Infiltration of acetochlor metabolites in two contrasted soils

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ABSTRACT

We studied the fate of two acetochlor metabolites, ethanesulfonic acid (ESA) and oxanilic acid (OA), in two contrasting soil types (luvisol and calcosol) under the same climatic conditions. The detection of the metabolites in the soils only 21 days after application, indicated a rapid onset of acetochlor degradation. Greater concentrations of ESA persisted in the calcosol compared to OA, regardless of time lapse or depth, as against an ESA/OA ratio that varied with both time and depth in the luvisol. Sampling the soils 55 days after application, revealed both metabolites at 93 cm depth in the luvisol, and ESA at 51 cm depth in the calcosol (maximum sampling depths).

INTRODUCTION

Acetochlor was registered in France in 2000 and now forms part of substitution programmes. Few data are available on the fate of the chloroacetanilides in general, very few for acetochlor, and even fewer for the acetochlor metabolites. Some laboratory studies have been carried out, but field studies are rare despite the fact that this is the only way to determine all the processes that are or could be involved in the fate of agrochemicals in the environment. Balinova (1997) has shown that acetochlor, like the other chloroacetanilides (metolachlor and alachlor), must be considered as a potential groundwater contaminant. Added to this, Kalhoff *et al.*, (1998) and Kolpin *et al.*, (1998) have detected that acetochlor and its major degradates in groundwater in the USA.

In order to assess the risk of groundwater contamination from acetochlor, a first step is to study the fate of the herbicide in the soil. Thus the purpose of the present study was to determine the fate of two acetochlor metabolites in two agricultural soils under the same climatic conditions.

MATERIALS AND METHODS

The study site is a small hydrogeological basin of some 3 km² whose outlet is a spring tapped for drinking water. It lies within the Paris Basin (70 km west of Paris). The two highly contrasted soils that were selected for the study are a deep silty soil (luvisol-FAO classification) and a shallower, more pebbly, more calcareous soil (calcosol-FAO classification) that is also slightly more clayey in the surface layers (around 20% vs. 15%).

The experimental fieldwork was carried out on two 100 x 70 m maize plots, one in each soil type. A commercial liquid pesticide (Trophee, Zeneca Sopra) was applied to the plots in pre-emergence by spraying directly onto the soil on 19 April 2000. This was the first time that acetochlor had been applied to these plots. A solution of KBr had been applied a few hours before the pesticide treatment. The average applications were (a) 1530 g/ha (+/-387 g) acetochlor and 19,967 g/ha (+/- 7638 g) bromide for the calcosol plot, and (b) 2021 g/ha (+/- 504 g) acetochlor and 32,589 g/ha (+/- 13,730 g) bromide for the luvisol plot.

A national meteorological network raingauge 3.5 km from the site records the daily precipitation. Due to the proximity (850 m) of the two experimental plots, the precipitation is considered as identical for both. The first rain (10 mm) fell on 20 April, *i.e.* one day after treatment.

Soil samples were collected both before the herbicide application and 7, 21 (calcosol) / 27 (luvisol), 55, 168 and 248 days after the application. The two plots were each divided into 4 equal area subplots from which 4 samples were taken during each campaign, thus giving a total of 16 samples per plot per campaign. A 10-cm-diameter percussion corer was used for the sampling, with the maximum sampled depth being 1.0 m in the luvisol, and less in the calcosol where the limestone substratum was at a shallower depth. After removal of the outer part, the cores were cut into segments corresponding to depth intervals of 0-5, 5-10, 10-20, 20-30 cm, etc. Each sample was dried at 40 °C for 3 days then ground to 2 mm.

Bromide was extracted from the soil in a solution of $CaCl_2$ $10^{-4}M$ with 40 minutes agitation, followed by centrifugation and filtering. The extracts were then analysed in an ion chromatograph (Dionex 4500i model) equipped with an As14 column. The two main acetochlor metabolites (Feng, 1991), *i.e.* ESA acetochlor and OA acetochlor, were determined through extraction with a water/acetonitrile mixture and analysed by HPLC/MS. The limits of detection are 0.5 µg/kg and 2.0 µg/kg for the ESA and OA compounds, respectively (Dagnac *et al.*, 2001).

DISCUSSION

Bromide concentrations measured for the soils before application are of the same order (below 0.28 mg/kg) of magnitude as those reported by Flury & Papritz (1993) for different soil types in several countries. The bromide analyses carried out on the 16 cores taken during each sampling campaign on the two plots show a high variability as regards both the measured concentrations at each depth and the overall profiles. On the basis of the bromide profiles (figs. 1 and 2) and mass balances (table 1) obtained for each campaign, two cores corresponding to extreme situations (marked preferential flow for one – PF – , and preponderant matrix transport – MT – for the other) were selected for analysis of acetochlor metabolites.

Both ESA and OA were detected in the two soils 21 (calcosol)/27 (luvisol) and 55 days after treatment (Figs. 1 and 2). At the end of 21 (calcosol)/27 (luvisol) days, the sum of the metabolites present along the profile were, depending on the core, between 8.9% (figure 1: luvisol PF) and 31.2% (figure 1: calcosol MT) of the average applied dose of acetochlor; the onset of acetochlor degradation was thus rapid. These observations are in agreement with the less than 10-day DT50 for acetochlor (Feng, 1991; Mueller *et al.*, 1999) observed in previous incubation experiments and in situ tests.

At 55 days after application, the metabolite percentages in the profiles of the two cores from the same soil are close, whereas at 21/27 days after application the difference between the two cores was much higher, in particular for the calcosol.

Table 1. Percentage of bromide (Br), acetochlor ESA and acetochlor OA in each soil column relative to the average applied doses.

Core	Days after treatment	Cumulative precipitation (mm)	Br % appl. dose	ESA % appl. dose	OA % appl. dose	ESA+OA % appl. dose
Calcosol MT	21	95	127	20.2	11.0	31.2
Calcosol PF	21	95	55	6.1	3.4	9.5
Calcosol MT	55	184	111	6.1	0.2	6.3
Calcosol PF	55	184	36	5.3	0.7	6.0
Luvisol MT	27	115	136	7.5	14.5	22.0
Luvisol PF	27	115	29	3.1	5.8	8.9
Luvisol MT	55	184	69	7.6	5.1	12.7
Luvisol PF	55	184	60	7.4	7.4	14.8

Between 21/27 and 55 days after treatment, the diminution of the metabolite percentages (with respect to the parent molecule) is more obvious in the calcosol than in the luvisol. The fourth campaign (168 days after treatment) showed that the metabolite percentages continue to diminish in both soil types (results not presented). This decrease could be due to different factors. For example, the ESA and OA metabolites could themselves degrade into other subproducts not looked for in the study. They could also become fixed to the solid matrix due to the formation of non-extractible residues. Finally, the degradates could be leached to deeper horizons that were not sampled (*i.e.* to a soil horizon deeper than 1 m and to consolidated limestone); that such leaching is probably not insignificant is indicated by the fact that ESA was detected in the deep horizons of the calcosol after 21/27 days, and that both ESA and OA were found at deeper levels of the luvisol after 55 days than after 21/27 days. As the metabolites were detected in the deepest horizons sampled, it is quite likely that they occur at even deeper levels. The bromide data provide some clues with this respect.

The bromide quantities present in the profile decreased indeed significantly with time (Table 2). Therefore, considering that i) uptake of bromide by maize is limited and ii) bromide does not decay or become fixed to the soil, the bromide losses can only be explained by lateral flow or leaching. The first hypothesis can be excluded due to the absence of a less permeable pedological horizon to give rise to lateral flow. The bromide loss therefore reflects leaching below the sampled horizons, particularly so in the luvisol.

Table 2. Cumulated bromide present in the soil profile expressed as percentage of the applied dose (average of 16 soil cores by period and soil type).

Days after treatment	Cumulative precipitation (mm)	Calcosol (%)	Luvisol (%)
7	46	117	69
21/27	95/115	138	85
55	184	121	56
168	398	14	13

The hypothesis that the acetochlor acid metabolites are leached to depths greater than those sampled here, is also supported by the results of measurements made on 88 wells in the United States (Kalhoff *et al.*,1998; Kolpin *et al.*,1998), which showed that acetochlor degraded to mobile metabolites that were then transported to groundwater before complete mineralization of the parent compounds. We can thus consider that the ESA and OA metabolites are prone to leaching.

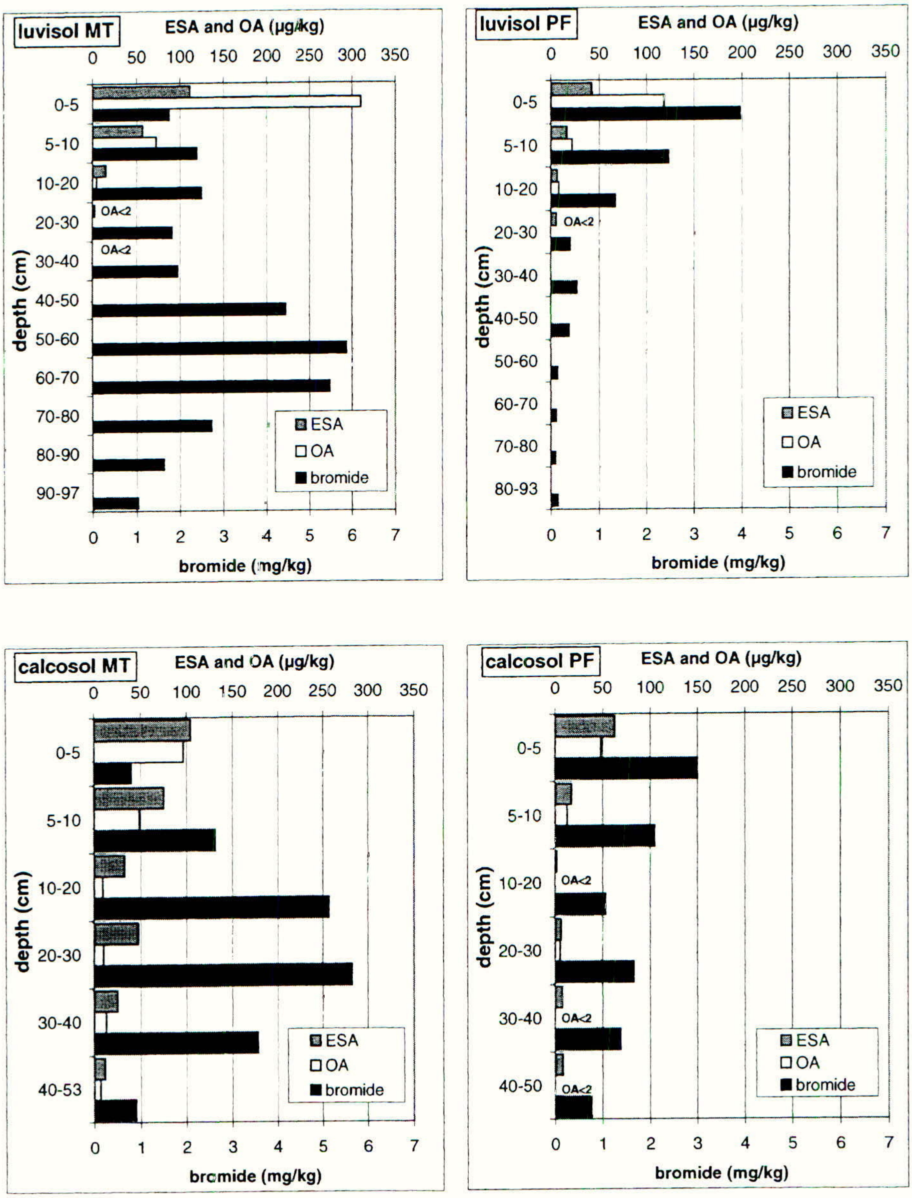

Figure 1. Depth profile of acetochlor ESA and OA, 21 (calcosol) or 27 (luvisol) days after application.
Luvisol MT / Calcosol MT: luvisol/calcosol core with Br profile suggesting matrix transport
Luvisol PF / Calcosol PF: luvisol/calcosol core with Br profile suggesting preferential flow
Detection limit for OA = 2 µg/kg; detection limit for ESA = 0.5 µg/kg

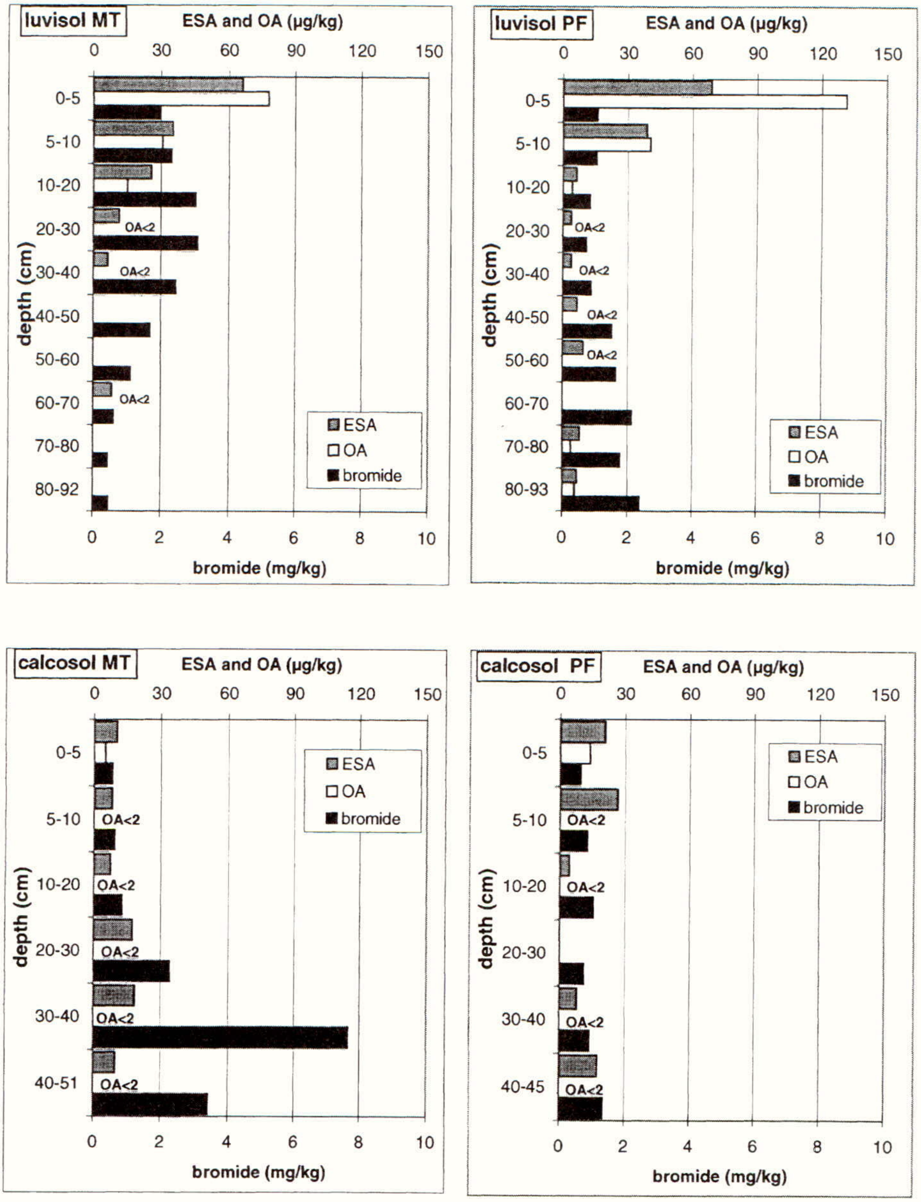

Figure 2. Depth profile of acetochlor ESA and OA, 55 days after application.
Luvisol MT / Calcosol MT: luvisol/calcosol core with Br profile suggesting matrix transport
Luvisol PF / Calcosol PF: luvisol/calcosol core with Br profile suggesting preferential flow
Detection limit for OA = 2 µg/kg; detection limit for ESA = 0.5 µg/kg

Another interesting observation concerns the differences between the soil types in relative contributions of the two acetochlor degradates. In the calcosol, the ESA concentrations are greater than the OA concentrations in all the horizons; the OA metabolite, 55 days following application, was no longer detected at the surface. In the luvisol, on both the second and third campaigns, the OA concentrations were equivalent to or much higher than the ESA concentrations in the uppermost 10 centimetres, whilst in the deeper horizons it is the ESA concentrations that are highest and OA may sometimes no longer be detected. Moreover, the OA concentration 55 days after application is proportionally less than the ESA concentration, as compared to the situation 21/27 days after application. The disappearance of OA with time could indicate that this compound is less stable, is more mobile, or a greater proportion has become non-extractable residues.

Although the bromide data show a greater leaching in the luvisol than in the calcosol (table 2), more ESA and OA remain in the luvisol than in the calcosol (table 1). This strongly suggests that the formation and/or persistence of ESA and OA is different in the two soils. The differences in moisture content and temperature – two parameters that are dominant in the degradation of agrochemicals – resulting from the different soil textures and structures most likely play a key role here.

Based on the data available, a risk of groundwater contamination by ESA and/or OA is strongly suggested, even though no definite conclusion can be drawn on the comparative risk between by ESA and OA on one hand, and between calcosol and luvisol on the other hand.

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Sorption properties of isoproturon and diflufenican on ditch bed sediments and organic matter rich materials from ditches, grassed strip and forest soils.

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ABSTRACT

In order to limit non-point source pollution from agricultural pesticides, research programs have been developed to study the different transport and dissipation mechanisms of pesticides from fields to rivers. Sorption is considered as one of the major processes responsible for the decrease of pesticide concentration in run-off. Sorption is thought to be especially important in buffer zones installed to reduce pesticides losses by runoff from agricultural areas. This can occur in grassed areas, such as grassed buffer strips, or forested land, and also in linear ditches collecting surface and drainage waters. Buffer zones contain many elements which could influence pesticide sorption. For example, in ditches a great variety of solid materials may act as sorbents: grasses, tree leaves, woody materials in different states of decomposition, organo-mineral particles or sediments originating from soil erosion. Laboratory experiments were carried out to investigate some of the intrinsic properties of different types of sediment/organic litter. Adsorption and desorption kinetics were studied with the herbicides isoproturon, and diflufenican. Batch experiments were used to determine sorption isotherms and Kd values. The comparison of the different results shows that beside the sorbent organic matter content, which was the main contributory factor for herbicide sorption, organic matter decomposition and origin had to be taken into account to explain the differences observed between ditch, grassed soil and forest litter materials.

INTRODUCTION

Agricultural non-point pollution originates from land areas which intermittently contribute to the transfer of pollutants to water by runoff, drainage, and leaching. Many methods and levels of actions can be developed to reduce the transfer. First, new or improved agricultural practices can be set up, such as choosing the best application period, controlling toxic substance impacts, and combining with non-chemical practices (Baker *et al.*, 1995). However, pesticide losses from fields cannot be totally eliminated. Pesticides leaving a plot may pass through landscape components before reaching rivers; including other fields, ditches, brooks, and vegetative or wooded buffer zones. Since 1992, two French Research Institutes Cemagref and INRA, in collaboration with the Institut Technique des Cereales et des Fourrages (ITCF), have studied the role played by grassed buffer strips in reducing the contamination of runoff water (Patty *et al.*, 1997; Benoit *et al*, 1999). Concerning farm ditches, different experiments have been carried out by Cemagref, on natural sites in Western France (Garon-Boucher *et al.*, in press) and by the Centre for Ecology and Hydrology (CEH) in the Oxfordshire (Williams *et al.*, 1999). Reduction of maximum concentrations and fluxes have been noticed for each site and buffer zone. Pesticide dissipation seems strongly linked to the nature of substratum and also to the physico-chemical properties of the molecules. Furthermore, the diversity of vegetative materials greatly varies spatially and over the season. Therefore, it is important to characterise the relationship between the nature of sorbents found in such buffer zones and pesticide sorption characteristics, namely kinetics, capacities and reversibility.

Research has been carried out on these aspects in rural ditches, grassed strip and forested land in France and the UK. Different natural organic and organo-mineral materials have been sampled in ditches, surface layers of grassed and forest soils. Sorption and desorption properties of these materials were characterised in laboratory classical batch experiments for two ^{14}C labelled herbicides, isoproturon, (3-(4-isopropylphenyl)-1,1-dimethylurea) and diflufenican (2',4'-difluoro-2-(α, α, α-trifluoro-m-tolyloxy)nicotinanilide).

MATERIALS AND METHODS

Chemicals

Isoproturon was uniformly ^{14}C-labelled on the phenyl ring with a specific activity of 2.66×10^9 Bq mmol^{-1} and a radiopurity greater than 95%. It was purchased from Amersham. ^{14}C diflufenican labelled on C2 position of the nicotinamide ring was purchased from Aventis. Specific activity was 7.19×10^8 Bq mmol^{-1} and a radiopurity of 99%.

Table 1. Properties of the studied herbicides

Characteristics	Isoproturon (IPU)	Diflufenican (DFF)
Solubility in water (mg/litre)	65 (22°C)	0.05 (25°C)
Koc (ml/g)	120	1990
Kow	2.5	4.9

Natural sorbents

Ditch bed sediments were collected in two different natural sites in France and the UK. The French one was sampled in Roujan (southern France). The soils of this catchment are developed from marine, lacustrine or fluvial sediments. The other site in the UK is the Oxford University Farm at Wytham, Oxfordshire. The predominant soil type is heavy clay from the Dentworth series. Both sediments were dried at 40°C, sieved using a 2-mm sieve and analysed for carbon (C) and nitrogen (N) contents (Table 2) before sorption studies.

Dead leaves that can be found in natural ditches in France are commonly oak and chestnut tree leaves. For this study, leaves were collected in autumn and dried at about 30 °C. Other organic materials were collected from an 8 years old grassed strip and a forest floor in an oak forest. Both sites were located at the experimental farm of the ITCF "La Jailliere" (western part of France). The soil is an hydromorphic silt loam on schists of the Massif Armoricain. For the forest floor, the litter was sampled between 0-2 cm after removing from the surface the coarsest debris mainly made of oak leaves in early decomposition. For the grassed strip, the surface layer 0-2 cm, an organic mat with a high density of collar and roots with fine soil aggregates attached to the roots, was separately sampled from the underneath horizons (Benoit *et al.*, 1999). The grassed strip was planted with perennial rye-grass (Lolium perenne) in 1992 (Patty *et al*, 1997). Above ground plant debris as stems and dead leaves at the surface of the mat were collected by cutting before sampling the 0-2 cm layer. From the two litters, light organic fractions (LOF) of the 0-2 cm layer were separated by dry and wet sieving. In both cases, the debris > 2 mm were considered similar to the fractions previously collected at the surface, respectively grass and leaves fraction. The sieved fraction (< 2 mm) was dispersed in water and passed successively through 200 µm and 50 µm sieves. From both size fractions 2mm-200µm and 200-50 µm, and LOF were separated by flotation in water and by successive washing in order to eliminate as far as possible coarse mineral particles. All the organic sorbents were air dried and stored before use in sorption experiments. They were analysed for total C and N content using a CHN autoanalyser. LOF fractions represented early decomposed materials as shown by the decrease in C/N ratio and the decrease in C content with the decrease in particle size (Table 2)

Table 2 Characteristics of the sediments and the organic materials

Samples	Organic C (g/kg)	Total N (g/kg)	C/N
Sediments			
Roujan (F)	10	-	-
Wytham (UK)	36	-	-
Dead leaves	492	12	41
Grassed Strip			
Grass fraction > 2mm	320	16	20
Litter LOF 2 mm – 200 µm	323	13	25
Litter LOF 50-200 µm	243	15	16
Forest Litter			
Leaves > 2 mm	449	14	32
Litter LOF 2 mm – 200 µm	348	15	23
Litter LOF 50-200 µm	340	17	20

Sorption experiments

Ditch sediments

The experiment was carried out for 5 sorption times (5, 20 minutes, 1, 5 and 24 hours) with 3 replicates. In each tube 10 g dry sediments were added to 10 ml 0.22 µm filtered ditch water and the appropriate volume of radiolabelled herbicide solution to reach a final concentration of 5 µg/litre. The mixtures were left on orbital shaker (about 200 shakes/minutes) at room temperature for the appropriate sorption time. After centrifugation, 1 ml of the 0.45 µm filtered supernatant was transferred into scintillation flask for radioactivity measurement by liquid scintillation counting. The herbicide concentrations in supernatant solution (C, in µg/ml) were calculated from the supernatant radioactivity measurements. The amount of sorbed herbicide, x, per mass of sorbent, m (in µg/g sorbent) was calculated from the difference of herbicide concentration before and after sorption. Sorption coefficients K_d were calculated from sorption data at 24 hours to estimate maximum sorption capacities of sediments. K_{oc} coefficients were derived from the K_d values (see equations 1 and 2):

$$Kd = \frac{x/m}{C} \quad (1) \qquad\qquad Koc = \frac{Kd}{OC} \times 100 \quad (2)$$

with OC: organic carbon content of the solid phase (%)
Desorption was then continued with the sorption tubes for 24 hours. The water left in the tube was removed and replaced by fresh water. The tubes were shaken for 30 minutes. Scintillation of the filtered supernatant was measured allowing the calculation of desorbed amounts. Desorbed amounts were expressed as % of initially sorbed amount.

Litter and organic materials

Solutions of ^{14}C-isoproturon and ^{14}C-diflufenican were prepared in calcium chloride (0.01*M*). Three milliliters of these solutions were added to 100 mg of organic fractions in glass centrifuge tubes with Teflon caps. Triplicate samples of each OM were used with one single concentration: 200 µg/litre for isoproturon and 30 µg/litre for diflufenican. Sorbed amounts were evaluated after 24 h shaking at 23 ± 1°C by the same procedure as described above. Contact times of 24 hours were considered sufficient to estimate sorption coefficients K_d and K_{oc} in order to compare the different organic materials. Desorption was evaluated after 24 h sorption. The supernatant was replaced by the same volume of 0.01M $CaCl_2$ solution and the suspensions were shaken at 23 ± 1°C. Desorption time was 30 minutes for dead leaves and 24 h for grass and forest organic materials. Then the suspensions were centrifuged and desorption was determined as previously described.

RESULTS AND DISCUSSION

Sorption kinetics. Contact time had a great effect on isoproturon sorption particularly on leaves (Figure 1) showing a continuous increase in sorption versus time. This agreed with other studies on isoproturon sorption in soils (Gaillardon & Durr, 1995; Walker & Jurado-Exposito, 1998).

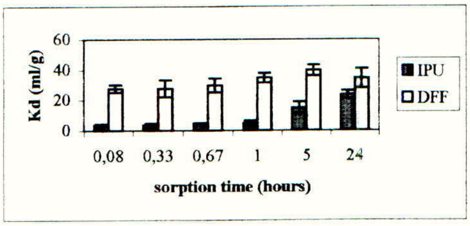

Figure 1. Sorption kinetics on leaves

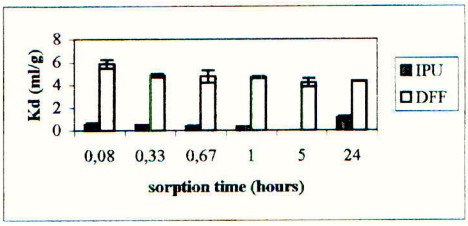

Figure 2. Sorption kinetics on Roujan sediments

On the contrary diflufenican sorption reached an equilibrium after 5 minutes (Figuress 1 and 2). Considering that short contact times of 5 or 10 minutes are relevant to the natural processes occurring in ditches, these results confirmed field studies showing a greater dissipation in ditches for diflufenican (Williams *et al.*, 1999; Garon-Boucher *in press*).

Sorption capacities

Sediments - Koc values measured for isoproturon on both sediments could be compared with those found in the literature. Common values for soil are 80-230 ml/g. Sorption capacity of diflufenican on sediments was very low, compared to the literature for soils (Table 3).

Litter and organic materials - Comparing K_d and K_{oc} obtained at 24 hours contact time showed that isoproturon sorption on the dead leaves from the ditches was comparable to sorption on leaves from the forest floor (Table 3). For diflufenican, however strong differences were observed between sorption capacities on dead leaves and other organic materials. For isoproturon and diflufenican, sorption on grass was significantly lower than sorption on leaves from the forest floor. Despite higher C content, the grass and leaves fractions had generally lower sorption capacities than the LOF fractions (Table 3). K_d and K_{oc} increased as the size of the LOF decreased, i.e. as decomposition proceeded. This indicated that changes in OM composition during first decomposition stages increased the sorption capacities of both the grass and leaf residues.

Table 3 Sorption coefficients (K_d and K_{oc}) and desorbed amounts in one single desorption (% of initially sorbed amount) for isoproturon and diflufenican on sediments and organic materials.

	Isoproturon			Diflufenican		
	K_d (l/kg)	K_{oc} (l/kg)	% desorbed	K_d (l/kg)	K_{oc} (l/kg)	% desorbed
Sediments						
Roujan (F)	1 ± 0.1†	110 ± 15	5 ± 3	4 ± 0.1	440 ± 10	14 ± 1
Wytham (UK)	2 ± 0.2	63 ± 5	33 ± 3	29 ± 4	805 ± 110	16 ± 2
Dead leaves	23 ± 3	48 ± 6	23 ± 16	34 ± 6	70 ± 13	7 ± 2
Grassed strip						
Grass fraction	10 ± 1	32 ± 3	42 ± 1	322 ± 22	1007 ± 70	5 ± 3
>2mm	32 ± 1	100 ± 2	40 ± 2	733 ± 62	2269 ± 191	2 ± 1
LOF 2 mm-200 µm	30 ± 1	122 ± 3	32 ± 2	663 ±122	2730 ± 501	3 ± 1
LOF 50-200 µm	24 ± 1	54 ± 3	37 ± 2	666 ± 68	1482 ± 151	5 ± 3
Forest litter	40 ± 1	117± 1	33 ± 1	438 ± 66	1258 ± 190	2 ± 1
Leaves > 2 mm	39± 7	114 ± 21	30 ± 6	714 ± 82	2100 ± 240	4 ± 1
LOF 2mm-200 µm						
LOF 50-200 µm						

† means and standard errors of three replicates

Sorption reversibility - Desorption

The reversibility of sorption was assessed by the proportion of desorbed herbicides after one single desorption period of 30 min (sediment or dead leaves) and 24h (litter OM.).
For the sediments from Roujan, desorption of diflufenican (14%) seemed to be greater than isoproturon (5%). On Wytham sediments and on the organic rich materials, the contrary was observed (Table 3). The behaviour for Roujan may be explained by the sediment nature and the low C content, that meant different interactions between the sorbents and the herbicides. After 30 minutes, 23% of initially sorbed isoproturon was desorbed from dead leaves, but only 7% of initially sorbed diflufenican (Table 3). After 24 hours, 37% of isoproturon was desorbed from forest floor leaves, but only 5% of diflufenican. This indicated that the kinetics of desorption was probably slower for diflufenican than for isoproturon. The comparison of grass and forest litters showed that isoproturon desorption was easier from grass materials (42% from the grass fraction). Again for the more decomposed fractions 50-200 µm LOF, differences between grass and forest litters were smaller. For diflufenican, only 2 to 5 % could be desorbed after 24 h. This confirmed that decomposed organic matter

such as plant residues can play a significant role in non reversible sorption of herbicides (Reddy *et al*., 1997; Benoit *et al*., 1999).

CONCLUSION

The present results suggest that origin and degree of decomposition of OM are important factors affecting the sorption of non-ionic herbicides with strong (diflufenican) or medium (isoproturon) hydrophobic characteristics. Non-specific interactions such as partitioning into organic matter are thought to be a major mechanism to explain sorption of such molecules on plant residues (Lickfeldt & Branham, 1995). Increased sorption with decomposition could be explained by as rapid changes in plant residues chemistry with preservation of aliphatic (cutins) or aromatic (lignins) structures or increased specific surface areas. Some extra laboratory experiments are now planed to characterise the organic materials in relation to the observed pesticide adsorption.

The comparative study between herbicide sorption/desorption on sediments and organic materials demonstrated that the presence of organic sorbent in buffer zones or farm ditches could significantly reduce pesticide occurrence in surface water. These laboratory experiments confirmed preliminary results at fields (Garon-Boucher *et al*., in press; Patty *et al*., 1997).

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Pesticide penetration and groundwater recharge on a chalk hillslope in southern England

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ABSTRACT

Pesticide penetration and groundwater recharge monitoring on a chalk hillslope in southern England identified very different mechanisms of contaminant transport related to the water table depth. On the interfluve, where the groundwater was 18-20 m below the surface, matrix flow only through the deep chalk unsaturated zone was observed. In contrast, the dry valley bottom with a shallow (4-6 m deep) water table experienced rapid preferential water/contaminant transport, as well as matrix flow, to the groundwater.

Unsaturated soil/chalk hydrology demonstrated the importance of the shallow groundwater capillary rise in keeping the unsaturated profile well supplied with water resulting in a reduced storage capacity for rainfall pulses; little water is required to wet the shallow profile before rapid preferential flow events occur. Storage sites on chalk surfaces and at "contact points" remain empty where the groundwater is deeper and rainfall pulses are attenuated as these sites absorb the downward water fluxes. Consequently preferential events here are rare.

The maximum potential mass load of pesticide that might be transported to the groundwater in the preferential events in 1996-7 was determined from bromide tracer studies. Calculations under the worst case scenario showed no more than 0.13 % of the applied pesticide would be transported to the water table rapidly at the shallow groundwater site. A more realistic estimate was between 0.04 % and 0.07 % of the applied pesticide. The work indicates contamination of groundwater by pesticides applied following normal agricultural practice over unconfined chalk can occur, however the major pollution sites are likely to be restricted to the dry valley areas at least in the short term.

INTRODUCTION

With the chalk aquifers of SE England contributing 55% of all groundwater use in the UK, the water quality of this resource is an important issue. Large tracts of the typically thin soils overlying these unconfined aquifers are under arable land use with agrochemical pollution an increasing concern. Chalk is a dual porosity system where water can move through both the matrix and through fractures (Price *et al.,* 1993). Water fluxes through the matrix are relatively slow (~ 1 myr^{-1}) whilst movement through the fissures can be orders of magnitude greater. Consequently, contaminant transported by water through the fissures will arrive quickly to the groundwater with very little opportunity for attenuation and degradation soon after application; whilst the slow transport through the chalk matrix means there is a considerable amount of time likely to be available for attenuation and potential degradation before it reaches the groundwater.

Previous work in southern England on unsaturated Upper chalk over a deep water table (>30 m) determined that preferential fissure flow in the chalk would only occur when the hydraulic conductivity of the matrix has been exceeded (Cooper *et al.,* 1990). This was found to occur rarely, only once in a 5 year study on the Upper Chalk in Hampshire, UK. Importantly, the threshold matric potential above which fissure flow began was identified as -5 kPa suction (Wellings, 1984).

However, some of the cultivation over the chalk is likely to be in the characteristic dry valley bottoms where the groundwater is relatively close to the surface. Under these conditions preferential fissure flow may be more significant, and these areas may represent zones of high risk for agrochemical contamination of the groundwater. A detailed physico-chemical study was established at a chalk site in Hampshire, southern England, to compare recharge processes over shallow and deep ground waters and to determine the implications for contaminant transport. This paper presents some of the results from the 1996-1997 field season.

METHODS AND MATERIALS

The study site was situated on a sloping arable field on the Upper chalk in Hampshire, about 24 km north of Winchester, and comprised of 2 instrumented stations. Station WON 7 was located on the interfluve where the groundwater was 18-20 metres below ground level (mbgl), whilst station WON 4 was located on the dry valley floor where the water table was 4-6 mbgl (Figure 1). Site WON 4 was 382 m down slope of WON 7.

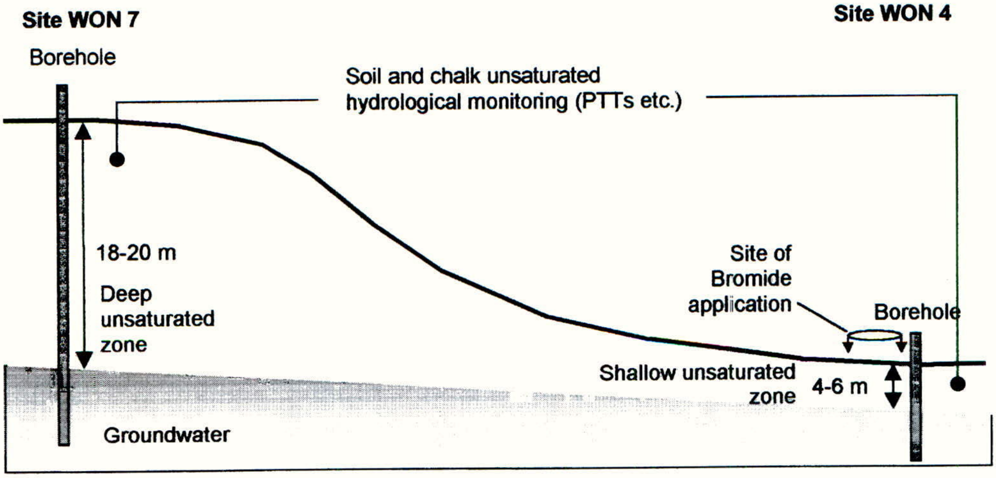

Figure 1. Schematic diagram of the experimental site showing relative locations of instruments.

The soils are Andover series and, along with the site, are described in more detail by Johnson *et al.,* (2000). Boreholes, installed at both sites using a dry percussion drilling method, were used to take weekly groundwater samples. Additionally, automated daily water samples were collected at WON 4 after pesticide application to assess pesticide concentrations arriving at the groundwater immediately following rainfall.

The pesticides Isoproturon (2.5 $kgha^{-1}$ total in 1994) and Chlorotoluron (2 $kgha^{-1}$ on 30th October 1996) were applied at both sites. Unsaturated chalk water potentials at both sites were measured using pressure transducer tensiometers (PTTs), logging hourly, at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 m depths. On 22nd February 1995, 48 L of 50,000 mgL^{-1} KBr tracer solution was applied just upslope of the borehole at WON 4. Profiles of chalk cores were extracted on 28th September 1996 and again on 22nd September 1997 and analysed for Br. By the use of pesticide concentrations measured in the boreholes immediately following rainfall, MORECS data, and by studying the Br peak displacement, a worst case estimate of preferential pollutant transport could be made for the period between core extractions at WON 4.

RESULTS AND DISCUSSION

Weekly baseline borehole sampling showed that where the groundwater was deepest (WON 7), little or no herbicide detections were made. However, where the groundwater was only 4-6 mbgl (WON 4), a regular baseline pesticide signal of around 0.1 μgL^{-1} was distinguished. This suggests that no significant pesticide concentrations are reaching the groundwater at WON 7 whilst there is a regular input of pesticide reaching the groundwater at WON 4. Over the winter recharge period the automatic sampling at WON 4 revealed periodic high spikes of 0.4-0.8 μgL^{-1} of pesticide following rainfall. The high spike concentrations observed in the groundwater immediately following rainfall were strong evidence of rapid preferential contaminant transport taking place through the fissure pathways at this part of the field.

Different recharge processes between the deep groundwater site (WON 7) and the shallow groundwater site (WON 4) are clearly identified by the PTT data for a storm in February 1997. Figure 2 shows time series data of hydraulic potential response to rainfall, for 0.5 m to 3.0 m depths, for WON 7 and WON 4. Matric potentials may be calculated by subtracting the gravitational potential from the hydraulic potential. There are two main points of interest in Figure 2. First is the response in peak flux to peak rainfall down the profile, identified when the hydraulic potential is closest to zero (these are marked on Fig.2 by the short vertical lines crossing the lines of hydraulic potential). At WON 4 peak flux at 3.0 m is approximately 1 day after peak rainfall, whilst at WON 7 peak response at 3.0 m takes 7 days. The second noteworthy point is the difference in matric potential during peak flux at 3.0 m, for the February 1997 storm, at both sites. The matric potential at WON 7 did not exceed -17 kPa whilst at WON 4 it reached -3 kPa. According to previous research, preferential flow will only begin in the chalk when the matrix conductivity has been exceeded, and this only occurs in the Upper chalk at matric potentials greater than -5 kPa (Wellings, 1984). Thus, these conditions were met at the shallow groundwater site (WON 4) but not at the deep groundwater site (WON 7) during this rainstorm.

Why these differences should exist, at the two locations with different depths to the water table, can be explained by the capillary fringe above the water table effectively reducing storage in the chalk. The concept of chalk being a dual porosity system only, where the uniform matrix porosity is clearly differentiated from fissure porosity needs re-thinking since

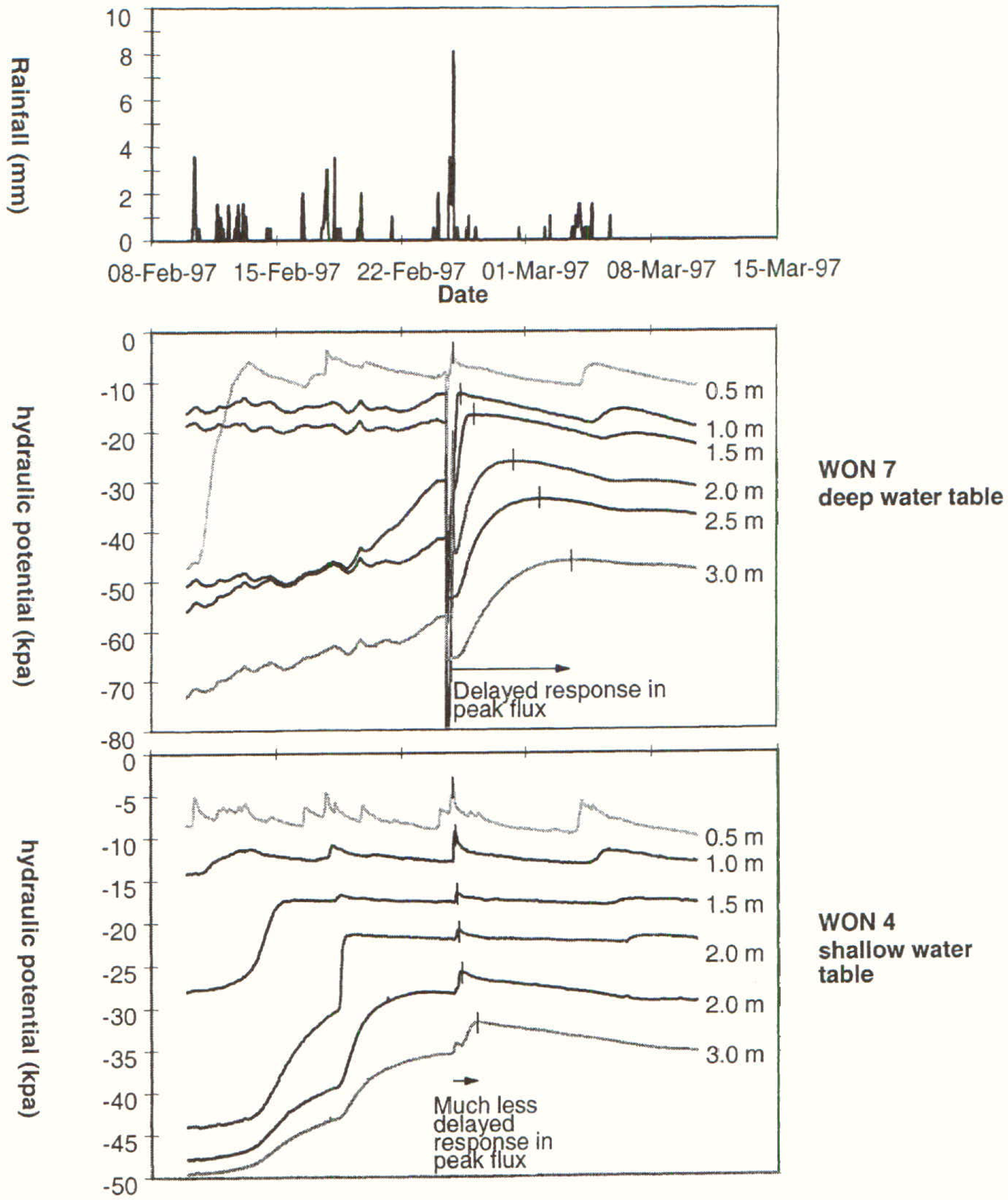

Figure 2. Time series data of hydraulic potential response to rainfall, for 0.5 m to 3.0 m depths, at WON 7 and WON 4.

clearly an intermediate, or more accurately a range of intermediate pore sizes exists. The concept is shown in Figure 3. This intermediate porosity need not be volumetrically great but it appears to be very important in providing storage sites at WON 7 which attenuate pulses of rainfall such that the resulting fluxes at lower depths are through the matrix only. At WON 4, where the intermediate porosity is largely water filled because of groundwater capillary effects, rainfall pulses quickly fill the remaining intermediate storage sites and further drainage "overflows" into the fissures. These storage sites have recently been investigated by

Price *et al.,* (2000), who identified sites on chalk block surfaces. Other possible loci of intermediate porosity may be at contact points between chalk blocks. Additionally, the profile at WON 7 may have had a bigger moisture deficit from the previous summer; at WON 4 upward gradients from the shallow water table in the summer mean the chalk here would not be as dry.

The bromide profiles (not shown) determined by coring at WON 4, described water movement through the chalk matrix, with the peak Br concentrations representing mean pore water velocities. Knowledge of chalk properties and looking at Br peak displacement enabled calculation of the flux of water through the matrix between core extractions. Using MORECS hydrometric data, and peak pesticide concentrations reaching the groundwater following rainfall, it was possible to estimate the amount of pesticide transported preferentially through the fissures for the period between core extractions. Calculations under the worst case scenario, assuming an effective matrix porosity of 0.5 v/v (Barraclough et al., 1994), predicted that 0.13% of pesticide applied reached the groundwater through the fissure system between 28th September 1996 and 22nd September 1997. More realistic estimates, assuming an effective matrix porosity of 0.85 v/v (Besien *et al.,* 2000), were between 0.04 % and 0.07 % of the pesticide applied reaching the groundwater at WON 4 through the fissure system.

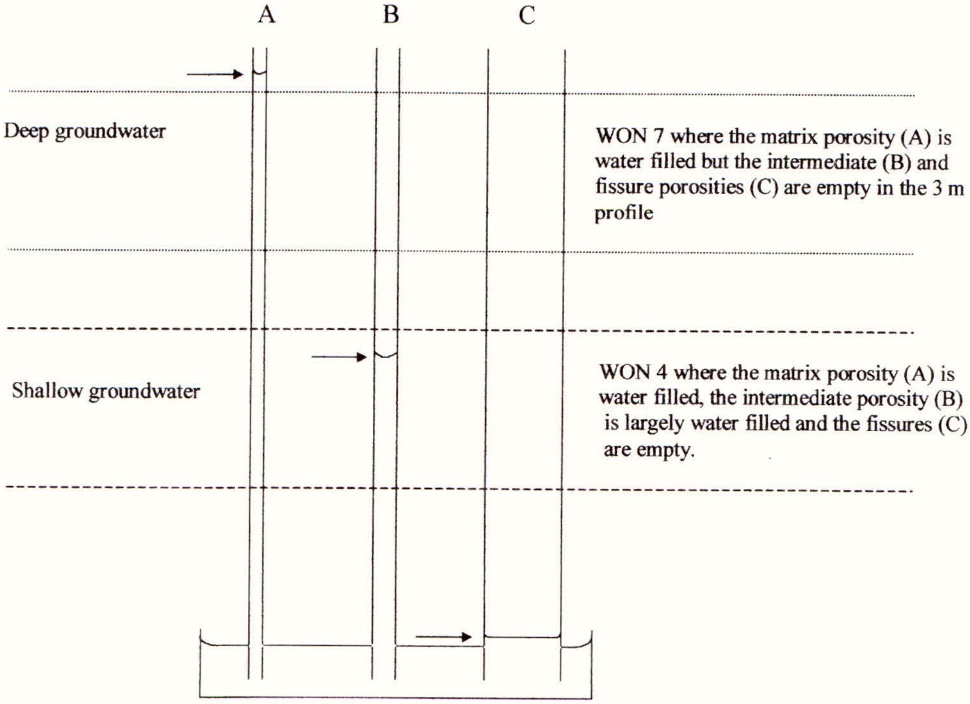

Figure 3. Conceptual model explaining the effect of the capillary fringe in reducing storage sites in the unsaturated zone close to the water table.

CONCLUSIONS

Winter recharge processes to the Upper chalk aquifer can be very different depending on distance to the water table. At the shallow groundwater site, the near water table capillary fringe effectively reduced the intermediate storage potential in the unsaturated chalk above. Recharge fluxes very quickly wet the profile to a point where the fissures began to operate. For the same storm the recharge at the deep groundwater site was through the chalk matrix only. The resultant pesticide contamination by preferential fissure pathways was shown not to exceed 0.13% of that applied in the 1996-1997 field season. However, this value will vary depending on many factors such as the depth of the water table, rainfall patterns, pesticide used etc. The implications for winter cereal production over shallow unconfined chalk aquifers, due to the potential preferential contaminant transport to groundwaters, needs to be researched further.

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