry soils at unit equilibrium solution concentration, are summarised in Table 2. They indicate much reduced adsorption in soils from the deeper horizons which would be expected on the basis of their lower organic carbon contents (Table 1).

Although the above method for measuring adsorption of pesticides by soils is the standard procedure for deriving distribution coefficients, it is somewhat unrealistic compared with the situation in soils in the field. In the field, water containing pesticide will flow through moist soil, and with intense rainfall events, the residence time might be quite short. A series of experiments was made to measure the rate of adsorption of the herbicides by fresh soil samples that were not vigorously shaken. With the highly structured clay soil, different sized aggregates were also studied (< 3 mm; 3-6 mm; > 6 mm). Adsorption measurements were made in a 1:1 soil:solution mixture and the samples were mixed by very gentle swirling at the beginning and end of each equilibration period. Three initial soil moisture contents were studied - 25, 50 and 100 % of the 33 kPa moisture content (Table 1). The results with isoproturon and the Denchworth clay are shown in Figure 2. There was little difference in the results between the different initial moisture contents, and the results shown are for the wettest treatment only. They indicate slow adsorption over the 8 hour experimental period, with marked differences between the different sized aggregates. In the system most close to the field situation (large, moist aggregates), adsorption in the first 0.5-1 hour was very low indicating that under conditions of high water flow, the extent of equilibration with soil surfaces during downward transport of pesticide may be limited. Results with the non-structured sandy soil (not shown) also demonstrated slow adsorption by fresh soil in static systems, although the measured K_d-values were similar to those measured by the shaken slurry technique within about 4 hours. The results with alachlor were similar to those with isoproturon. A definition of adsorption distribution coefficients is a key component of any model of pesticide transport in soils, and the present data strongly suggest that particular attention must be paid to the way in which this parameter is derived.

Mini-lysimeter experiments

After initial application of a pesticide to the soil surface, subsequent movement in the soil will be controlled in part by the rate of degradation of the chemical in the soil which will determine the total concentration remaining, and by the partition of the total residue between the adsorbed and solution phases. Mini-lysimeter experiments were made with the non-structured sandy loam and moderately structured clay loam soils to investigate these two parameters in the field. Attempts were made to use the highly structured clay soil in the same types of experiment, but the techniques used were not appropriate to this type of soil when wet in the winter months. Plastic columns (20 x 20 cm) were inserted into the sandy loam and clay loam soils at the field sites immediately prior to spraying the herbicide alachlor. They were carefully removed after spraying and mounted in a mini-lysimeter system exposed to natural conditions outdoors. They were prepared such that drainage water could be collected from three replicate samples of each soil. A further three replicate samples of each soil were used to assess total (acetone) extractable residues, and aqueous available residues in the top 2.5 cm of soil. The latter were measured by placing a number of small soil cores in the body of a disposable plastic syringe plugged with glass wool, adding sufficient water to raise moisture content to field capacity, and centrifuging after 30 minutes equilibration time. In a sequence of experiments made over a 3-year period, it was demonstrated that the rate of decline in aqueous available residues was consistently faster than the rate of decline in total extractable residues (example in Figure 3), with again clear implications for the availability of herbicide for transport in the aqueous phase.

Sectioning of the soil columns at the end of the experiments demonstrated only limited movement of alachlor in the soil with residues largely confined to the top 10 cm, whereas analysis of leachate water demonstrated significant concentrations of the herbicide (up to 18 g/l) on most occasions when water was collected. Additional studies were also carried out with undisturbed soil columns taken from the field which included dye tracing studies to characterise flow pathways and structural features, monitoring of soil water status in the surface to determine when macropore flow and matrix flow were generated, collection of leachate from macropores and the soil matrix and the application of different artificial rainfall regimes.

Lysimeter studies with large soil columns
More detailed, direct comparative studies of the behaviour of alachlor and isoproturon were made in a lysimeter system involving the sandy loam and clay loam soils. The lysimeter system comprised 12 rigid PVC columns, 50 cm long and 30 cm diameter, 6 of which contained the sandy loam soil and six contained the clay loam. They were taken from the field sites in April 1993 and May 1994, mounted in the lysimeter station, and used in the autumn of the two years after 6-month equilibration periods. Alachlor and isoproturon were sprayed on the soil surface of all lysimeters at the normal dose on 23 October 1993 and 17 October 1994. The herbicide pendimethalin was also applied for comparative purposes. Pendimethalin is stable (field DT50, 50-80 days) and strongly adsorbed (Koc, 1600-2000). In the 1993 experiments, tensiometers were introduced into replicate lysimeters of each soil at depths of 5, 15, 25, 35 and 45 cm with recordings taken via pressure transducers. Recording at 5 minute intervals was triggered by a rain gauge, and all data was stored on an automatic data-logger. Measurements taken included the vertical redistribution of residues in the lysimeter columns by destructive sampling of single large columns at monthly intervals. Changes in available concentrations near the soil surface were also measured as above, and drainage water concentrations were measured following significant rainfall events. The results were generally consistent with the laboratory data. The order of persistence was alachlor < isoproturon < pendimethalin. Mobility in soil was in the order isoproturon > alachlor > pendimethalin. Leachate concentrations were also in the order isoproturon > alachlor > pendimethalin, with greater losses from the clay loam soil than from the sandy loam soil in both years of the experiment (summarised in Table 3). The tensiometer data were consistent with matrix flow in the sandy lysimeters with evidence for the progressive movement of a wetting front through the soil. After the first major rainfall event, the time taken for the wetting front to move through the 50 cm soil column was approximately 18-20 hours. There was evidence for bypass flow in the clay loam lysimeters since a pressure head of water developed in the surface soil layers with no indication of a change in soil water potential at depth even though similar volumes of leachate water were collected from both soil types. These contrasting patterns of water flow are entirely consistent with the differences in leachate amounts shown in Table 3.

Field studies

Approach and methods

Non-structured sandy loam soil
Three replicate plots of 20m x 20m were instrumented within a field drilled with oil seed rape. Alachlor was applied as a pre-emergence herbicide at a rate of 1.92 kg/ha on 18 September 1991 and on 21 September 1992. Different fields were used in each year but soil types were selected to provide similar texture, organic matter and structure for the experiments. Data collected during a 1990 experiment were also available to the project. Instrumentation was installed to monitor and sample the vertical soil water fluxes in the profile. Suction samplers were used to abstract soil water as it moved down the unsaturated soil profile. Overland flow

was monitored after it became apparent that capping of the soil surface generated the lateral movement of water.

Structured clay loam soil
Instrumentation at the clay loam site was similar to the sandy loam site but sampling depths were varied to take account of differences in the soil profile. 'Grab samples were taken from artificial drains (of approximately 40m spacing and 0.6m depth) and surface waters following rainfall events of 10mm or more. Alachlor was applied on the same days as the sandy loam sites.

Structured clay soil
In response to rainfall, changes in soil hydrology and water flow were measured automatically in a mid slope field plot. The 600 m^2 field plot was hydrologically isolated from the rest of the field by a series of ditches and flow capture devices. Equipment was established to monitor water flows over the soil surface (overland flow), within the upper soil horizon (lateral subsurface flow) and in the field and mole drains (drain flow). The fieldwork was continued for three seasons, with isoproturon applied at 2.5 kg/ha to winter cereals on 10 February 1993, 12 March 1994, and 17 November 1994.

Soil samples were taken from areas adjacent to all the monitoring plots to determine field dissipation rates.

The relative importance of different flow routes for water movement
Sandy loam and clay loam field sites were not automatically monitored so comprehensive data on hydrological balances cannot be provided. Data from surface traps collected after rainfall events during October 1992 suggested that up 0.54 % of rainfall was monitored as overland flow at the sandy loam site whilst up to 3 % of rainfall was monitored as overland flow at the clay loam site.

The total amounts of rainwater that were measured as flowing out of the clay soil plot ranged from 8 to 24 % in the 1993-94 season. Of this proportion, 63 to 87 % left the plot in the drainage system. On the events when it occurred, no more than 3 % of the outflowing water left the plot via overland flow. The quantity of outflow water in lateral subsurface flow varied between 13 and 34 %. The largest proportion of lateral subsurface flow water as a proportion of the whole was on 31 March 1994, and the smallest on 25 May 1994.

It is important to note that only a fraction of water monitored as overland flow from within hillslope plots on all soil types was actually seen to directly enter surface waters. Field topography usually promoted the infiltration of water at downslope locations. Vegetated headland areas of approximately 0.5-1m width intercepted remaining water.

Figure 4 shows the dominant flow pathways for the contrasting soil types studied and gives approximate proportions of water flow for the different routes.

The relationship between water flow and soil structure

Non-structured sandy loam soil
Fluxes of water in this soil were predominantly vertical and classical convective movement was concluded on the basis of tensiometer data from both lysimeter and field data. Dye tracing studies showed that limited preferential flow did occur via worm channels in the topsoil,

particularly after heavy rainfall had broken the weakly structured surface aggregates and the bare soil surface 'capped over. Surface infiltration capacity was restricted by this process and it was at this time that overland flow was generated.

Structured clay loam soil

Surface aggregates in the clay loam soil were larger and of greater strength than the sandy loam site and retained their structure during the period of pesticide application and several weeks after. Infiltration capacity of the topsoil was never exceeded as water moved between aggregates. Worm channels, ped faces and incorporated straw at the base of the topsoil appeared to act as preferential pathways for water. The coarse porosity of the subsoil matrix decreased down the profile and water movement occurred in the occasional worm channel or between the faces of the prismatic structures. A perched water table developed in autumn of both years at the base of the plough layer and a deeper water table which was monitored at 80 cm depth rose to 25 cm during the wettest periods of monitoring. It is anticipated that the perched water moved laterally and infiltrated the subsoil via the preferential flow routes. Drain flow commenced before profile field capacity was reached indicating preferential pathways in this soil were responsible.

Structured clay soil

There was a clear delineation between an upper soil horizon with a bulk density of 1.24 g/cm^3 and a lower horizon of 1.5 g/cm^3. The soil matrix in both horizons have a very low hydraulic conductivity (they possess a clay content of 57-63 %). Such that in response to rainfall it could be reasonably expected that a wetting front would reach the mole drains (at 50 cm) only after several days. However, during winter it may take not more than 2 hours for the drains to start flowing in response to rainfall. This rapid response is achieved by water by-passing the soil matrix via macropores. In the critical winter period these macropores include inter-aggregate spaces, fractures, worm burrows, plant roots and the moling fissures. The substantial shrinkage fractures which appeared in summer did not coincide with the herbicide application/rainfall period. Results from tensiometers and dye experiments suggested that lateral water movement was concentrated not at the interface between the two horizons but within the top 6 cm of the soil. Water could flow laterally between the aggregates of 0.4-1.5 cm diameter present in this layer. Most probably the structure in this upper part of the soil was a result of a rotavation cultivation technique. Thus, once the upper horizon had saturated to within 6 cm of the soil surface then significant drain flow could be detected. Once top soil saturation has occurred the route taken by the new rainwater and its load of pesticide may therefore be via (a) inter-aggregate spaces, (b) worm burrows, and (c) moling fissures until it reaches the drains. It does not interact or become diluted in a deeper water table. This macropore journey may take only a matter of minutes, such a short transport period clearly limits the opportunities for pesticide readsorption. An aspect of the speed of vertical water movement once drainflow has been established can be seen in the low chloride/sulphate drain water concentration compared to the soil matrix. The movement of chloride/sulphate present in the soil pore water in the soil matrix into the macropores is limited by the diffusion rate. Only when the water is moving slowly through the soil can requilibration occur and the drainwater chemistry begin to reflect the soil porewater (see Figure 5).

The relative importance of different flow routes for pesticide transport

Non-structured sandy loam soil

When water was able to infiltrate the topsoil hydrological monitoring data showed that it moved down the profile mainly as a chromatographic flow. However in October 1991 alachlor was detected in soil water samples at 150 cm depth within 14 days of application. This followed a period of three days when 55 mm of rain fell (an event equivalent to a 1 in 5 year return period). Inspection of the installation of the sampling equipment revealed that the coarse porosity of the repacked sandy material was up to 40 % greater than the surrounding undisturbed soil and preferential flow was actually initiated by the sampling process (Table 4). In 1992 bentonite was backfilled around installed equipment and the majority of pesticide in the soil solution was observed at 25 cm depth (maximum of 51.8 g/l) with amounts of 1 g/l or less detected in the deeper soil layers. The impact of leachate on groundwater quality (which was present at approximately 2 m depth at both sandy loam sites) was minimal. Concentrations of overland flow were highest (1.95 mg/l in October 1991) at the sandy loam sites (Figure 6) and losses as a percentage of applied active ingredient were 0.68 %* and 0.002 %* for 1991 and 1992 respectively.

Structured clay loam soil
Water and thus soluble pesticide transport appeared to occur mainly in macropores or inter-aggregate spaces and was confirmed by dye tracing studies, though there was a certain amount of diffusion of dye into the immediate surface of aggregates. Soil water sampling indicated that preferential flow had occurred as concentrations of alachlor were on occasions greater at 40 cm than at 25 cm. The maximum concentrations detected in soil water were 1.06 g/l and 2.84 g/l at 40cm depth in 1991 and 1992 respectively and are slightly greater than those observed in the sandy loam subsoil. Concentrations in drain water (approx 60 cm depth) were very similar to those detected in soil water at 40cm suggesting a by-pass mechanism to the artificial drainage system. The concentration of alachlor in overland flow was greatest during the first event after application with a maximum of 161 g/l in October 1991 (Figure 6). Losses as a percentage of applied active ingredient were <0.08 %[1] and 0.008 %[1] for 1991 and 1992 respectively.

[1] values are calculated for a 5.5 m^2 area within the field and do not reflect amounts lost from the field as a whole, they could however represent an extreme worst case assessment.

Structured clay soil
Of the three preferential flow routes discussed, the lowest concentrations of pesticide were found in the lateral subsurface flow water. The concentrations in drain water being 1.5 to 1.6 times higher at times of maximum flow. The overland flow water and drain water pesticide concentrations were very similar. If all of the preferential flow water initially collects its pesticide from a pool at the soil surface before being transported in different directions, then the lateral subsurface flow water loses approximately one third of its pesticide as it flows out of the plot. This is in contrast to other solutes such as nitrate and chloride in which the same proportions are carried as in the other flow routes (see Figure 7). This suggests that pesticide is being readsorbed as it travels through the soil via lateral subsurface flow.

Although high pesticide concentrations could be found in overland flow water, as little of the rainwater left the plot by this route, no more than 3 % of the pesticide was lost from the plot in this manner. Notwithstanding the depth of the drains from the soil surface, the drain concentrations were very similar to those found in overland flow. This suggests that little pesticide was readsorbed as it moved down vertical macropores, and within the drainage system. This is despite organic matter coatings on any of the worm burrows which functioned as macropores and ped faces. The use of a dye with undisturbed soil in the mini-lysimeter experiment (see Figure 8) illustrated the important role of worm burrows in conveying water below 12 cm. Thus, due to the large volumes of water and high pesticide concentrations the drainage system carried 75 to over 90 % of the pesticide lost from the plot in the different rain events.

Comparison of pesticide behaviour and transport

Non-structured sandy loam and structured clay loam soils

In autumn 1991 two rainfall events of 25 and 31 mm within 8 and 10 days of alachlor application caused soil water to drain in the soil profile. Much larger concentrations were detected in soil water at the sandy site and whilst leaching to depth has been attributed to problems associated with equipment installation, the low organic carbon content of this soil (0.9 %) may have exacerbated the leaching potential of this soil type. In 1991 the Kd for alachlor in the sandy loam soil was 2.16 compared to 4.37 in the clay loam soil and differences in concentrations and loadings of alachlor were probably due to differences in sorption and aqueous availability. In autumn 1992 rainfall was 129 % of the average but only 3 events exceeded 10mm. Alachlor residues at 60 days after application at both sites were similar to those detected in 1991 after 111 days suggesting that dissipation was faster in 1992 than 1991 due to greater leaching (excess winter rainfall in 1992 was 45 mm greater than 1991). In autumn 1992 concentrations of alachlor in overland flow were similar for the clay loam and sandy loam sites, but loadings for the clay loam site were higher due to the greater volume of run-off. The sandy loam soil did not cap and therefore infiltration of rainfall was greater. Preferential flow pathways in the subsoil of the clay loam site appeared to provide the opportunity for greater concentrations of herbicide to be transported via drain flow to a water resource as drainflow concentrations were greater than soil water concentrations measured in the sandy subsoil. The lack of interaction with the total soil matrix decreases sorption despite the higher K_d value of the clay loam soil. Laboratory experiments have indicated that the standard slurry test may not be a good indicator of sorption in these structured soils particularly when flow can be relatively fast.

Structured clay soil 1993 and 1994

In the 1993 season pesticide degradation followed the expected pattern until late May. From then on the small amount of residues left showed an increased persistence. Although the remaining pesticide appeared more persistent it could still be mobilised in rain events. Similarly in 1994 from late April onwards the pesticide appeared to be more persistent. Analysis of the weather and soil hydrological data for 1994 showed a developing soil moisture deficit in the topsoil during this period. This would reduce microbial activity due to moisture stress and so reduce degradation. It is interesting to note that after the rain storm in May 1994 the pesticide residues decline again more rapidly than before.

As in the 1993 season the pesticide was applied in late winter/early spring and rain events leading to drain flow occurred in March and April. A max concentration of 500 ppb was noted in the drain water on 1 April 1993 and 290 ppb on 31 March 1994. However, for the 1993 event more pesticide was present in the soil (2.9 mg/kg) than for the 1994 event (1.4 mg/kg). A greater amount of water and thus loss of pesticide through the drains occurred in the 1993 events. For the 1 April 1993 event of 12.7 mm rainfall, 32 % exited via the field drain. The estimated cumulative loss of applied pesticide to the drainage system for the 1992-93 season was 1.5 %. For the 31 March 1994 event (day 19) 10 mm of rain fell but only 5.7 % exited via the field drain. For this and other events, more rainwater appeared to be held by the soil in 1994. This can possibly be attributed to the mole drain network decaying from the previous season when it had only recently been created. The cumulative loss of applied pesticide for the 1993-94 season is shown in Figure 9.

Summary of observations

1) Isoproturon residues could be found in soil water from the previous years application, long after it would have been expected to be all degraded. Alachlor appeared to degrade relatively quickly and monitoring concentrations were negligible by 120 days after application.

2) If it is assumed the worm burrows and inter-ped spaces play a major part in conveying water to the drainage system, the similarity in overland flow and drain flow isoproturon concentrations at the clay site suggested that the worm burrows and ped faces did not adsorb significant quantities of pesticide, despite their potential for increased sorption. More sorption was apparent in the less well structured clay loam soil as concentration in drainflow were similar to those at 40 cm and not in the topsoil or overland flow. The standard slurry sorption test can no longer be considered appropriate for structured soils on the basis of the information generated from these experiments.

3) Over the course of the field season, notwithstanding variations in rainfall intensity, volume and antecedent soil conditions, calculations suggest that less of the aqueous phase of the pesticide is transported in successive storm events. This may indicate a change in adsorption equilibrium over time.

4) Hydrological, hydrochemical and soil physical evidence at the clay site suggested that the main part of the soil involved in lateral water flow, apart from the drains is the 0-6 cm layer of the soil. Infiltration was deeper at the clay loam site and lateral transport appeared to occur at the base of the plough layer where a perched water table developed.

5) Wide variations were observed in the performance of mole drains spaced only a few metres apart. This included both volumes of water and loads of pesticide transported. The major influence on this variability believed to be differential decay of the mole drain network.

6) Overland flow as a mechanism for pesticide transport was insignificant compared to other flow routes although pesticide concentrations were high. If this flow (particularly that which occurs following pesticide application) were to enter surface waters, environmental problems with respect to water quality and acute effects on aquatic flora and fauna might be experienced.

7) Lateral subsurface flow was more important than overland flow although less than drain flow in terms of load of pesticide carried at the clay site. An important factor in terms of the relatively low pesticide concentrations in lateral flow was believed to be the increased opportunity for readsorption to soil particles compared to the other flow routes. This is supported by the clay loam site where soil water residence time appeared to be longer than the clay site and pesticide concentrations much lower.

8) The drainage system was the major route for the exit of pesticides from the field in the clay loam and clay soils. When permeable fill was used in conjunction with the drainage system, flow and pesticide losses were more rapid and of greater concentrations.

9) The employment of mini-lysimeters and rainfall simulators suggested that rainfall intensity had a major influence on the quantity of pesticide released from the soil surface.

Conclusions

Alachlor was detected below the plant rooting zone in soil water taken from both the permeable sandy loam soil and the slowly permeable clay loam soil in 1991 and 1992. Leaching of solutes to depth is often considered to be greater in sandy soils than in clayey soils, yet similar concentrations were found at the greatest sampling depth in both soils emphasising the contribution of by-pass flow which is common in these soils. Alachlor concentrations in the drainflow were influenced by the effectiveness of the drainage systems with the more modem drains with gravel backfill allowing greater and more rapid movement of water and pesticide to surface water. Concentrations of alachlor in overland flow were very variable for each year and soil type. The highest concentrations were detected on the sandy loam site when rain fell shortly after application and overland flow interacted with newly applied chemical at the soil surface. Whilst this water was not observed to directly enter surface waters it is possible that infiltration caused the development of zones of enrichment and thus elevated concentrations in drain water.

Monitoring data showed that detections of alachlor on both soil types, particularly in the first few weeks after application were most dependent on antecedent conditions and the intensity of rain storm events. Laboratory data for the subsoils particularly the sandy loam suggested that alachlor could be very persistent, but data from soil water suction samplers suggested that field dissipation was much more rapid and consequently no large concentrations of alachlor were monitored entering surface water.

The high pesticide losses from the Wytham field site, which are amongst the highest reported in the European literature can be ascribed to (a) the rapidity of water movement through the soil minimising the opportunities for pesticide readsorption, (b) there is no interaction of this storm water with a deeper water table where dilution might take place, and (c) the efficiency of the drainage network in collecting the new storm water.

Even with farmers following good agricultural practice, on a clay drained soil, herbicides applied to winter cereals will reach nearby streams and ditches at levels which should give rise to concern. There is no advantage in spraying in early spring rather than late autumn. The largest pesticide losses which we observed were following early spring pesticide applications.

Water companies have now highlighted agricultural use of isoproturon as a major factor in non compliance with the EC water quality targets. The current design of uncultivated buffer strips can prevent direct overspraying and reduce drift into water courses. They may also prevent overland flow from directly entering streams and ditches. However, our research has highlighted the role of the drainage system in transporting pesticide to the nearby stream. As the drains run through the buffer zone they cannot affect this major pollution route.

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Further reading

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Table 1. Soil properties

Soil	Depth (cm)	Organic matter (%)	pH	Moisture content (% at 33kPa)	Biomass mgC/kg	Respiration mgC/kg/day
Unstructured sandy loam						
	0 - 20	2.05	5.75	15.95	452	7.25
	20 - 40	0.72	6.52	5.59	65	3.91
	40 - 60	0.32	6.47	4.09	52	3.56
	60 - 80	0.52	6.59	7.40	n.d.	5.02
Moderately structured clay loam						
	0 - 20	4.15	6.72	23.12	784	10.21
	20 - 40	2.13	6.28	14.43	108	2.87
	40 - 60	1.47	6.43	14.15	88	2.80
	60 - 80	1.58	6.79	19.65	64	2.66
Highly structured clay						
	0 - 25	3.10	7.80	45.60	n.d.	13.69
Straw layer		5.33	8.20	45.52	n.d.	21.30
	25 - 30	1.55	8.20	37.00	n.d.	5.40
	30 - 50	0.90	8.20	37.00	n.d.	3.30
	>50	0.40	8.30	37.30	n.d.	3.00

n.d. = not determined

Table 2. First-order half-lives and adsorption distribution coefficients for the herbicides in the different soils. (All data are means of 3 replicates).

Soil and depth	Alachlor half-life	Isoproturon half-life	Alachlor K_d-value	Isoproturon K_d-value
Unstructured sandy loam				
0 - 20	23.4	36.4	2.16	0.62
20 - 40	111.9	117.7	0.59	0.31
40 - 60	143.4	212.2	0.41	0.19
60 - 80	80.3	n.d.	0.38	n.d.
Moderately structured clay loam				
0 - 20	12.2	22.5	2.79	0.78
20 - 40	95.3	30.0	0.74	0.70
40 - 60	88.4	128.4	0.44	0.40
60 - 80	385.3	n.d.	0.65	n.d.
Highly structured clay				
0 - 25	n.d.	18.23	n.d.	3.25
Straw layer	n.d.	11.24	n.d.	n.d.
25 - 30	n.d.	22.75	n.d.	2.01
30 - 50	n.d.	56.45	n.d.	1.32
>50	n.d.	125.54	n.d.	1.22

n.d. = not determined

Table 3. Total cumulative loss of herbicides in leachate water from lysimeter studies in 1993 and 1994.

Soil	herbicide	% of total applied dose in leachate	
		autumn 1993	autumn 1994
Unstructured sandy loam			
	isoproturon	0.44	0.99
	alachlor	0.21	0.13
	pendimethalin	0.006	0.003
Moderately structured clay loam			
	isoproturon	4.20	2.41
	alachlor	1.30	0.18
	pendimethalin	0.012	0.002

Table 4. Comparison of undisturbed and re-packed material in Newport suction sampler installation

Depth (cm)	47-52	57-62	67-72	77-82	87-92	97-102	107-112	117-122
Coarse Porosity (Ca %) *Re-packed*	17.52	16.76	17.41	18.29	18.97	15.63	15.86	14.25
Coarse Porosity (Ca %) *Un-disturbed*	14.37	12.89	14.47	12.75	15.45	13.67	11.95	8.53
Bulk Density (Db g/cm^3) *Re-packed*	1.41	1.465	1.44	1.51	1.55	1.59	1.52	1.56
Bulk Density (Db g/cm^3) *Un-disturbed*	1.57	1.500	1.66	1.70	1.69	1.67	1.64	1.69

Un-disturbed values mean of 3 tins
Re-packed values mean of 2 tins

a:awfin1

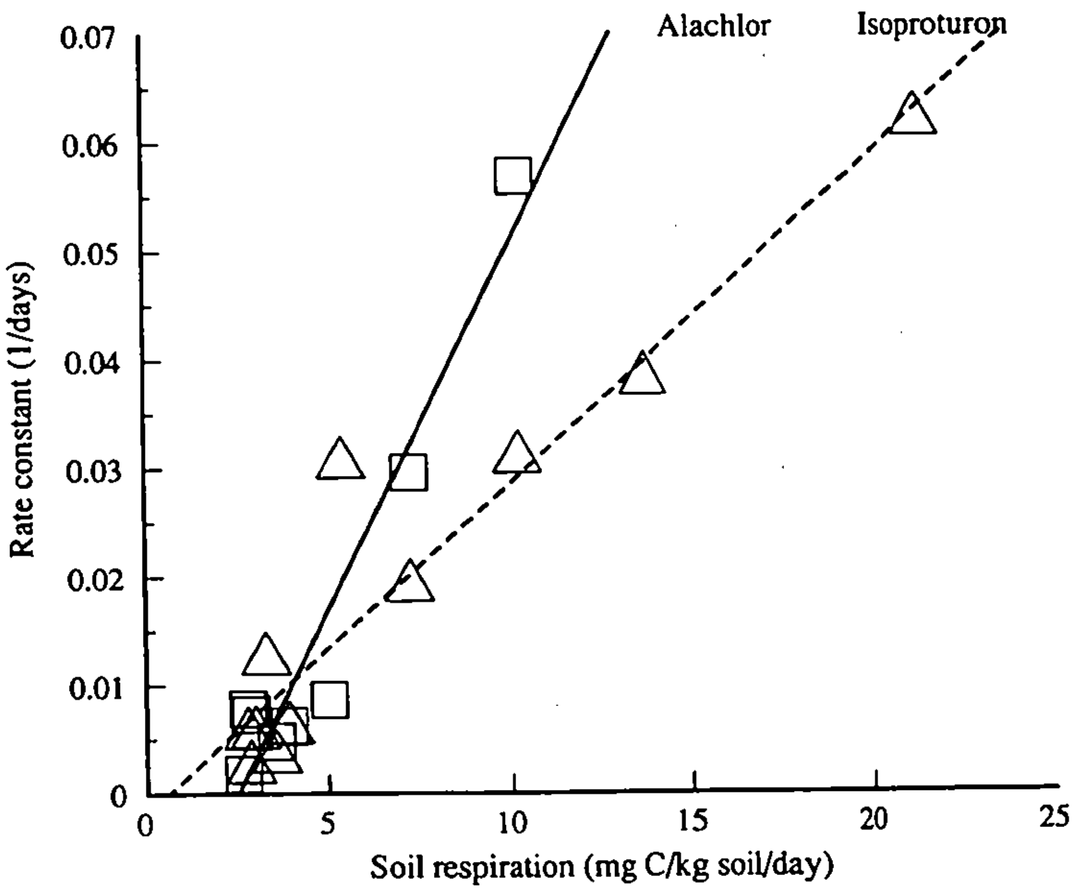


Figure 1 Relationship between alachlor and isoproturon degradation rates and soil microbial activity

a:awfin2

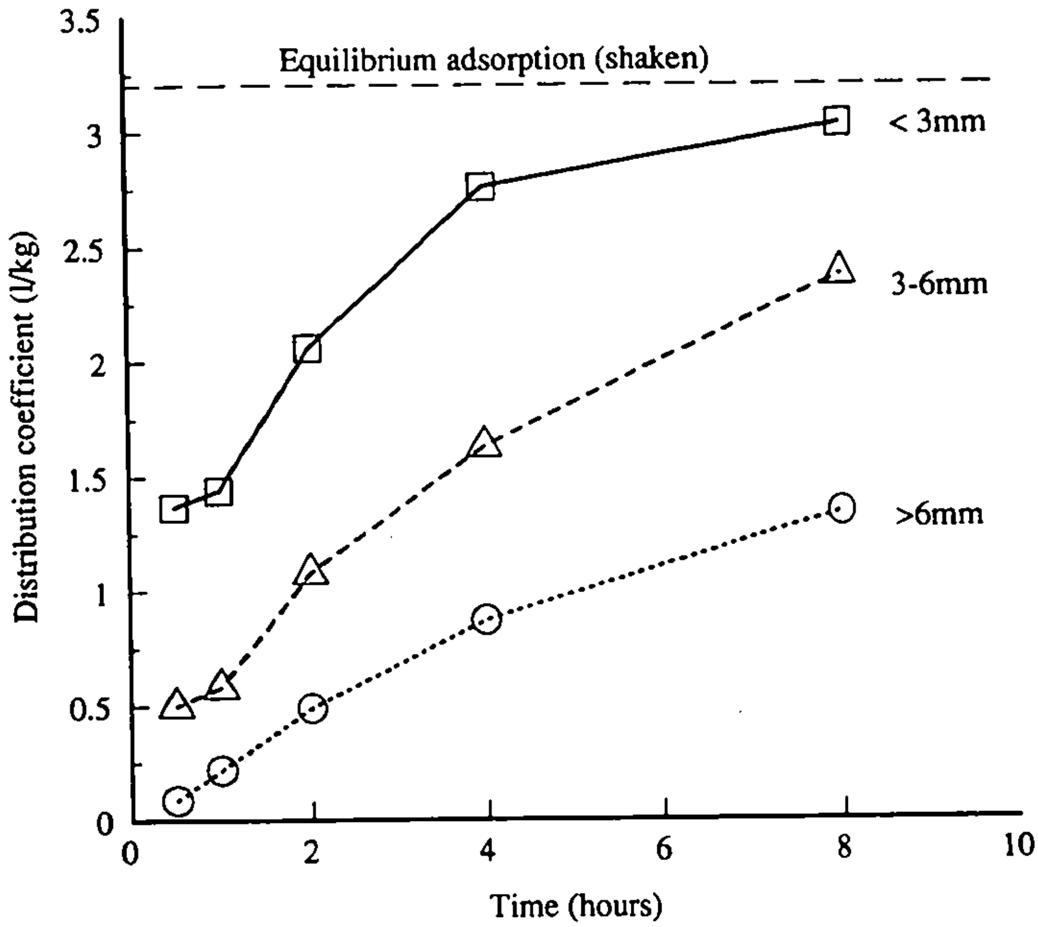


Figure 2 Rates of isoproturon adsorption by different-sized aggregates of a heavy clay soil

a:awfin3

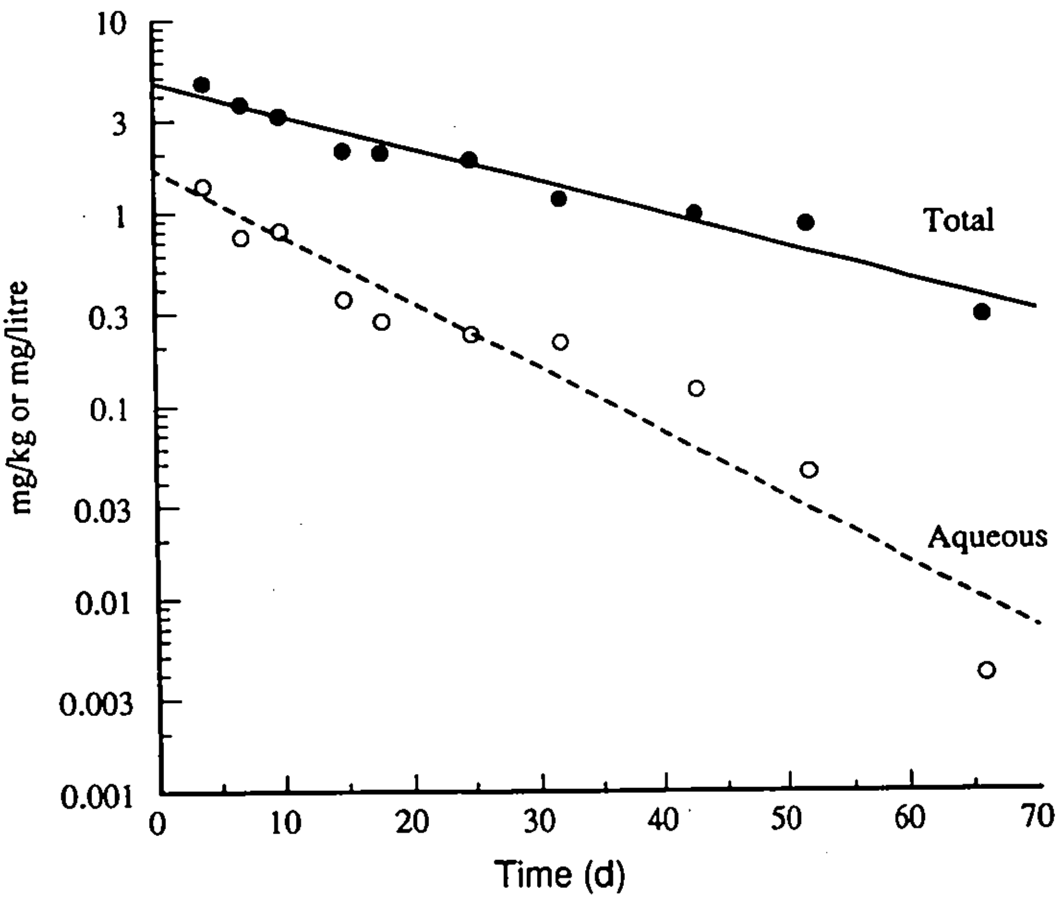


Figure 3. Changes in total and aqueous extractable residues of alachlor in the surface 2-cm of soil

a:awfin4

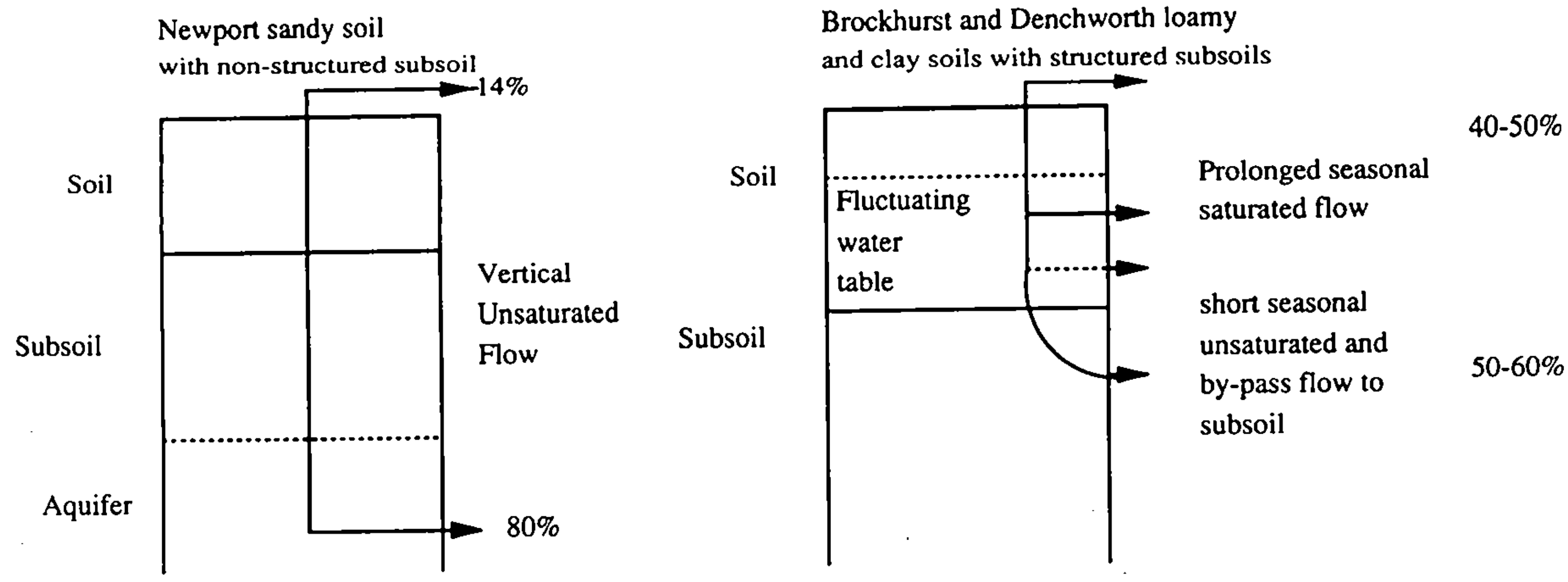


Figure 4 Major water flow pathways in the different soils

a:nercfin1

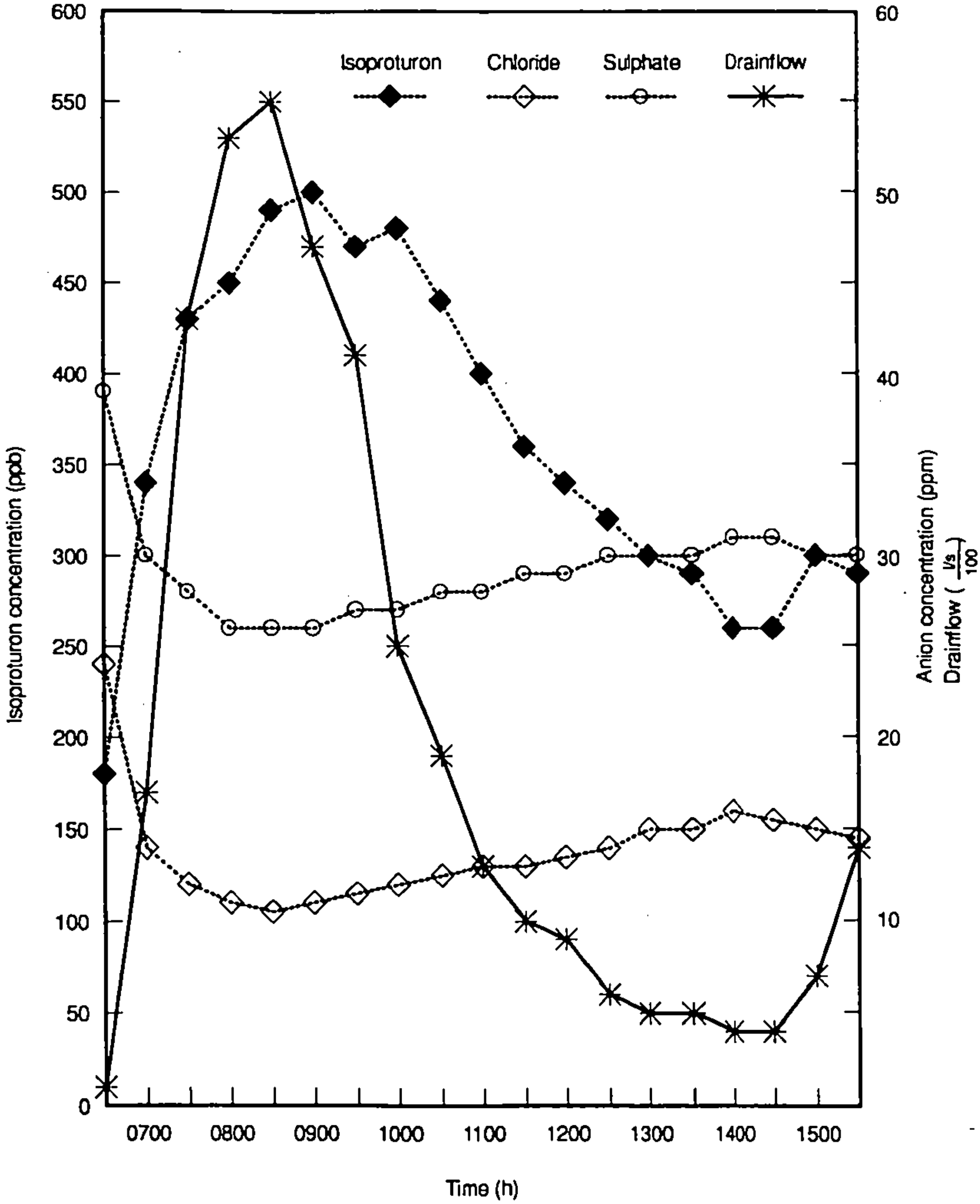
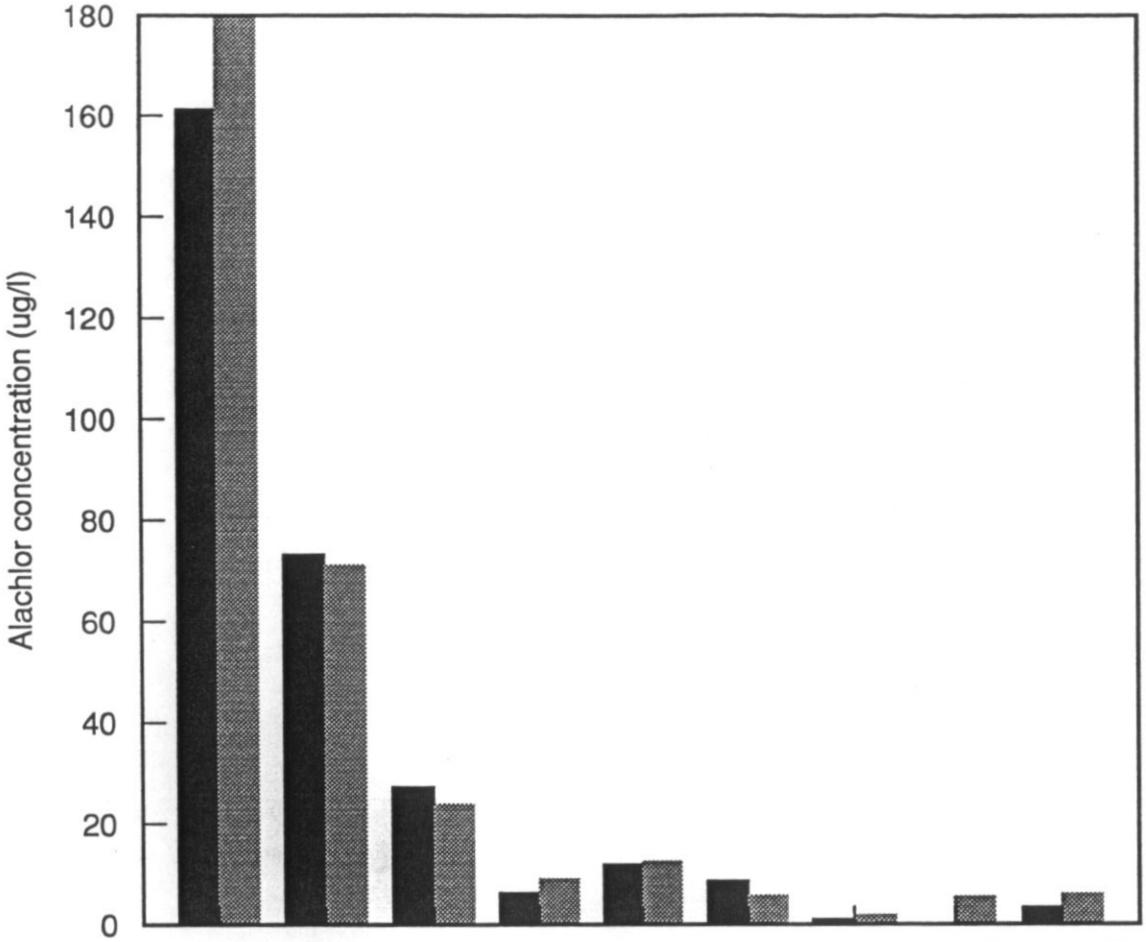


Figure 5. Comparison of solute concentrations with drainflow for the storm event on 1 April 1993.

a:acfin6



Date	02/10/91	18/10/91	30/10/91	04/11/91	11/11/91	05/01/92	10/01/92	30/01/92	27/02/92
Clay loam	161.3	73.2	27.2	6.3	11.9	8.6	1.0	0.0	3.4
Sandy loam	1,957	71.0	23.8	8.9	12.5	5.7	1.8	5.4	5.9

Figure 6. Concentrations of alachlor in surface runoff

a:nercfin2

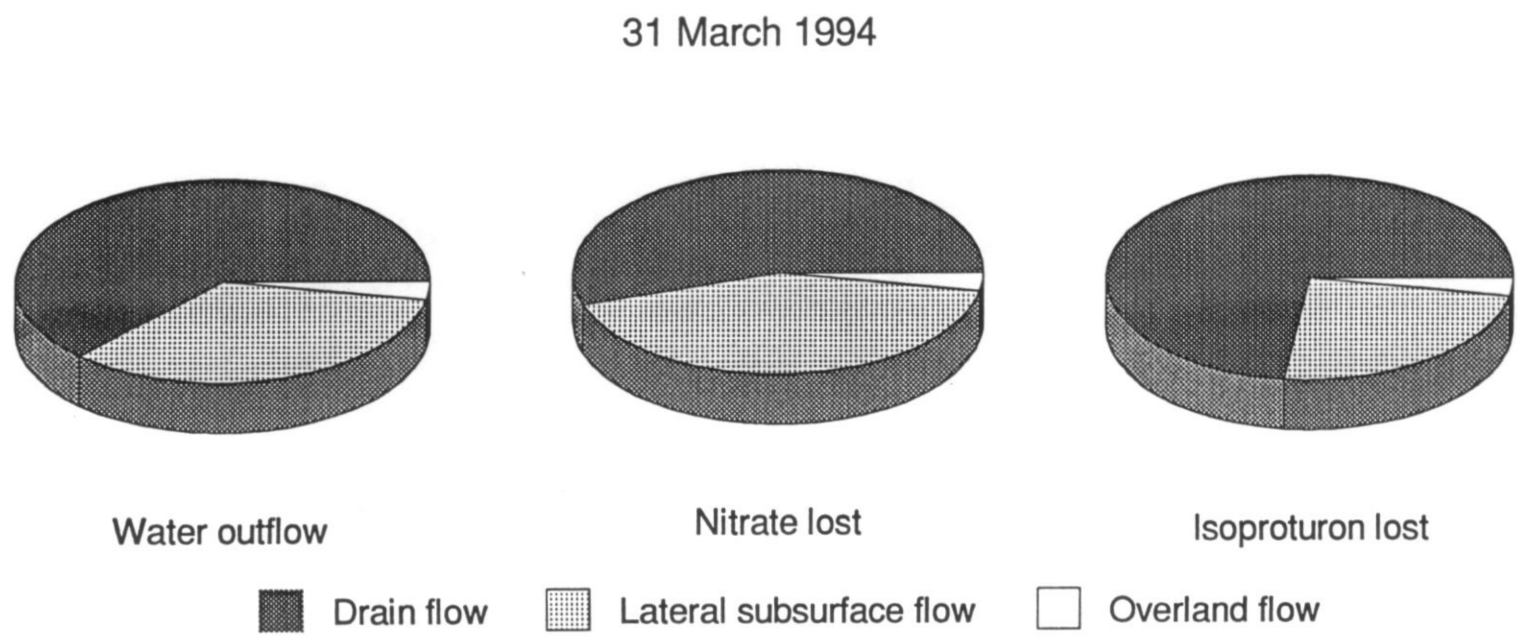


Figure 7. Typical example of the distribution of water loss from the plot together with distribution of nitrate loss (non-sorptive ion) and isoproturon loss (sorptive organic)

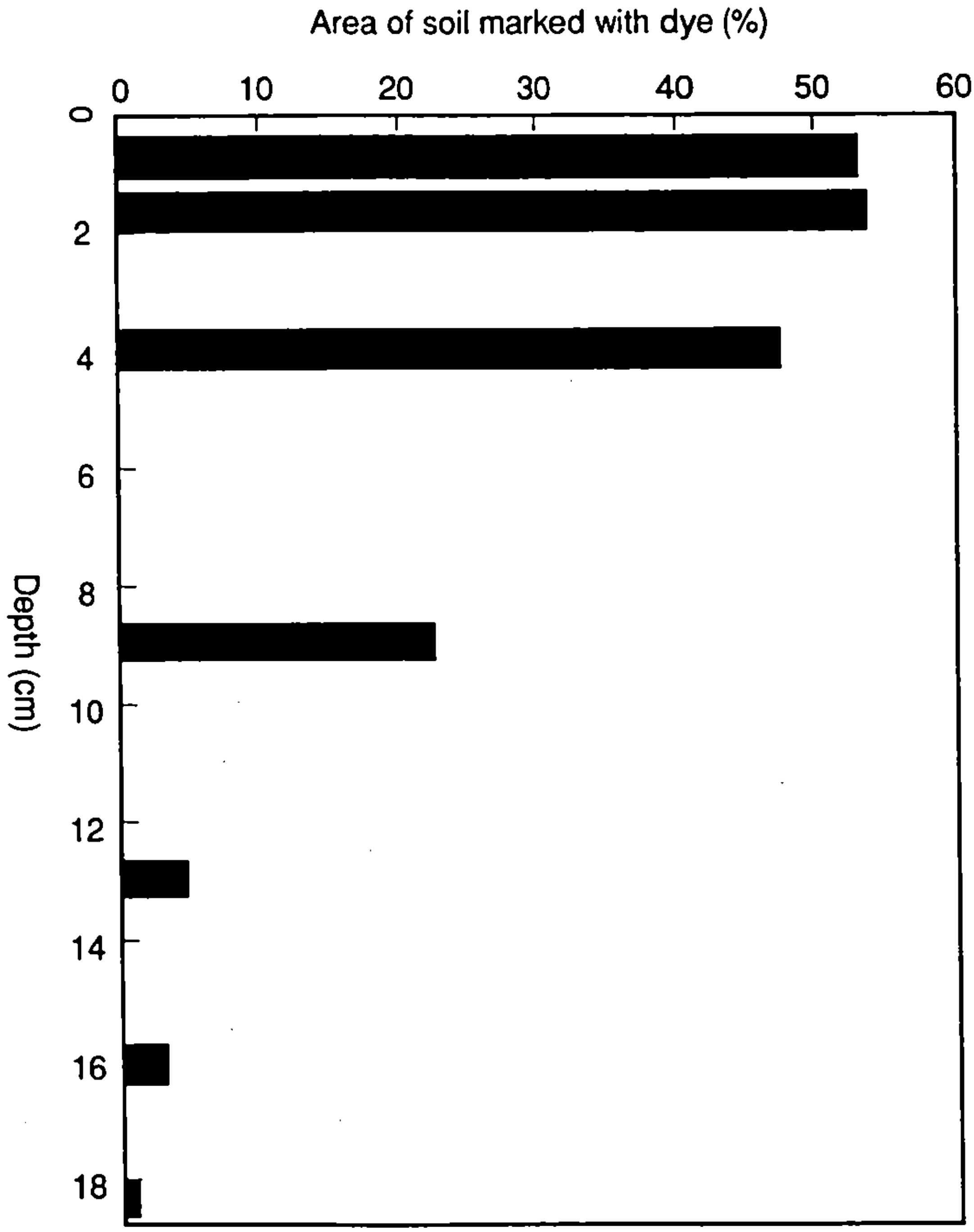


Figure 8. Proportion of soil in undisturbed soil column stained by dye. A reflection on the amount of soil which interacts with by-pass flow water in the Denchworth series clay soil

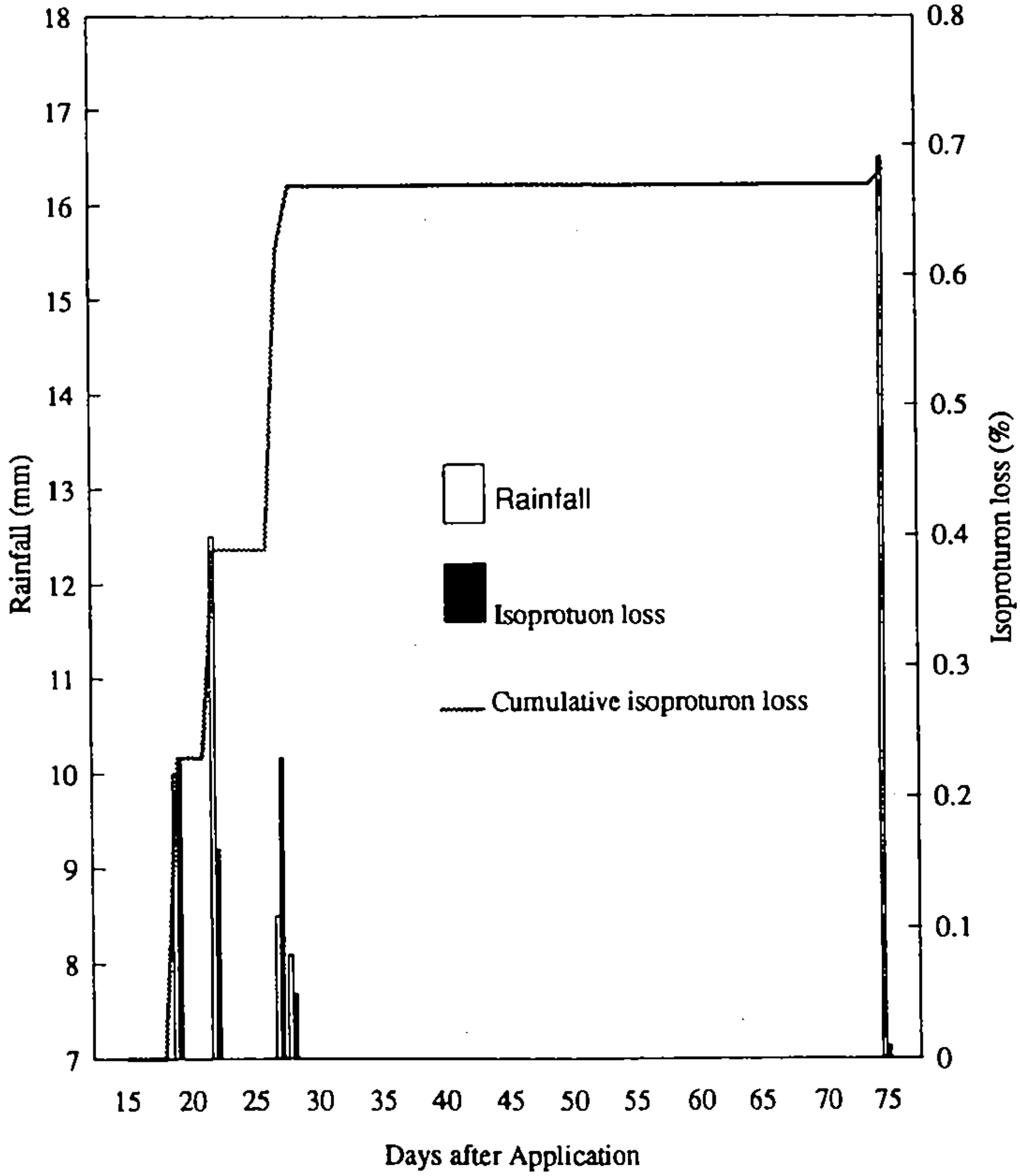


Figure 9. Cumulative loss from the clay soil field plot of isoproturon applied in March 1994