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A field study to determine the fate of diuron and its metabolites in calcareous sediments

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BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/022

A field study to determine the fate of diuron and its metabolites in calcareous sediments

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Front cover

Photograph of experimental plot 338 days after diuron applied.

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Summary

An experimental plot has been established on a calcareous soil in southern England to investigate the fate and transport of diuron (*N*'-[3,4-dichlorophenyl]-*N,N*-dimethylurea), a commonly used phenylurea herbicide. In early January 2001 an agricultural grade of diuron was applied to the soil surface at a rate of 6.7 kg/ha along with a potassium bromide conservative tracer applied at 200 kg/ha. Hand augured samples were taken at regular intervals over the next 50 days, and then again after 338 days, with samples collected down to 54 cm. Porewaters were extracted from the soil cores by using high speed centrifugation and the supernatant fluids were retained for analysis by HPLC for diuron and three of its metabolites, *N*'-[3,4-dichlorophenyl]-*N,N*-methylurea (DCPMU), *N*'-3,4-dichlorophenylurea (DCPU) and 3,4-dichloroaniline (DCA). The centrifuged soil was retained and then extracted with methanol prior to HPLC analysis for the same suite of phenylureas. A mass balance approach showed large variations in diuron distribution but on average accounted for 104% of the diuron applied. Concentrations of diuron and its metabolites were roughly five times higher in the soil than in the soil porewaters. After 50 days metabolites comprised 10% of the total diuron present in the porewater and 20% of the total diuron sorbed to the soil matrix. After 36 days a large pulse of diuron and DCPMU appeared in the porewaters and soil matrix at a depth of 54 cm, travelling an average of 0.15 cm/d faster than Br. A preferential route for diuron transport is suggested. There is evidence to suggest that degradation occurs at depth as well as at the soil surface. Metabolites generally appear to move more slowly than the parent compound. All metabolites were encountered but interpreting transport and degradation processes simultaneously proved beyond the capability of the study. Diuron was detected once in a shallow (5 m) observation well situated on the experimental plot. High concentrations of diuron and metabolites were still present in the soil and soil solutions after 50 days. After 338 days diuron was absent from the porewaters but still resided in the solid phase. The metabolite DCPU became the dominant compound in the soil solution whereas DCPMU was dominant in the sorbed phase. Both compounds remained as a source of potential groundwater contamination.

1 Introduction

Contamination of groundwater by pesticides has brought increased environmental concern over the past decade (Foster et al., 1991; Soutter and Pannatier 1996; Chilton et al., 2000; Foster 2000; Gaus 2000). In the United States, a considerable body of work exists relating to the occurrence of both parent compound pesticides and their metabolites in aquifers (Thurman et al., 1992; Baker et al., 1993; Lawrence et al., 1993; Kolpin et al., 1996; Kolpin et al., 1998; Kolpin et al., 2000a; Kolpin et al., 2000b). In the UK the number of field studies has been limited (Clark et al., 1991; Gooddy et al., 2001; Johnson et al., 2001) with researchers often concentrating on laboratory studies of transport and degradation potential (Johnson et al., 1998; Besien et al., 2000; Johnson et al., 2000).

The major aquifer in the UK, the Cretaceous Chalk, is a soft microporous and fractured calcium carbonate commonly overlain by thin (<1 metre) calcareous soils. It is a complex natural system and consequently is very difficult to measure or sample in a systematic manner. Once a pesticide enters the chalk rock, the potential for biodegradation is substantially reduced (Johnson et al., 2000). With effect from December 2003, the European Union Drinking Water Directive (Council Directive 98/83/EC) has set limits of 0.03 µg/L for certain pesticides. Under the Directive there is currently no requirement for water supply organisations to measure pesticide metabolites despite evidence that their toxicity can be higher than the parent compound (Tixier et al., 2000; Tixier et al., 2001). There is a clear need therefore, to better understand the movement and transport of pesticides and their degradation products in both the thin soil zone, where most retardation and degradation is likely to take place, and in the aquifer itself. In this study we have applied diuron and bromide, as a conservative tracer, to a trial site. By improving existing analytical methods we have made a series of field measurements to determine the movement and transport of both diuron and its metabolites under normal herbicide application rates and environmental conditions.

Diuron (*N*'-[3,4-dichlorophenyl]-*N,N*-dimethylurea) is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds. It is used on many agricultural crops such as fruit, cotton, sugar cane, alfalfa, and wheat but is more widely applied for long-term pre-emergence weed control in non-crop areas (Tomlin, 1994) especially along railway lines (Schweinsberg et al., 1999). It may be found in formulations as wettable powders and suspension concentrates. Diuron works by inhibiting photosynthesis. It is relatively persistent in soil, with half-lives from 1 month to 1 year (Wauchope et al, 1992). Its persistence in soil is due to a combination of three properties: chemical stability, low water solubility and strong adsorption to soil particles (Walker and Jurado-Exposito, 1998). Microbial degradation is considered to be the primary mechanism for its dissipation from soil (Tixier et al., 2000). Under well oxygenated conditions, this is believed to occur by successive demethylation of the urea group followed by hydrolysis to produce a chlorinated aniline (Figure 1). The metabolites are generally less mobile than the parent compound (Howard, 1991).

This report details the findings from the first year of an on-going project into the fate of herbicides and their metabolites in the unsaturated zone of UK aquifers.

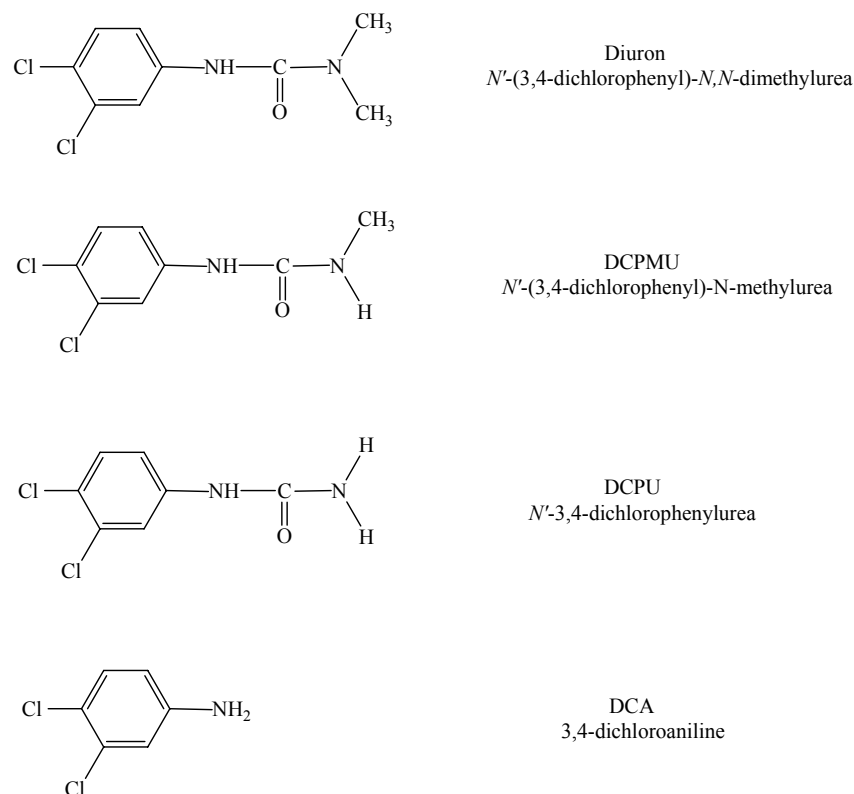


Figure 1 Chemical structure of diuron and three sequential degradation products, DCPMU, DCPU and DCA.

2 Methods

2.1 FIELD SITE AND SAMPLING

The field site is situated near Wallingford, UK (NGR 46141898, 1°06' W 51°36' N). The site lies 250 m west of the topographical gradient change indicating the edge of the outcrop of the Lower Chalk and is situated over 1st (Flood Plain) Terrace deposits of Younger River Gravels in the valley of the River Thames (Avery, 1980). The soil is roughly 50 cm thick and is typical of brown calcareous earths of the Coombe 2 series, although near to the boundary of the argillic brown earths of the Sutton 2 series. Below 50 cm, a thin band of Chalk is encountered but no River Gravels were excavated as auguring was ceased at 54 cm. No previous pesticide applications have been made for at least 30 years and the land is left under grass, being regularly cut during the summer months.

To investigate the in situ degradation and mobility of diuron we devised a small experimental plot as shown in Figure 2. The plot comprises a 3x3 m grid with a small, 5 m deep observation borehole constructed towards its northern end. On the 9th January 2001 at 11.30 am, a solution containing 6.03 g of an agricultural grade of a commercially available form of diuron, Karmex® (Du Pont chemicals), and 180 g of KBr in 9 litres of Wallingford tap water (approximately pH 7) was prepared in a clean 10 L watering can and applied to the plot by hand. The concentration of diuron applied is equivalent to 6.7 kg/ha which is the maximum recommended application rate.

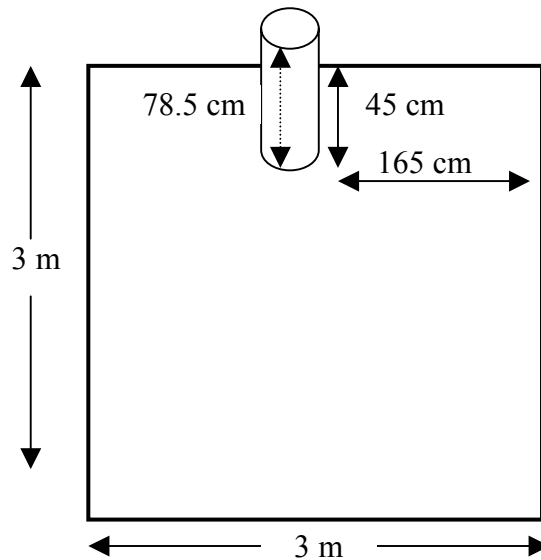


Figure 2 Schematic diagram of experimental site.

The KBr application is equivalent to 200 kg/ha or 134 kg/ha of Br and was applied to act as a conservative tracer of the downward flux of water.

Precipitation was measured by a local rainfall collector situated roughly 50 m from the experimental plot. Figure 3 shows the distribution of rainfall that occurred during the first 50 days of the monitoring period. A total of 109 mm fell on the 26 days when rainfall occurred. On 19 occasions daily rainfall exceeded 1 mm. No rain fell on the day of application. During the complete period of January-February 2001 a total of 129.2 mm fell in the area, this compares with a 20 year median for the site of 96.3 mm which suggests this part of the winter was wetter than normal.

Soil profiles down to 54 cm were obtained with an Edelman (Dutch) auger. Samples were taken every 9 cm and profiles were taken in duplicate with equivalent depths mixed in a polythene bag. Groundwater samples were taken at the same time from the observation borehole by using a small, battery powered submersible pump. The groundwater at the site is comparatively shallow, varying between 1.00 m and 1.40 m. Samples for both soil profiles and groundwater were taken after 1, 8, 15, 22, 29, 36, 50 and 338 days.

In the laboratory approximately 300 g of soil from each of the samples were loaded into the buckets of a six arm JA 14 fixed angle rotor in a refrigerated Beckman J2-21 high speed centrifuge. Specially made Delrin liners with collection cups and pre-filters held the soil in the centrifuge rotor. The samples were centrifuged at 14,000 rpm (equivalent to a driving force of about 1.7 MPa) for 35 minutes at 4°C, and the pore water was extracted using the centrifuge drainage method (Edmunds and Bath, 1976). Great care was taken to avoid contamination and to minimize evaporation. Pore waters were extracted on the same day as soil sampling. During the first sampling exercise the resultant porewaters were divided into 4 fractions: 4ml 0.45 µm-filtered and unacidified for anions (including the bromide tracer); 5ml 0.45µm-filtered and acidified for cations; 4ml unfiltered and unacidified for dissolved organic carbon (DOC); and 10 ml unfiltered and unacidified for diuron and its metabolites. For subsequent sampling the porewaters were split into just 2 fractions: 2ml unfiltered and unacidified for bromide and a minimum of 10ml unfiltered and unacidified for diuron and metabolites. The centrifuged soil residues were preserved in a refrigerator at 4°C for 1 day prior to extraction by methanol and subsequent analysis for diuron and metabolites. These residues represent diuron and metabolites that are sorbed to the soil surface.

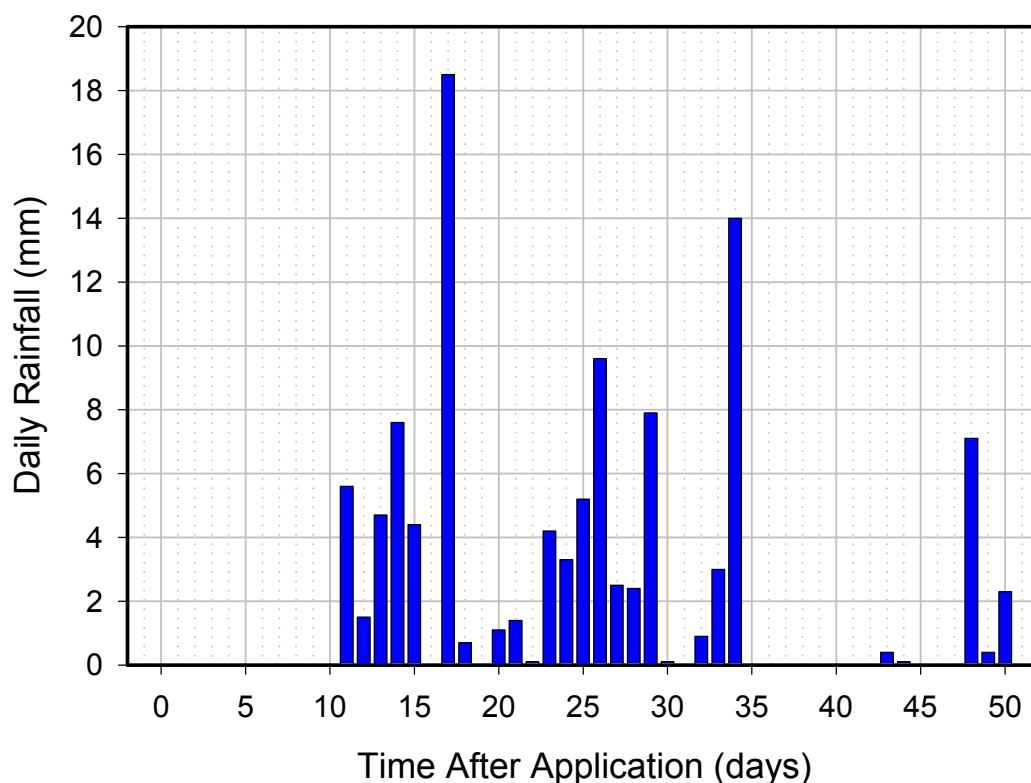


Figure 3 Bar chart showing rainfall at the site over the initial 50 days of intensive sampling.

2.2 SOIL CHARACTERISATION AND CHEMICAL ANALYSIS

Filtered acidified porewaters were analysed using a Perkin Elmer Optima 3300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) which is calibrated using standard solutions for the following 19 elements: Na, K, Ca, Mg, B, Ba, P_{total}, SO₄, Si, Sr, Zn, Cd, Cu, Co, Cr, Ni, Mn, Fe_{total} and Al. All analyses were blank corrected and detection limits defined as 6 times the standard deviation of the blank. Nitrate-nitrogen (NO₃-N), ammonium-nitrogen (NH₄-N), and Cl were determined using standard Auto Analyser II colorimetric methods (Kinniburgh and Miles, 1983) on the filtered, unacidified water fraction. Nitrate-nitrogen was determined by the cadmium column reduction method since the high dissolved organic carbon content of the samples can cause suppression of the baseline when the hydrazine/copper reduction method is used. Bromide was measured on a separate sample and analysed by a bromide ion selective electrode. pH was measured with a glass micro electrode and bicarbonate (HCO₃) determined with an automated Radiometer titrator. Dissolved organic carbon (DOC) was measured on the unacidified, unfiltered sample with a TOCSIN II aqueous carbon analyser. Analyses were verified against standard reference materials.

Chemical characterisation of the solid phase was carried out by using a weak nitric acid solution. The efficacy of this method for providing data on exchangeable cations in sandy acid soils has previously been demonstrated (Boekhold et al., 1993) and has a number of benefits over more specific extractants (Goody et al., 1995). In calcareous soils the extractant will considerably overstate the exchangeable base cation concentration but still provides useful information on other elements present. Five grams of dry soil from each 9 cm interval were placed into a pre-weighed 250 ml Oak Ridge polypropylene centrifuge tube to which was added 50 ml of 0.43 M HNO₃ (Analytical Reagent grade). The tubes were shaken on a box shaker for 2 hours before centrifuging for 10 min at 14,000 rpm. The coloured supernatant liquids were then filtered

through 0.45 µm filters prior to analysis by ICP-OES as above. All extractions were performed in duplicate.

Total organic carbon of the solid phase was determined by a Carlo Erba NA1500 CNS analyser fitted with a Porapak column operated isothermally at 70°C.

2.3 DIURON AND METABOLITE ANALYSIS

Initial HPLC method development was based on a previously published method (Field et al., 1997). The method involved the separation of diuron and its metabolites on a base-deactivated reversed-phase C18 Supelco LC18-DB column. However, in contrast to Field and coworkers, it was found that gradient elution was not necessary to provide good chromatography. Preliminary experiments using solutions of pure diuron and pure metabolites (QM_x Laboratories, Saffron Walden, UK), in conjunction with various isocratic compositions of a simple binary mobile phase consisting of acetonitrile and water, resulted in the formulation of an optimum mobile phase composition of 35% acetonitrile : 65% water. Chromatograms produced with this gave retention times of *ca.* 8 mins. for DCPU, *ca.* 11 mins. for DCPMU, *ca.* 14 mins for diuron and *ca.* 20 mins. for DCA. Detection was conducted with a sensitive UV/Vis detector (Waters 2487) set at 252 nm. By using a large sample introduction loop of 1 ml capacity a detection limit in the region of 50 ng/L was achieved. Good detection limits on small volumes of sample is crucial to this study due to the serious time penalty of centrifuging large masses of soil to obtain enough water for a pre-concentration step. Small sample size also meant that many samples could be taken from the study plot without causing the serious disruption to the site that shallow coring using a drilling rig would cause.

A 2 mg/L aqueous solution of the commercial agrochemical form of diuron (Karmex) was prepared and analysed by HPLC. The chromatograms obtained indicated that the formulation contained 84% weight for weight (w/w) diuron (compared with 80% stated by the manufacturer) together with 0.1% w/w DCPMU, 0.1% w/w DCA and 0.01% w/w DCPU.

Porewater was analysed directly by injection of 1 ml onto the HPLC system. On completion of an HPLC analysis the column was backflushed with 80% aqueous acetonitrile to remove any strongly retained materials that might otherwise elute on later runs with possibly deleterious effects on peak quantification.

For the soil samples, roughly 200 g of a given post-centrifuged soil was transferred into a conical beaker and accurately weighed. To this was added twice as much methanol by weight. The mixture was carefully stirred with a large palette-knife type spatula which was also used to breakdown large soil aggregates. The beakers and their contents were then placed in a heated ultrasonic bath (40°C) and sonicated at intervals over a 24 h period. Further stirring with the spatula was performed intermittently over a 24 h period. The contents of each beaker were then transferred to a Buchner funnel and filtered through Whatman No. 41 filter paper. The residue was rinsed with methanol and the filtrate was reduced in volume on a rotary evaporator until the methanol had been removed. The resulting mainly aqueous suspension was made to an appropriate volume with pure water, sonicated and a 1 ml volume injected through the HPLC system. Again a post-run backflushing regime was employed to preserve the column and avoid quantification artefacts.

3 Results

3.1 POREWATER INORGANIC CHEMISTRY

Major ion data from the porewater profile sampled 8 days after diuron and bromide application is presented in Table 1. The predominance of calcium and bicarbonate ions demonstrate the porewaters to be of a calcium carbonate type. Nitrate concentrations are above EU drinking water standard and considered high when compared with those found beneath non agricultural grassland (Campbell et al., 1989). This may reflect some post-war agricultural activity on the land although any such activity is very unlikely to have involved application of diuron or similarly structured herbicide. The high concentration of potassium and chloride in the top 9 cm reflects the application of KBr, with chloride present as a trace impurity present in the reagent. The pH of the soil solution averages 8.02 which is indicative of mildly alkaline conditions.

Table 1 Major ion chemistry for porewater profile sampled 8 days after application.

Depth (cm)	pH	mg/L										
		Na	K	Ca	Mg	Si	HCO ₃	Cl	SO ₄	NO ₃ -N	NH ₄ -N	P
9	7.93	15.3	35	229	8.13	23	144	368	19.4	7.2	0.77	0.54
18	8.02	11.1	0.5	82.2	1.80	8.3	123	25.8	25.3	21.9	4.3	0.36
27	8.03	13.6	0.6	86.2	1.37	5.1	107	19.1	19.2	28.7	0.15	0.39
36	8.02	10.7	0.5	77.1	1.32	5.0	112	16.4	18.9	23.0	0.15	0.42
45	8.04	9.8	0.5	78.2	1.70	4.7	124	18.5	19.4	19.2	0.12	0.43
54	8.05	9.4	0.6	79.1	1.65	4.3	126	19.2	19.5	17.6	0.11	0.34

3.2 SOLID PHASE EXTRACTIONS

Data for the solid phase inorganic chemistry are presented in Table 2 for the weak nitric acid extractable cations. For most elements a clear trend of decreasing concentration with depth can be observed. The exceptions to this are the concentrations of calcium and strontium, both of which increase with depth. The calcium values are erroneously high and do not reflect extractable cations as the calcium has been dissolved from the soil matrix. This is likely to also be the case for strontium, although the other two base cations, magnesium and barium, follow the decreasing concentration with depth trend. Higher concentrations of calcium appear at depth as some weathered chalk bedrock is present below 50 cm. Low concentrations of both iron and manganese throughout the profile suggest the soil is well aerated and not subject to gleying. This reflects the oxidising conditions in the soil thereby facilitating breakdown of diuron by an aerobic route through successive demethylation of the urea group. The low concentration of iron also precludes any significant sorption to iron hydroxides. The high calcium concentrations clearly indicate that the soil is calcareous and as such the conditions are alkaline and well buffered.

Table 2 0.43 M HNO₃ extractable cations from calcareous soil.

Depth cm	mg/kg													
	Na	K	Ca	Mg	Si	Ba	B	Fe	Mn	Sr	Al	Zn	Ni	
0-9	242.3	637.5	56138	315	105	10.13	2.25	1.91	188	83.6	3.59	183	0.58	
9-18	99.0	60.0	58313	222	87	8.44	1.50	0.71	132	88.9	1.97	32.1	0.34	
18-27	94.5	48.8	60788	191	75	7.95	1.50	0.19	87.0	94.9	0.46	21.4	0.30	
27-36	105.0	75.0	58125	235	92	8.40	1.50	0.60	125	94.5	<0.05	2.93	0.23	
36-45	98.3	69.0	60338	198	80	8.06	1.50	0.34	105	94.9	0.47	1.35	0.29	
45-54	81.0	48.8	61350	179	77	5.43	<1.50	<0.15	74.3	98.3	0.16	0.79	0.27	

3.3 DISSOLVED AND SOLID PHASE ORGANIC CARBON

The carbon content of both the soil and the soil solution is expected to have a significant effect on diuron transport since sorption is considered a key process in attenuation (Madsen et al., 2000). The relative proportions of solid phase organic matter and dissolved organic matter effectively compete for hydrophobic organic molecules. Figure 4 shows how organic carbon varies with depth. Organic carbon in the solid phase (TOC) varies from 4.97 to 0.94% whereas dissolved organic carbon ranges from 112 to 28 mg/L. TOC shows a good decreasing trend with depth, with concentrations declining at roughly 0.1% organic carbon per cm. DOC also shows a general decreasing trend with depth although the lowest DOC measurement occurs at 18 cm rather than at the profile bottom. DOC concentrations decline at roughly 2 mg/L per cm. The ratio between solid phase and dissolved phase carbon is approximately 500:1. At the application rate used, the diuron added should have contributed no more than 1 mg/L to the DOC.

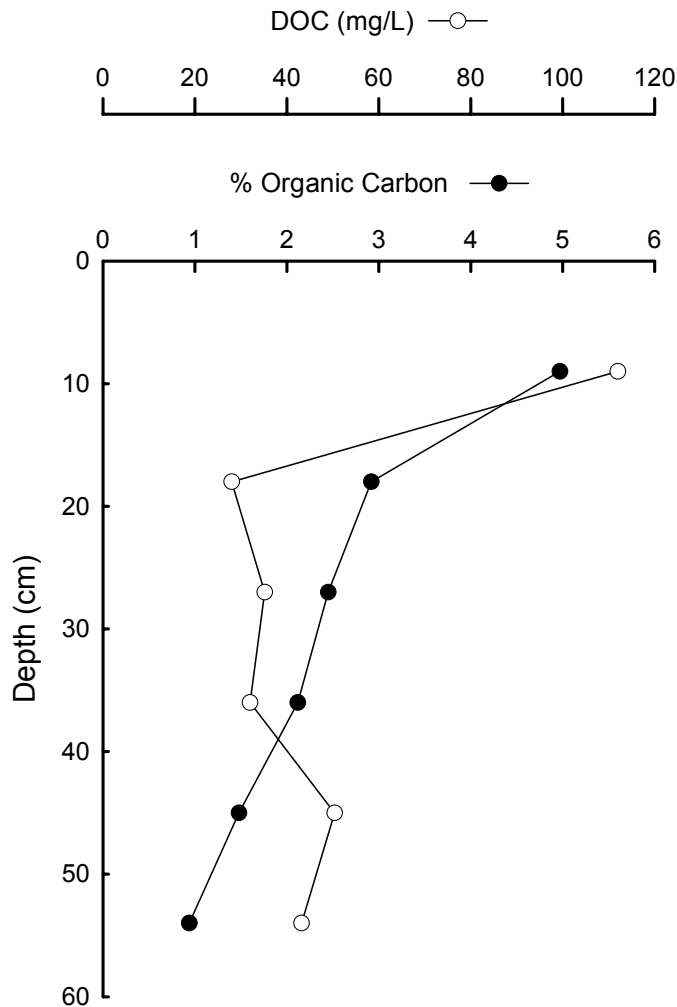


Figure 4 Concentration with depth profiles for dissolved organic carbon (DOC) and total organic carbon in the soil.

3.4 MOISTURE CONTENT AND YIELDS

Over the first 50 days of the experiment the moisture content of the soil ranged from a maximum of 88% at the top of the profile to a minimum of 22% at 54 cm. Interestingly, the moisture content varied most greatly with time at the top of the profile with a coefficient of variance (CV) of 22%. At 27 cm the moisture content remained remarkably constant with a CV of just 1%. Water yields vary more greatly than the moisture contents with a maximum yield of 36% at the

top of the profile and a minimum of 7% at 45 cm. Although the moisture contents for 27 cm remained remarkably constant, yields from this depth showed the greatest variance over time, with a CV of 36%.

3.5 DIURON DETECTIONS

Significant concentrations of diuron (7 µg/L) and DCPU (0.5 µg/L) were found in the porewaters recovered from below 50 cm just 8 days after application. After the same interval, detectable concentrations of diuron (17 µg/kg), DCMPU (0.6 µg/kg), DCPU (0.2 µg/kg) and DCA (2.0 µg/kg) were all found in the soil residue material from this depth.

A mass balance approach has been used in Figure 5 to show the percentages of total diuron and bromide recovered on each sampling occasion from the whole soil profile during the intensive sampling regime as a function of the original amount applied. The effect of heterogeneity is clearly demonstrated as bromide recovery varies between 64 and 440% of that originally applied (mean recovery is 174%). Recovery of total diuron (the sum of diuron and its metabolites) as a percentage of that originally applied as active agent accounts for between 1 and 43% in the porewaters (mean recovery 15%). From the solid phase of the soil the range is 21-183% (mean recovery 89%). The mean concentration of the total amount of diuron and metabolites recovered (porewaters and solid phase) accounted for 104% of the amount applied but ranged between 22-226%. This suggests that during the first 50 days the majority of diuron remains in the soil zone.

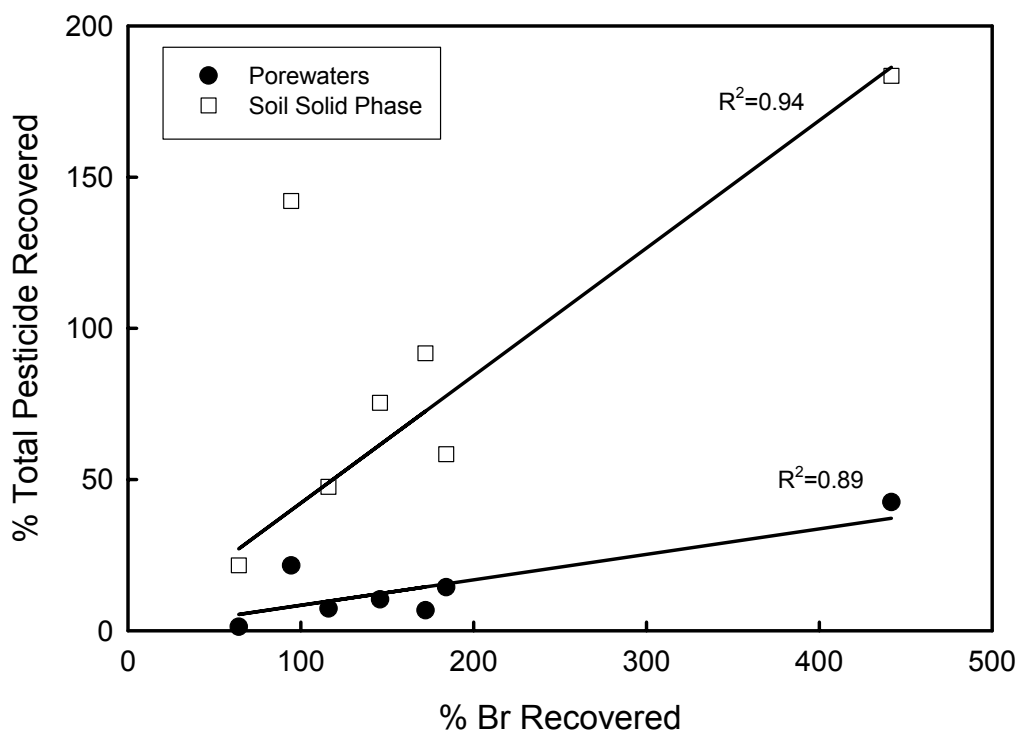


Figure 5 Cross plot of percentage bromide recovery against total diuron and metabolites in the porewaters and total diuron and metabolites sorbed to the soil matrix.

Two best fit linear regressions have also been plotted on Figure 5. The regressions have been calculated based on the omission of the data from 15 days of sampling where 95% of the bromide was recovered. The reasons for this data point falling off the linear trend are unclear. Although it is reasonable to assume that the amount of porewater bromide and total diuron extracted should have a linear relationship, the relationship between bromide and the amount of total diuron residing in the solid phase suggests some form of equilibrium state between the solid

and liquid phases. Total diuron concentrations in the soil are roughly five times greater than in the porewaters.

Table 3 summarises the percentage of porewater samples found to exceed two threshold values, 0.1 µg/L and 1 µg/L. These have been chosen because 0.1 µg/L is the current EU admissible maximum and 1 µg/L is a factor of ten greater and as such allows for dilution effects in groundwater. Diuron occurs throughout the porewater profile at concentrations greater than 0.1 µg/L for the whole 50 days of the intensive monitoring programme and at concentrations greater than 1 µg/L for 97 % of the measurements made. DCPMU, the first recognised metabolite of diuron was found in porewaters at concentrations greater than 0.1 µg/L for 69% of measurements made with the number of detections at this concentration generally showing a decreasing trend with depth. DCPU, the second sequential metabolite of diuron was detected on a surprising 92% of occasions at a concentration greater than 0.1µg/L. At the higher threshold value of 1 µg/L, DCPMU and DCPU are detected roughly the same number of times with the number of positive detections decreasing with depth. DCA was detected at concentrations greater than 0.1 µg/L on roughly a third of occasions with the majority of these occurring in the lower 20 cm of the profile.

Table 3 Percentage of samples exceeding 1 µg/L and 0.1 µg/L in porewater samples taken at depths between 9 and 54 cm over a fifty day period.

Depth (cm)	Diuron	DCPMU	DCPU	DCA
Porewater > 1µg/L				
9	100	100	86	0
18	100	43	0	0
27	86	0	0	0
36	100	0	17	17
45	100	17	17	0
54	100	0	17	0
	97	28	23	3
Porewater > 0.1µg/L				
9	100	100	100	14
18	100	86	71	0
27	100	43	86	0
36	100	83	100	50
45	100	67	100	67
54	100	33	100	50
	100	69	92	28

Table 4 summarises the percentage of soil samples found to exceed threshold values of 0.5 µg/kg and 5 µg/kg. These have been chosen based on the maximum admissible concentration and an assumed average water content of 200 g/kg. Diuron occurs throughout the profile at concentrations greater than 0.5 µg/kg on all extractions carried out and at concentrations greater than 5 µg/kg on 89% of measurements made. At this higher threshold the number of positive detections declines with depth. DCPMU is detected on the majority of occasions (95%) at concentrations greater than 0.5 µg/kg and on half of the samples at concentrations greater than 5 µg/kg, where they all occur in the top 27 cm. DCPU is detected 58% and 18% of the time at concentrations exceeding 0.5 µg/kg and 5 µg/kg respectively. Detections generally decline with depth. The greater positive detection of DCPMU over DCPU in the soil is in contrast to what is found in the porewaters where DCPU tends to prevail at concentrations between 0.1 and 1 µg/L. DCA occurs in the top 27 cm on a several occasions at concentrations greater than 5 µg/kg at concentrations greater than 0.5 µg/kg is commonly found throughout the profile.

Measurements made on groundwater found concentrations of diuron and DCPMU greater than 0.1 µg/L on just one occasion 8 days after application. No other metabolites were found and neither was bromide detected at the water table.

Table 4 Percentage of samples exceeding 5 µg/kg and 0.5 µg/kg in solid phase samples taken at depths between 9 and 54 cm over a fifty day period.

Depth (cm)	Diuron	DCPMU	DCPU	DCA
Soil > 5µg/kg				
9	100	100	100	57
18	100	100	0	14
27	100	71	0	14
36	83	0	0	0
45	67	0	0	0
54	60	0	0	0
	89	53	18	16
Soil > 0.5µg/kg				
9	100	100	100	57
18	100	100	100	57
27	100	100	71	29
36	100	100	17	0
45	100	100	17	67
54	100	60	20	20
	100	95	58	39

3.6 TEMPORAL CHANGES IN DIURON AND METABOLITES

An assessment of how the relative proportions of diuron and its metabolites vary with time in the porewaters is shown in Figure 6. A gradual decline in parent proportion can be observed so that after 50 days diuron accounts for 90% of the total diuron and metabolites found in the porewaters of the entire profile. This decline is not however completely smooth, with an apparent slight increase in relative diuron porewater concentrations after 29 and 36 days. The second most dominant compound detected is DCPMU which initially accounts for 0.25% of total diuron and metabolites after 1 day and 9% after 50 days. DCPU accounts for just over 1% of total diuron and metabolites detected after 50 days with the relative proportion growing from 0.1% on day 1. DCA first contributes 0.1% of the total after 22 days and this contribution is then relatively constant throughout the remainder of the monitoring period.

A similar assessment has been carried out for the centrifuged soil and is shown in Figure 7. The parent compound is again dominant, accounting for initially 96% of the total amount of diuron and metabolites present. After 50 days this has declined to just over 80%. A slight increase in the relative proportion of diuron again occurs after 29 and 36 days. DCPMU is again the dominant metabolite, accounting for 17% of total diuron and metabolites sorbed to the solid phase after 50 days. From 15 days DCPU starts to account for between 1 and 1.5% of total diuron and metabolites detected. DCA starts to account for roughly 1% of the total found after 22 days and remains at a fairly constant concentration.

Data from the sampling after 338 days shows a considerable decrease in diuron and metabolite concentrations (Table 5). Diuron is absent from the porewaters and the dominant metabolite is DCPU, accounting for 78% of the total herbicide in the soil solution. DCPU concentrations show an increasing trend with depth. In contrast, diuron and all metabolites are detected in the solid phase material, with the dominant compound DCPMU, which accounts for 62% of total sorbed herbicide. Concentrations are highest at the top of the profile with a gradual decrease with depth, although a slight increase in concentration occurs at the profile base.

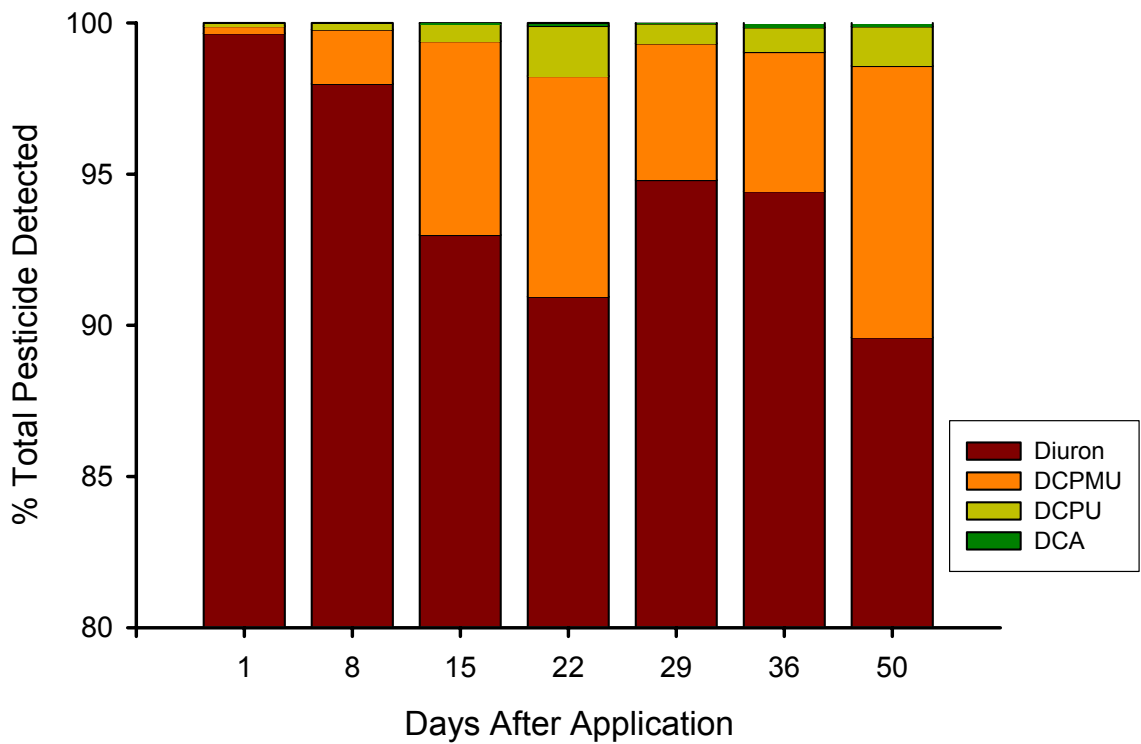


Figure 6 Bar chart showing the relative proportions of diuron and metabolites detected in the porewater solution as a function of the total detected in the soil solution with time.

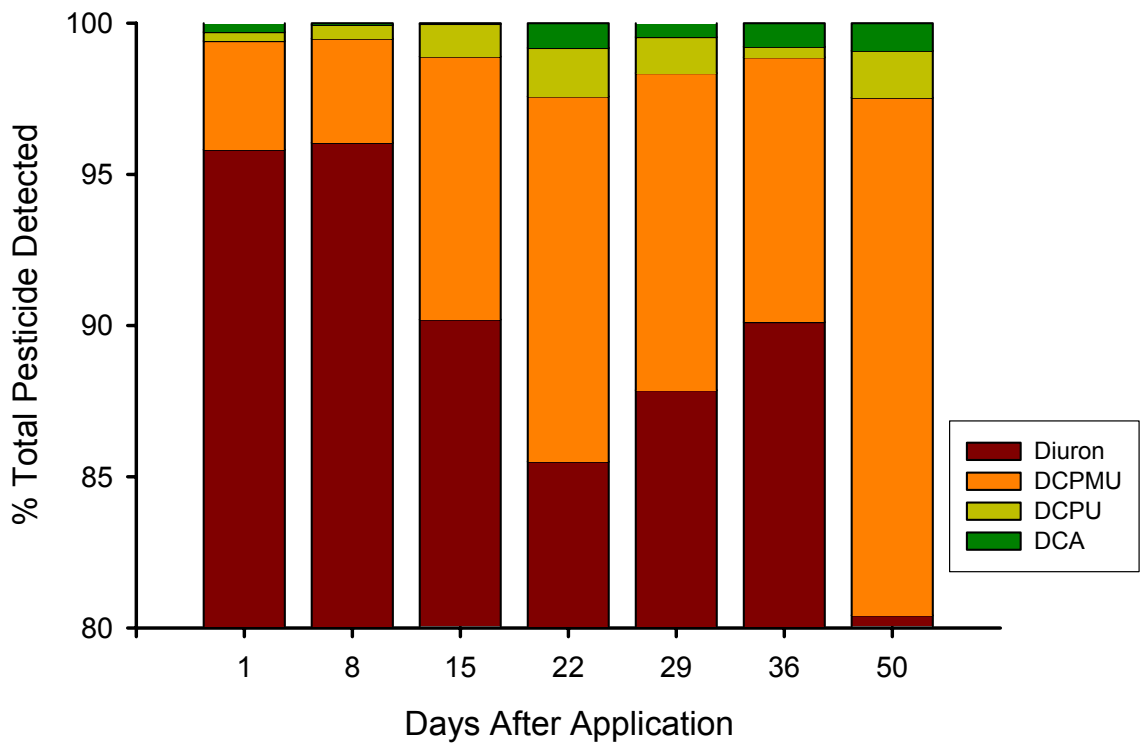


Figure 7 Bar chart showing the relative proportions of diuron and metabolites detected in the soil as a function of the total detected in the solid phase with time.

Table 5 Concentration of diuron in porewaters and in solid phase after 338 days.

Depth (cm)	Diuron	DCPMU	DCPU	DCA
Porewaters ($\mu\text{g/L}$)				
9	0.00	0.00	0.15	0.00
18	0.00	0.00	0.21	0.00
27	0.00	0.07	0.22	0.00
36	0.00	0.00	0.25	0.32
45	0.00	0.01	0.44	0.02
54	0.00	0.01	0.42	0.10
Solid Phase ($\mu\text{g/kg}$)				
9	22.1	135	9.79	42.1
18	2.95	13.6	3.72	6.95
27	2.64	8.25	1.11	2.03
36	1.07	1.98	0.70	2.12
45	0.09	1.95	0.09	0.91
54	1.14	3.49	1.83	1.86

3.7 DETERMINING BROMIDE AND DIURON TRANSPORT

Movement of bromide and diuron has been determined to assess the rate at which they migrate to groundwater and whether or not any preferential movement or attenuation occurs. Concentration against time curves have been determined for all the analytes in both the porewaters and in the soil to show when the bulk of the fluid movement is occurring. These curves have been normalised for each analyte in a given depth range. An example for the movement of bromide and diuron is given in Figure 8. The curves show how the relative concentrations of a given analyte change with time. In the 18-27 cm sampling interval bromide reaches a peak concentration after 29 days. For the peak in bromide to reach the 36-45 cm interval takes a further 7 days, therefore the bromide is moving over this range at an average rate of roughly 2.5 cm/d. For the data plotted (Figure 8) diuron and bromide show very similar rates of transport.

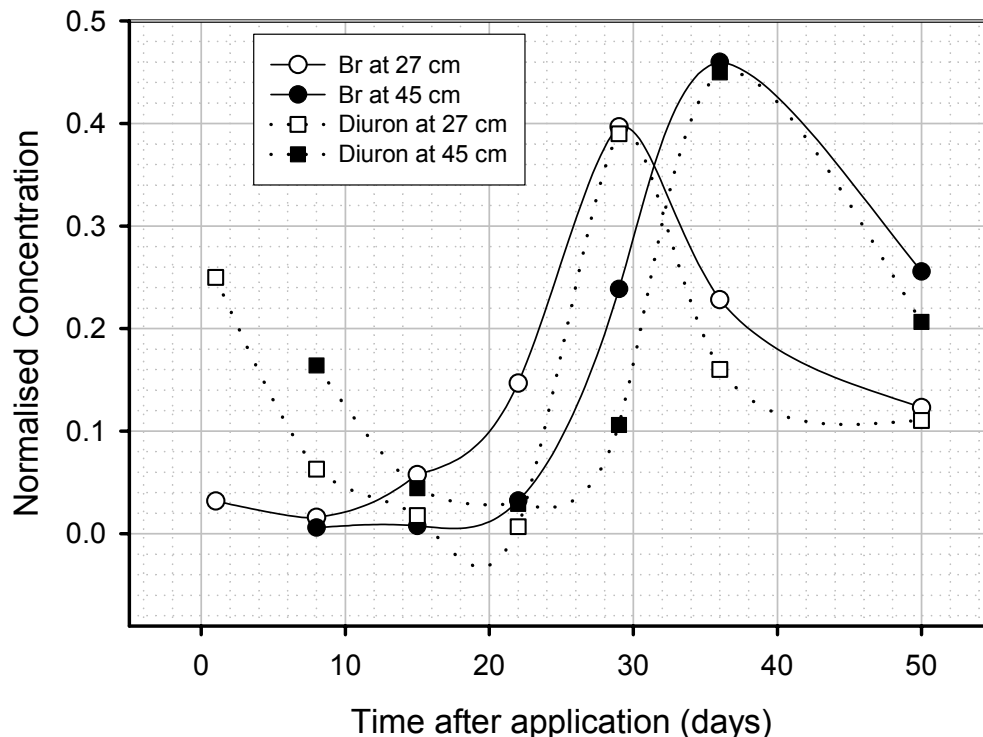


Figure 8 An example showing the method used to determine the time taken for peaks in porewater concentration for both bromide and diuron to move through the soil profile.

By finding the maxima in concentration at each depth range it is possible to compare the rates of movement of bromide with diuron and its metabolites. Figure 9 displays a plot showing the time at which a peak in concentration occurred at a given depth for the sampled porewaters. Bromide moves through the entire profile at an average rate of 1.1 cm/d, although in fact the plot displays a break in gradient around the 27 centimetre point with movement occurring at 0.6 cm/d before this point and 2.25 cm/d after it.

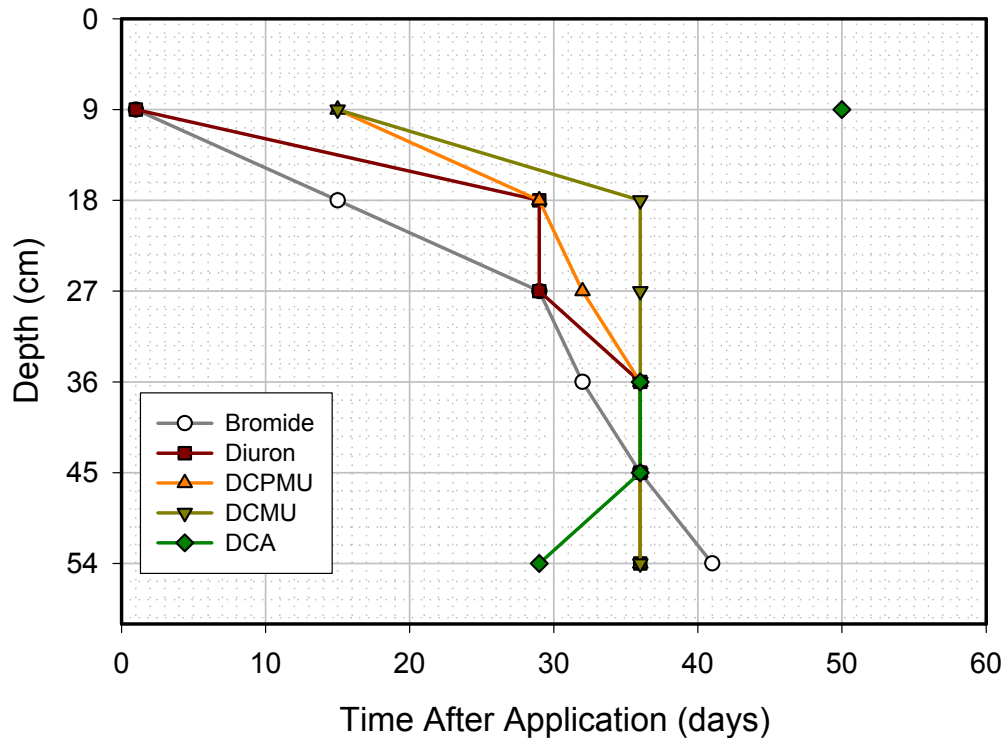


Figure 9 Time taken for peak concentrations to move through the porewaters for bromide, diuron and its metabolites. No DCA was detected at 18 cm or 27 cm.

Diuron does not appear to move in the same way as bromide. It takes twice as long to get to 18 cm, however once at this point it has also been able to migrate further in little or no time indicating some preferential movement. Diuron is then apparently retained relative to bromide, with a peak in concentration at 36 cm occurring 4 days after bromide has reached this point. However, from here on diuron moves more rapidly than bromide. Diuron reaches the profile bottom 5 days before bromide and has an average velocity of 1.25 cm/d.

DCPMU and DCPMU are retained for longer than diuron in the top part of the profile and can not of course occur until diuron starts to degrade. DCPMU then follows a similar pathway to diuron although does not appear to move more rapidly between 18 and 27 cm taking 3 days longer than diuron to reach this point. DCPMU is retained for longer than DCPMU and takes 36 days to reach 18 cm. However, DCPMU then moves rapidly with diuron and DCPMU. Both of these degradation products have reached a peak at the bottom of the profile before bromide. DCA reaches a maximum concentration in the top soil after 50 days.

Figure 10 displays a similar plot to Figure 9 but is for the soil residue data. Diuron follows a similar pattern to the porewaters although moves more rapidly between 18 and 45 cm than in the porewater. Diuron has distributed itself throughout the solid phase at the same rate as it has through the porewaters (1.25 cm/d). DCPMU is again retained in the top soil and then continues to move throughout the profile in a similar manner to diuron although is generally displaced by 3-5 days. This may reflect both the rate of degradation of diuron and attenuation of DCPMU. DCPMU and DCA both behave in a manner considerably different to the porewaters. Initially DCPMU is retained for 15 days in the top soil but then takes a further 35 days to move down to 18 cm.

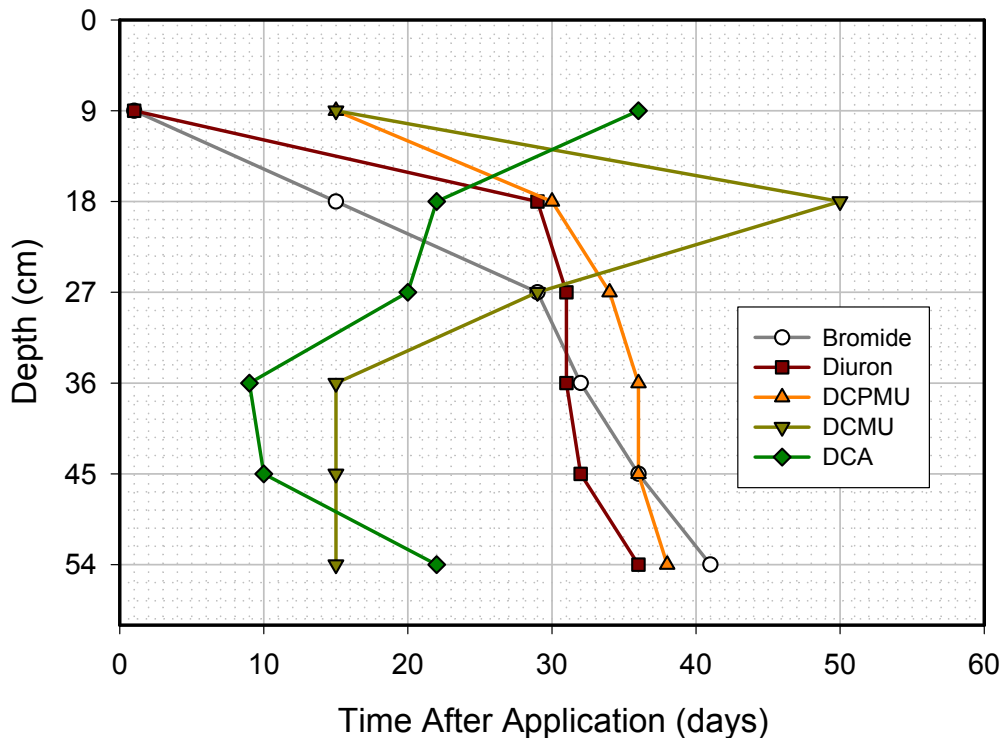


Figure 10 Time taken for peak concentrations to be detected in the soil solid phase for diuron and its metabolites. Bromide determined from the porewaters is shown as a reference.

4 Discussion

Movement and partial degradation of diuron, applied at normal concentrations under realistic environmental conditions, has occurred rapidly. It is generally assumed that the majority of the parent and daughter compounds will remain in the top soil (Tworkoski et al., 2000), however diuron and its metabolites have been found at depths in excess of 50 cm in 8 days in both the porewaters and associated with the soil solid phase. As the concentration of organic carbon decreases with depth, adsorption is also diminished in effectiveness. As the concentration of organic carbon declines so too does the microbial activity, further reducing the magnitude of biodegradation. Once the diuron has escaped from the soil zone there is little to prevent it reaching the unsaturated zone of an aquifer and ultimately the water table.

Several previous studies have observed preferential flow mechanisms operating in soils (Harris et al., 1994; Johnson et al., 1996) and this appears to be occurring at this site. Rainfall data (Figure 4) shows heavy precipitation in the days just before the major pulse of diuron and its metabolites migrate more rapidly through the soil after 36 days. Consequently there is little time for sorption to take place (Walker and Jurado-Exposito, 1998) and the relatively high concentration of organic carbon has little effect on attenuation. Although data from the moisture contents and yields shows considerable variation in the top 9 cm, there is no other evidence for a large pulse of water moving through the profile, therefore it is further support for water movement by a preferential pathway. It has been shown that the formulation of diuron can influence its mobility (Chaplain et al., 2001) and it is proposed therefore that the suspension produced for the environmental application of diuron attaches itself to particles and moves as colloids through the soil profile (Grolimund et al., 1996) and is transported more rapidly than the average downward flux of recharge. This has previously been proposed as a mechanism for pesticide movement in a chalk aquifer (Goody et al., 2001).

The dynamics and kinetics of diuron sorption and desorption are clearly complex (Alva and Singh, 1991; Reddy et al., 1992; Gaillardon, 1997) and hard to establish from a field experiment especially in the competing presence of metabolites. The high speed centrifugation process is assumed to remove all the mobile water, however water carrying diuron has clearly been able to travel throughout the depth of the soil and sorb to the soil surface. The greater amount of DCPMU found in the soil compared with the porewater solutions (where higher relative amounts of DCPU are found) may reflect structural differences between the two compounds, with DCPMU more readily sorbed to organic matter than DCPU due to its additional methyl group. The form of the carbon and hence competition for sorption sites in both the dissolved phase and in the solid phase will also influence the partitioning of these degradation products. Unfortunately, no data have been found for Koc values or solubilities for DCPMU or DCPU. Alternatively this reversal may be indicative of their relative rates of production and/or removal.

It is not possible to quantify how much transport of the metabolites occurs as a result of formation at the surface or formation in situ as diuron moves through the profile. The profile for DCA in porewaters (Figure 10) does not display a continuous flow path through the profile which suggests that in situ degradation of DCPU is occurring. Consequently although a peak in DCA is found at the profile bottom after 29 days this could be due to some degradation resulting from the leading tail of DCPU. In the soil profile, both DCPU and DCA show peak concentrations arriving at depth well before the parent compound or DCPMU. This certainly suggests some in situ degradation but could also represent colloidal transport of these two metabolites. It is important to note that the concentrations of the maxima are both relatively low, roughly 0.5 µg/kg for DCPU and 1 µg/kg for DCA compared with a concentration in the top soil of 100 µg/kg and 60 µg/kg for DCPU and DCA respectively. Any such colloidal movement would be likely to be highly dependant on the charge of the particles (Grolimund et al, 1996) which in turn is influenced by the pH of the soil system. Additionally it is possible that the peak in porewater DCA at the profile bottom may be caused by gradual desorption of DCA from the soil matrix.

The disappearance of diuron from the soil solution after more than 300 days is encouraging in respect of groundwater pollution. However DCPU is found at concentrations above the MAC and so poses a very real threat. Relatively high concentrations in the soil may act as a potential source of contamination for years to come. It is unclear why DCPU should be dominant in the porewaters whereas DCPMU is dominant in the solid phase, although this may relate to sorption/desorption processes.

5 Conclusions

Through carrying out a field experiment rather than laboratory column studies it has been possible to observe what happens to diuron and its metabolites under physical and chemical conditions typical of a soil overlying the Chalk. The use of a bromide tracer has assisted in understanding the rate of fluid movement through the soil and is invaluable for comparison with the diuron data. The development of a low volume, high sensitivity analytical method has enabled relatively cost effective, high resolution measurement of environmental processes. Despite the resolution used, it is still not possible to quantify the processes in detail due to the considerable degree of heterogeneity encountered. The complexity of the system has made it impossible to determine the rate at which degradation occurs under typical conditions. There is good evidence to suggest that metabolites formed in the top few centimetres of soil are able to migrate through the profile, sorbing and desorbing from the soil matrix. Field evidence also suggests the continued formation of degradation products as the parent compound continues to leach through the soil. Preferential flow has been observed at the field site and this is thought to be caused by intensive rainfall and by the sorption of the parent and metabolites to colloidal

material. Migration in this way means that groundwater is particularly vulnerable to contamination, since it can be penetrated before complete degradation has had time to take place.

The study has demonstrated the importance of determining both the parent compound and its respective major metabolites. After 50 days, 10% of total pesticide compounds in the porewater consisted of degradation products. After the same time period, nearly 20% of total pesticide found in the soil matrix consisted of degradation products. Roughly five times more diuron and metabolites were found sorbed to the soil matrix than in the porewater solution. This suggests the desorption processes from the soil surface will provide a source of these compounds. After 338 days diuron is absent from the porewaters but still resides in the solid phase. The metabolite DCPU becomes the dominant compound in the soil solution whereas DCPMU is dominant in the sorbed phase. It is therefore important that analytical suites in the future include degradation products. Land where diuron has been applied may therefore remain a threat to groundwater quality especially if it is used indiscriminately on non-agricultural areas.

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