

SESSION 4D

**RESIDUES OF HERBICIDES IN
SOILS, CROPS AND WATER**

SESSION
ORGANISER MR C. S. SPELLER

POSTERS

4D-1 to 4D-11

RESIDUAL LEVELS OF ATRAZINE IN DIFFERENT SOILS OF TWO CORN PRODUCTION AREAS

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ABSTRACT

A survey of atrazine residues was carried out in two main corn production areas of Spain. About 50 fields were randomly selected in each area, Albacete and Badajoz. Soil cores, four per field, were sampled 10 months after herbicide application. Soil was extracted with ethyl acetate and atrazine analysed by GC with thermionic detection. Residue analysis showed that atrazine levels in more than 70% of the fields were equal or lower than 0.05 mg/Kg. About 20% of Albacete fields showed levels higher than 0.1 mg/Kg, which may be phytotoxic to susceptible crops in rotation with corn. Simple correlation coefficients between different physico-chemical properties of soil and residue levels were calculated. The results are discussed according with these correlation coefficients and in relation with other parameters implicated in the herbicide persistence.

INTRODUCTION

Atrazine, in binary mixture with a chloroacetamide herbicide, is widely used in pre-emergence of corn (*Zea mays* L.) with satisfactory full-season weed control. Nevertheless, the persistence of atrazine in soil and the phytotoxicity of its residues to other plants can reduce yields of subsequent crops (Frank *et al.* 1983, Ivany *et al.* 1985).

Persistence of atrazine in the soil depends on several factors like weather, i.e. rainfall and temperature, soil characteristics (Burnside *et al.*, 1969), cultural practices (Lowder *et al.* 1982, Gaynor *et al.* 1987) and application dose of herbicide (Hance *et al.*, 1971).

The aim of this work was to study the level of atrazine residues in soil in Albacete and Badajoz, two main corn production areas of Spain, and its relation with the physico-chemical properties of soil.

MATERIALS AND METHODS

Two important areas of corn production in Spain, Albacete and Badajoz, were surveyed. Except for soil type, acidic and sandy in Badajoz and with high pH and less sand content in Albacete, differences between these two areas in weather, cultural practices or herbicide doses were not outstanding. Rainfall and average temperature data during 1990, in both studied areas, are shown in Table 1.

About 50 fields were randomly selected in each area. Soil cores were

TABLE 2. Atrazine residues in soil.

Range of atrazine residues (mg/Kg)	Number of fields per site	
	Albacete	Badajoz
< 0.05	24	38
0.05-0.1	9	8
0.1-0.2	12	0

The physico-chemical properties of soils (organic matter, pH and texture), together with the atrazine concentrations found in the fields, are shown in Tables 3A and 3B.

TABLE 3A. Soil characteristics and atrazine concentration of Albacete soils.

Field	Atrazine (mg/Kg)	O.M. (%)	pH	Sand	Silt	Clay
1	0.13	1.22	8.3	46.5	28.8	24.7
2	0.09	1.43	8.2	36.3	29.9	33.8
3	0.10	1.69	7.9	35.5	20.0	44.5
4	0.02	1.69	8.0	29.7	38.4	31.9
5	0.09	0.72	8.6	30.7	36.2	33.1
6	0.01	0.73	8.6	60.5	18.5	21.0
7	0.18	1.31	8.0	36.7	38.1	25.2
8	0.15	0.99	8.3	33.0	28.0	39.0
9	0.10	0.99	7.8	33.2	24.8	42.0
10	0.16	1.22	8.4	37.1	59.2	3.7
11	0.04	1.10	8.2	18.8	53.2	28.0
12	0.04	0.99	8.4	30.2	44.5	25.3
13	0.03	1.10	8.4	7.6	58.8	33.6
14	0.09	1.49	8.4	9.4	47.7	42.9
15	0.13	1.98	8.4	4.7	54.6	40.7
16	0.18	1.55	8.3	23.0	43.3	33.7
17	0.07	1.30	8.3	24.8	42.5	32.7
18	0.10	1.39	8.3	26.1	38.1	35.8
19	0.04	0.90	8.5	36.3	21.7	32.0
20	0.07	1.80	8.3	44.0	29.3	26.7
21	0.02	1.32	8.3	54.0	22.0	24.0
22	0.04	1.87	8.4	53.3	21.1	25.6
23	0.02	0.97	8.2	49.3	23.0	27.7

Analytical methods: O.M.: Kjeldahl method; pH: 1:2.5 soil-water method; texture: classification U.S.D.A. (sand = coarse + fine); particle size analysis by pipette method.

sampled at 4 representative points per field, 10 months after application (April - May 1990). Atrazine residues in each sample were determined by gas chromatography (GC). Soil (30g) was extracted twice with ethyl acetate (100ml) on an orbit shaker for 30 min. The extract was filtered under suction and the filter cake washed twice with 40 ml of ethyl acetate. The solvent was evaporated to dryness, then the residue was dissolved in ethyl acetate and transferred to a 10 ml tube. An aliquot was analysed by GC on a 3% OV-17 glass packed column with thermionic detection.

In order to examine the relationship between the soil characteristics and the atrazine persistence, different physico-chemical properties of soil (pH, organic matter content and texture) were determined in 43 representative fields from both areas.

A statistical analysis of the obtained results was carried out by principal component analysis. The individuals were the fields and the parameters were the different soil characteristics and atrazine residue levels.

RESULTS AND DISCUSSION

Residue analysis showed that atrazine levels in most of the fields were equal or lower than 0.05 mg/Kg (Table 2). These low levels were more common in Badajoz, where they occurred in 80% of the fields sampled. Nevertheless, about 20% of Albacete fields showed atrazine levels higher than 0.1 mg/Kg, which may be phytotoxic to some corn rotation crops (Frank *et al.* 1983, Ivany *et al.* 1985).

TABLE 1. Rainfall and average temperature data in Albacete(A) and Badajoz (B) during 1990.

Month	Temperature(°C)		Rainfall(mm)		
	A	B	A	B	
January	5.2	8.5	18.3	35.0	
February	9.7	11.3	0.0	2.3	
March	9.6	13.0	16.0	20.3	
April	10.0	13.0	32.4	75.2	
May	16.0	19.3	24.9	7.1	
June	22.3	22.5	0.7	0.0	
July	25.3	26.5	10.1	6.5	
August	25.0	26.5	4.5	0.0	
September	22.4	23.4	64.4	34.7	
October	15.6	17.0	57.0	49.6	
November	8.9	10.9	59.7	34.4	
December	4.4	7.6	6.9	30.3	
			TOTAL	294.9	295.4

TABLE 3B. Soil characteristics and atrazine concentration of Badajoz soils.

Field	Atrazine (mg/Kg)	O.M. (%)	pH	Sand	Silt	Clay
1	0.02	2.85	6.0	60.9	35.4	3.7
2	0.02	0.97	6.3	59.4	26.0	14.6
3	0.02	0.69	5.5	64.4	19.8	15.8
4	0.03	0.70	5.9	64.7	21.5	13.8
5	0.03	1.00	6.4	57.8	26.0	16.2
6	0.02	0.90	6.1	73.1	18.2	8.7
7	0.02	0.91	5.6	50.5	27.4	22.1
8	0.02	0.85	5.5	65.1	20.0	14.9
9	0.05	1.03	5.1	50.4	34.1	15.5
10	0.01	1.25	6.1	45.7	35.8	18.5
11	0.02	0.78	5.7	79.1	18.4	2.5
12	0.01	1.23	4.6	63.4	32.5	4.1
13	0.01	0.81	6.7	39.6	46.7	13.7
14	0.02	0.73	5.8	42.1	41.2	16.7
15	0.00	0.61	6.1	41.7	25.4	32.9
16	0.06	1.02	6.5	43.5	35.1	21.4
17	0.07	0.48	7.3	48.2	33.5	18.3
18	0.02	0.71	7.1	43.5	39.2	17.3
19	0.00	0.43	5.6	75.8	19.8	4.4
20	0.04	0.55	5.5	62.3	24.2	13.5

Analytical methods: see Table 3A

Simple correlation coefficients calculated between all soil properties and residue levels are presented in table 4.

Atrazine concentration showed highly significant ($P < 0.01$) and positive correlation ($r = 0.56$) with soil pH, which is in agreement with previous reports of Best and Weber (1974) and Hiltbold and Buchanan (1977).

Soil clay content was significantly ($P < 0.01$) and positively correlated ($r = 0.47$) with atrazine level too. On the other hand, atrazine level showed strongly negative correlation ($r = -0.53$) with soil sand content, in accordance with other work that has shown decreasing half-life of herbicide with increasing sand content of the soil (Walker *et al.* 1983, Allen *et al.* 1987).

No correlation was found between organic matter content and atrazine level, which can be explained by the low organic matter content generally found in Spanish soils.

A negative correlation ($r = -0.69$) was found between soil sand content and pH. This correlation can be explained by the different soil types in the two studied areas, sandy and acidic in Badajoz and with high pH and lower sand content in Albacete.

TABLE 4. Summary of correlation coefficients in 43 fields between soil properties and atrazine concentration.

	Atrazine	Clay	Sand	pH	O.M.
Atra(mg/Kg)	1.00				
Clay(%)	0.47*	1.00			
Sand(%)	-0.53*	-0.78*	1.00		
pH	0.56*	0.70*	-0.69*	1.00	
O.M.(%)	0.31	0.25	-0.33	0.33	1.00

* correlation is significantly different from zero at 0.01 level probability

In order to evaluate the relative importance of these different soil characteristics in the persistence of atrazine, principal component analysis (PCA) was carried out using the 43 fields as individuals with their different soil characteristics and atrazine concentration as numerical parameters.

The first principal plan of the PCA contained 77.9% of total variance. In agreement with the above correlations the first axis separated fields with high residue levels, high clay content and alkaly soil pH, from fields with low residue levels, high sand content and acid soil pH.

Organic matter content is associated with a second axis, corroborating the independence of this soil characteristic and atrazine residue level in this case.

CONCLUSIONS

The main conclusion of this work is that atrazine residue levels, 10 months after application in the studied areas of Albacete and Badajoz were equal or lower than 0.05 mg/Kg in more than 70% of fields. These low levels were more common in Badajoz.

The other important result is that 20% of fields sampled in Albacete showed atrazine levels higher than 0.1 mg/Kg. This level may be phytotoxic for susceptible crops in rotation with corn.

Finally, atrazine levels showed a positive correlation with soil pH and clay content. No correlation was found between soil organic matter content and herbicide level, owing to the low content in organic matter of these Spanish soils.

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FIELD STUDIES TO DETERMINE THE POTENTIAL RISK OF CONTAMINATION OF GROUND AND SURFACE WATERS BY AN AUTUMN AND SPRING APPLIED HERBICIDE IN OILSEED RAPE AND FODDER MAIZE

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ABSTRACT

Monitoring equipment has been installed at four field sites, two sites for each of spring sown fodder maize and winter sown oilseed rape. Contrasting soil types with differing potentials for pollution to ground and surface waters are represented. The oilseed rape sites have been monitored since October 1990 following a post-emergence application of herbicide. Soil water, drainage water, ditch and stream water have been collected from the sites on a routine basis and after significant rainfall events. All water samples have been analysed for the presence of the herbicide. Monitoring equipment at the sites consists of pore-water suction devices, (nested at depths to 150 cm) piezometers, neutron-probe access tubes and rainfall monitoring equipment. Each of the sites has undergone an extensive profile and hydrological investigation. Alachlor has not been detected below 25 cm and 50 cm in the slowly permeable soil type and freely draining soil type respectively. A drain sample has given a concentration above the detection limit on one occasion after a large rainfall event. Data gained from these, and other studies is currently being used to assess a range of pesticide fate and behaviour models.

INTRODUCTION

It is difficult to assess the real risk of ground or surface water contamination by a pesticide when carrying out controlled laboratory or lysimeter studies. Pesticide fate is influenced by a wide range of factors including agricultural practice, weather, topography and proximity of water sources to the site of application (Hollis and Carter, 1991). Alachlor has physio-chemical properties that suggest moderate mobility based on its organic carbon partition coefficient and slight persistence (half life of 16 days). Leaching predictions show no movement of the compound below 30 cm indicating that contamination of water sources is not a potential problem. There have, however, been limited reports of contamination of groundwaters by the herbicide in countries where the product is extensively used (Dobbs and Roberts, 1991). Field studies were therefore established in the UK to determine the potential for alachlor to contaminate water sources, when used in autumn on oilseed rape and in spring on fodder maize. A groundwater vulnerability assessment was initially carried out in order to identify the potential experimental locations. The assessment was based on soil and climatic suitability for the cultivation of fodder maize and three soil hydrological classes:

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- Class 1 Very permeable soils over shallow (2-20m) or very shallow (1-2m) aquifers.
- Class 2 Less permeable soils over shallow or very shallow aquifers and other soils over deep aquifers (>20 m)
- Class 3 All other soils and geologies.

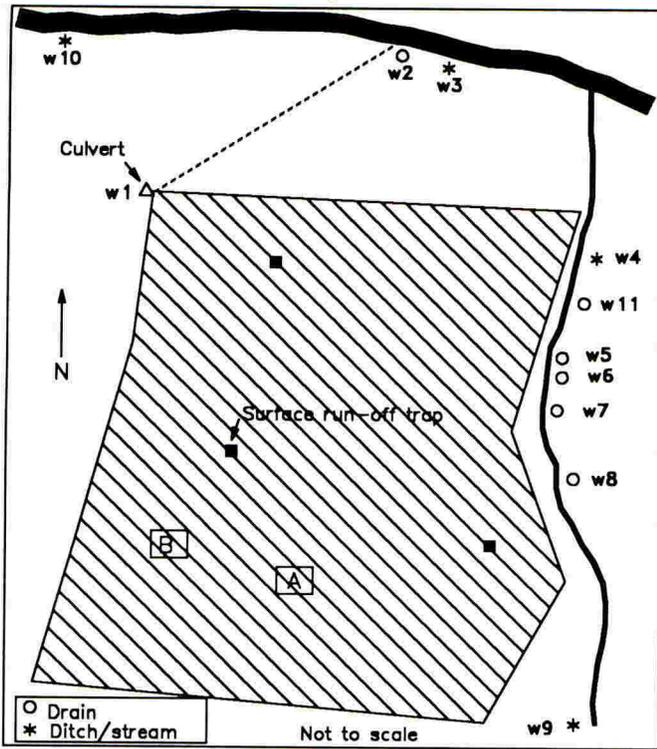
Class 1 land has the highest permeability and shortest travel time to the aquifer. The underlying substrates may be fissured or cracked. Spring and autumn applications of pesticides are more likely to reach groundwater. Class 2 land is less permeable than class 1 or the underlying aquifer is deeper. Spring pesticide applications will have less risk of ultimately entering groundwater than those applied in autumn. Class 3 land is slowly permeable and may not overlie aquifers and therefore autumn or spring applications of pesticides are less likely to contaminate groundwater reserves. Pesticides applied to class 3 land, however, have a risk of contaminating surface water since drainage water movement is predominantly lateral and may be via artificial drainage systems. Four field sites were therefore established, two on oilseed rape and two on fodder maize. Freely draining sandy soils with a very shallow water-table was chosen to represent class 1 land and slowly permeable, fine loamy soils with artificial drainage chosen to represent class 3 land.

EXPERIMENTAL SITE SELECTION

The two winter sown oilseed rape sites were located in a single field (Hag Field) south of Coventry at Temple Balsall. An extensive investigation of the soil profile and hydrological characteristics was carried out at this site after an initial suitability survey. The soils of the study field are developed from un-consolidated superficial glacial deposits. The underlying solid geology consists of reddish mudstone of the Mercian Mudstone group, formerly known as the Keuper Marl. The area around the site is covered by a mixture of reddish slightly stony clay till (boulder clay) and brown and reddish brown sands and gravels (Beard, 1984). The experimental field has a north/south ridge of sand and gravel material more than 2 m thick in places overlying the mudstone. In recent times erosion has created shallow valleys that flank the ridge, here clay occurs at shallow depth (35 cm in places) overlain by drift remnants and local material recently eroded from the upslope.

The dominant soils present at the field site are those of the Arrow (site A) and the Brockhurst series (site B). The Arrow series is classified as a gleyic brown earth developed in coarse loamy glacio-fluvial deposits and is freely draining. Mottling features below 40 cm indicate the presence of a fluctuating water table. The Brockhurst series is a slowly permeable, typical stagnogley soil developed in reddish fine loamy or fine silty head over Mercian Mudstone. Mottles are at less than 40 cm depth indicating a shallow but perched water table overlying the clay layer. The field drains to the north into a strongly flowing brook which empties into the river Blythe. A plan of the field site is shown in figure 1. The western half of the field drains into a shallow valley on its western margin into an underground drain which

Figure 1. Hag Field site diagrammatic plan.



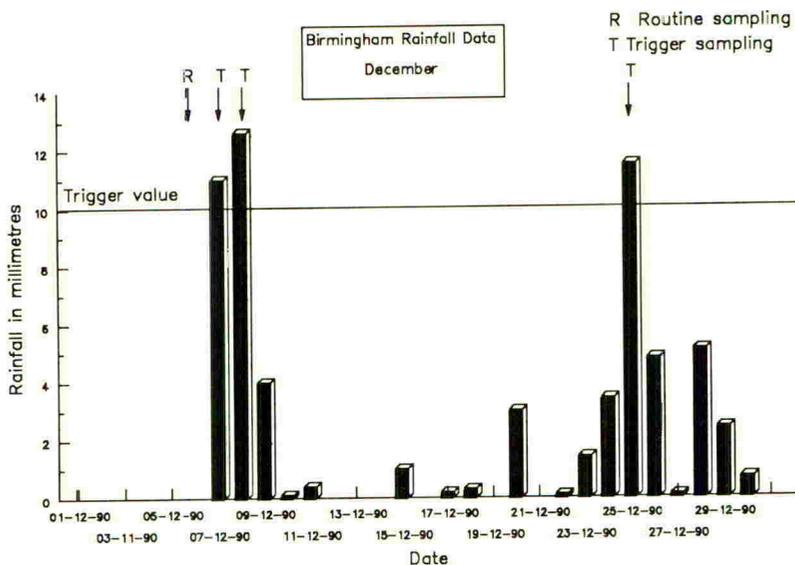
eventually emerges at sampling point w2. The field is drained on its eastern side via a number of land drains (sampling points w5, w6, w7, w8 and w11) into a ditch (sampling points w4 and w9) which joins the brook. Sites A and B were drilled with oilseed rape on 3 September 1990. The equipment was installed at the Hag field site on 10-11 October 1990 prior to an application of alachlor on 22 October 1990. Alachlor as 'Lasso' was applied at the 3-4 true leaf stage of the crop at a rate of 1.92 kg active ingredient ha⁻¹.

INSTRUMENTATION

One set of equipment was installed on the Arrow site and a similar set on the Brockhurst site. Each equipment set consisted of replicated suction samplers, neutron-probe access tubes and piezometers. The neutron-probe access tubes were used to measure soil water content at 10 cm increments up to a depth of 180 cm. Information gained was used to characterise water storage and movement thus giving information on likely pesticide behaviour. Piezometers constructed from 10 cm diameter PVC tube were installed to enable ground water to be sampled and water table depth to be measured (Carter, 1991). On the Arrow site piezometers were placed at a depth of 2 m, whilst on the Brockhurst site they were nested at different depths (25, 40, 80 and 150 cm) to sample the different layers of impeded water and to record the depth to groundwater. Suction samplers were placed at 50

and 150 cm depths on the Arrow site, whilst at the Brockhurst site samplers were nested at 25, 40, 80, and 100 cm depths. Further instrumentation at the site consisted of three surface run-off collection traps which were placed strategically at three sites where it was thought surface run-off was most likely to occur (ie. slope $>3^\circ$). Rainfall data was received from the Meteorological Office at Birmingham International Airport (10 km NNW of the site) on a daily basis by telephone to ensure an immediate response to trigger events (more than 10 mm precipitation in 24 hrs). A rain-gauge recorded on-site rainfall for inter-visit periods.

Figure 2. Rainfall data showing routine and trigger events.



SITE MONITORING PROCEDURES

Water samples from the site were taken initially on a routine fortnightly basis and immediately after significant rainfall events (figure 2). A total of 13 sets of routine and trigger event samples and Neutron-probe readings were taken in the period from 18 October 1990 to 20 May 1991, either routinely or after a rainfall event. 'Grab samples' from field drain, ditch and stream water sources were also taken routinely with the soil water samples. Samples were taken at all available drain outlets from the field also stream and ditch water was sampled both upstream and downstream of the field 'catchment'. Fifteen one litre samples of water from field drain w7 were taken on one occasion for storage degradation studies to be undertaken. The surface run-off traps were inspected on each visit to the site to determine any presence of run-off of water over the soil surface and possible pesticide loss by that route.

All the water samples were collected in amber glass bottles with Teflon lined caps and transported in refrigerated boxes from the field site and stored under refrigeration until analysed. A 250 ml sample was passed through a C₁₈ solid phase

extraction cartridge, eluted with 10% ethylacetate in iso-octane, dried with sodium sulphate, made up to volume and analysed using gc-ms.

A standard suction (0.7 bar) was applied to all the samplers using a hand suction pump and these were left to act for a minimum of two hours to allow a reasonable sample volume to be drawn into the tube from the surrounding soil. The applied suction has been shown to give an acceptable sample volume when the soil is at, or around field capacity and not to cause lasting depletion of the surrounding soil water (Earl and Carter, 1991). Water was drawn into a clean bottle by applying a small vacuum. Neutron-probe readings gave an estimation of the changes in water content throughout the soil profile by comparison with standard calibration curves. The water-table depth from the soil surface was measured using an electronic well monitor. The collection bottles on the surface run-traps were routinely inspected for the presence of any water which had run off the field. Surface water samples were taken from the centre of the ditch/stream to minimize collection of stream sediment with the sample, and always from areas of flowing water.

RESULTS AND DISCUSSION

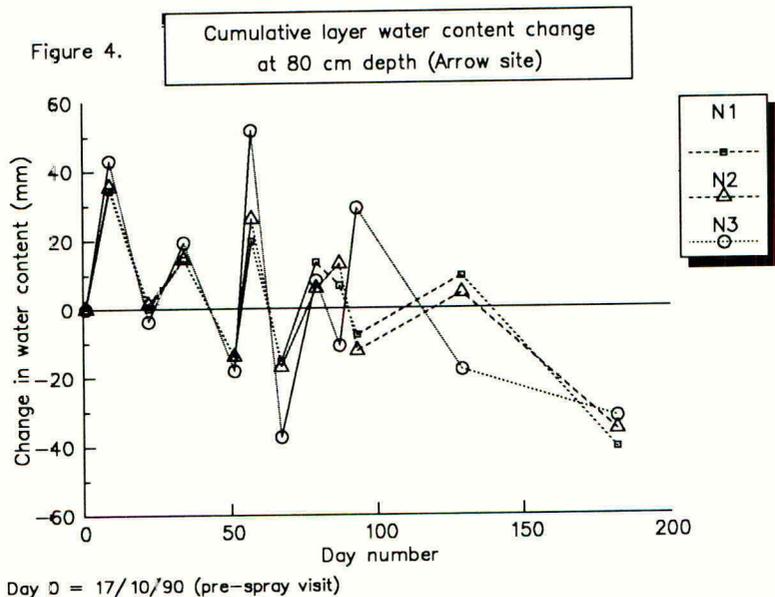
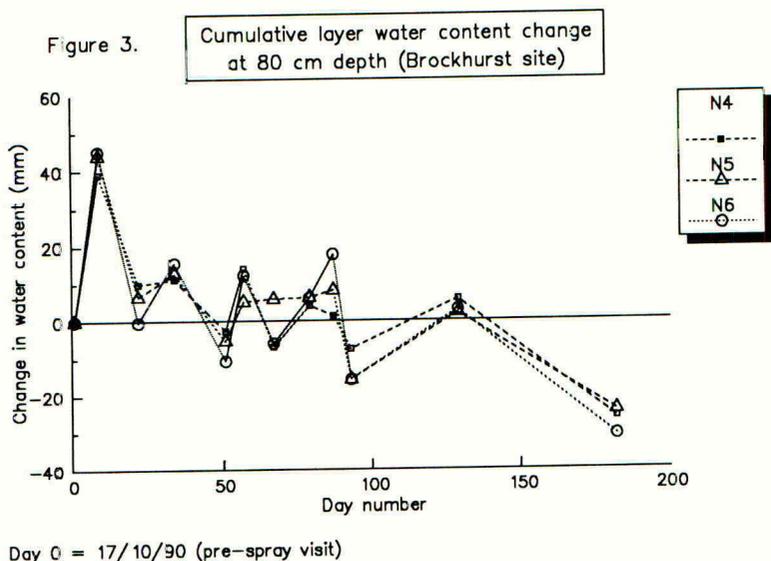
Soil water regimes

Studying the soil water regime of the experimental site is of paramount importance to understanding the fluxes of applied chemicals and for subsequent computer modelling of the system. Direct comparison between soil moisture contents and fluxes at sites A and B are possible and information valuable to the understanding of potential movement of the herbicide at the two sites has been gained.

The Brockhurst soil has a much higher cumulative water content than the Arrow. Less water is retained by the coarse textured Arrow series and therefore leaching is more likely to occur at the Arrow sites. Cumulative water content increases to around 26 November 1990 and then forms a plateau in both soil types. This plateau level represents a field capacity situation for each soil type and this level is much higher in the heavier textured Brockhurst series. At field capacity water moved through the profile to the water table and to artificial field drains, this downward water flux is reversed later in the year when the soil moisture deficit (SMD) increased and crop development and warmer temperatures caused evapotranspiration to increase, in turn causing the main water flux to be in an upwards direction. Leaching of applied herbicide to field drains was therefore only likely in a near field capacity situation or in a heavy rainfall event which was likely to cause flow through macropores. Rainfall in excess to that required to maintain field capacity caused excess water to drain through the soil profile to the water table or artificial drainage systems. No flow of soil water to drains was expected until the field capacity situation was reached, however local flow to drains from isolated masses of soil at field capacity and by-pass flow through cracks and macropores may have occurred giving possible drain flow before a universal field capacity situation was reached in the profile.

Figures 3 and 4 show the cumulative layer water content change at 80 cm for both sites. A general linear decrease in the water content of both the profiles can be seen as the study progressed and the SMD increased. The water content change

(0-80 cm) fluctuates to a much higher degree in the Arrow soil giving a more pronounced series of wetting and drying cycles.



The differences in water content fluctuations can be predicted by the texture of the soil, the Arrow series has a greater air space and therefore more temporary water

storage than the Brockhurst. Much less fluctuation in water content was experienced at depth in the Brockhurst due to the proximity of the water table capillary fringe and the relative absence of extracting root systems. Also at depth the soil is a relatively massive material giving a low air capacity value and therefore little ability to give wide fluctuations of water content. No water run-off was experienced at any time, on either soil types in the oilseed rape study.

Analytical results

A total of 132 water samples have been analysed for alachlor to date, of these only eight samples showed a concentration of residue above the limit of detection ($0.05 \mu\text{g l}^{-1}$). Five of these positive samples were taken from suction samplers at a depth of 25 cm on the slowly permeable Brockhurst site. The 25 cm suction samplers consistently gave concentrations of alachlor throughout the period of the study and $0.42 \mu\text{g l}^{-1}$ was still detectable in the soil water 124 days after application. There were two positive results from the site on the freely draining Arrow series at a depth of 50 cm ($0.12 \mu\text{g l}^{-1}$, 11 January 1991 and $0.10 \mu\text{g l}^{-1}$, 21 February 1991). The remaining positive result came from a field drain (site w7) on the western side of Hag field. The drain gave a concentration of $0.08 \mu\text{g l}^{-1}$ (11 December 1990) after a fairly large trigger event of 27.7 mm of rain in the preceding 4 days (figure 2). All other analysed water samples have shown no herbicide concentrations above the detection limit.

Alachlor was detected consistently in the soil water samples at 25 cm depth in the Brockhurst series, the appearance of the herbicide in only one drain sample suggests that a by-pass mechanism was responsible. Drain depth is not documented but is believed to be at 60-80 cm depth in the Brockhurst soil. Since no herbicide has been detected at 40 or 80 cm depth, by-pass flow to a drain or collecting area is the most likely explanation for the detection. Profile descriptions of the sites identify the presence of macropores in the 30-70 cm horizons. The presence of these macropores coupled with the preceding rainfall at the site whilst in a field capacity situation was likely to produce such a flow.

Alachlor was detected on two occasions in the Arrow series at 50 cm depth, since a coarse textured soil is considered to be the 'worst case' for leaching more detections of the herbicide might have been expected in the Arrow series. The predictive models CALF (Nicholls *et al*, 1982), PRZM (Carsel *et al*, 1984) and LEACHP (Wagenet and Hutson, 1989) are currently under investigation in order to simulate the current data set and to help provide explanations regarding the important processes controlling the fate and behaviour of the herbicide. Similar sets of monitoring equipment have been installed at each of two selected fodder maize sites. Post spray samples have been taken but have yet to undergo analysis.

CONCLUSION

The study area provides an ideal combination of contrasting soil types within the same field boundary. Results from the freely draining site, underlain by a shallow groundwater table, can be compared to data from a lysimeter, but the advantage of this field study is that the implications, of any herbicide concentration in excess of $0.1 \mu\text{g l}^{-1}$, to ground and surface water quality can be assessed. The importance of macropore flow as a process contributing an otherwise moderately

mobile pesticide to drain water is emphasised. Soil characterisation enables extrapolation of data to areas of similar soil and agroclimate, whilst validation of the models aids extrapolation to a wider situation. The characteristics of this study site have also been correlated with similar situations in France so that the experimental data can also be considered by French regulatory authorities.

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INFLUENCE OF COWPEA CANOPY ON THE PERSISTENCE AND DOWNWARD MOVEMENT OF IMAZAQUIN IN A TROPICAL ALFISOL

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ABSTRACT

The persistence and downward movement of imazaquin (2-(4,5-dihydro-4-methyl-4-(1-methyl ethyl)-5-oxo-1 H-imidazol-2-yl)-3-quinoline carboxylic acid) on a tropical alfisol was monitored after pre-emergence applications at 150 and 300g AI/ha on a field with and without a crop of cowpea (*Vigna unguiculata* (L) Walp) using a corn (*Zea mays* L.) shoot dry weight bioassay in the cropping seasons of 1990.

In general, imazaquin did not substantially leach beyond the 0-7.5cm soil depth at both rates of application with or without the canopy of cowpea. By 56-70 days after planting only between 10 and 20% of the initial application remained at the 0-7.5cm soil depth. The presence of cowpea did not have any significant effect on the period of persistence of imazaquin at the recommended rate of 150g AI/ha, however, residue of both rates of application at each sampling period and persistence at the 300g AI/ha rate were reduced under cowpea indicating that the cowpea plant contributed to the disappearance of imazaquin from the soil.

INTRODUCTION

Imazaquin is preferred as a herbicide in cowpea crops due to its ability to effectively control *Euphorbia heterophylla* L., a noxious weed of cowpea. One of the factors that make *E. heterophylla* a problem is that its seeds germinate several times during the crop life thereby posing serious problem of control (O'Makinwa, 1986). It is desirable therefore to examine how long imazaquin remains active in the soil and capable of giving effective control of emerging *E. heterophylla* seedlings in the presence of a cowpea crop.

Recent research in our laboratory has shown that imazaquin at the recommended rate of 150g AI/ha when applied on the soil without a cowpea canopy persists for a period of 8-10 weeks in the tropical soil (Akinyemiju *et al.*, 1989). This report also indicated that effective weed control from imazaquin probably ceases by about 6 weeks after application due to the fact that only 20% or less remains in the soil by this time. However, the influence of the cowpea crop on the persistence of imazaquin is not known.

In agronomic crops, the crop canopy can assist in the control of weeds especially where it closes quite early in the life of the crop. Weed control by herbicides can be augmented by the crop canopy especially if it is fully expanded before a substantial proportion of the herbicides dissipate in the soil. Also, research reports have indicated that crops

contribute to some degree in the disappearance of herbicides from the soil by directly absorbing the herbicide molecules even though the amount may not be sufficient to kill the crop or the crop may be tolerant of the absorbed herbicide (Akobundu, 1987).

The objective of the present study was to examine the influence of cowpea on the period of persistence of imazaquin in comparison with a non-crop situation.

MATERIALS AND METHODS

The experiment was conducted at the Teaching and Research Farm of the Obafemi Awolowo University in Ile-Ife, latitude 7° 28'N, longitude 4° 33'E and 244m above sea level, in the early and late cropping seasons of 1990. The soil used for the experiment (Table 1) was an alfisol of the Oba series (Harpsted, 1973) with a pH of 6.1 and organic matter content of 1.1%. It was cropped with maize in the 1989 season, but was in fallow in the previous five years. The land was conventionally ploughed and harrowed, using a tractor mounted disk plough and harrow, before the experiment was laid out. The piece of land was divided into two, one was earmarked for the late season repeat while the other was partitioned into 2 equal portions. One of the two portions was planted to cowpea while the other was left unplanted. Both the cowpea planted area and the unplanted were each further divided into 3 replicates, and each replicate was partitioned into the three imazaquin treatments (0, 1.5 and 3.0 g AI/ha). The herbicide plots, measuring 11m x 1m each, were further partitioned into 3 treatments of soil depth (0.0-75cm, 7.5-15.0cm, 15-22.5cm) of 1m x 1m each. Treatment plots, subplots and sub-sub plots were separated by appropriate buffer zones. The plots that were planted to cowpea had 120 stands of cowpea per plot (5 rows at 0.3m x 0.6m spacing). Cowpea variety Ife Brown was used for the experiment. Each treatment was randomised within appropriate plot or sub plot. Sampling was done immediately after application, and at 2 weekly intervals thereafter till 112 DAT. The experiment was a split-split plot with rate of application as main plot, soil depth as sub-plot and time after application as the sub-sub plot. The experiment was replicated 3 times and repeated in the late season.

Herbicide application was accomplished with a knapsack sprayer previously calibrated to deliver 200 l/ha spray solution at a pressure of 2-3kg/cm². Herbicide application was made on April 9, for the early season, and on September 17, for the late season, of 1990 respectively. Each herbicide application was made a day before cowpea seeds were planted. Weed was controlled manually, twice before crop harvest, in treatments that did not receive any herbicide. Insect pests were appropriately controlled in cowpea plots in both season (Akinyemiju and Echendu 1987).

At each sampling period, soil sample were taken with the aid of a soil auger of mouth diameter 8.5 cm, in all treatments plots. The residue of imazaquin was determined using a corn-shoot length bioassay as previously described by Akinyemiju *et al* (1989). The residue data obtained were analysed statistically and disappearance curves were plotted out separately for the plots that were planted to cowpea and those that were not. Because the curves were similar for both seasons, an average of the two seasons is presented.

TABLE 1. Physical and Chemical Properties of the Soil of Obafemi Awolowo University Teaching and Research Farm used for Bioassay and Persistence Studies.

Mechanical Analysis	% Sand	% Silt	% Clay
	81	8	11
Textural Class	Sandy loam		
% Organic matter	1.11		
pH (0.01M CaCl ₂)	6.1		
NO ₃ -N	260ppm		
Available P	81.6ppm		
Exchangeable Ca	3.69meq/100g		
Exchangeable K	0.50meq/100g		
Exchangeable Na	0.47meq/100g		
Exchangeable Mg	1.55meq/100g		

RESULTS AND DISCUSSION

Weather data in 1990 showed that the year conforms with the generally typical weather pattern of the humid tropical forest zone with its bimodal annual rainfall and high temperature and relative humidity (Table 2).

TABLE 2. Mean monthly weather data at the University Teaching and Research Farm in 1990.

Month	Rainy Days	Total Rainfall (mm)	Temperature 0°C		Relative Humidity %	Soil Temperature 0°C at		
			Max	Min		5cm	10cm	20cm
January	1	26.4	33.2	22.6	81.6	14.2	29.1	28.3
February	1	5.0	34.9	20.6	65.3	15.6	28.2	29.2
March	1	5.5	37.2	22.7	66.4	20.0	42.2	32.5
April	12	200.5	32.2	22.8	67.0	16.5	29.2	29.4
May	15	202.9	33.1	26.6	80.6	15.9	28.0	28.5
June	13	171.0	20.9	22.6	80.4	15.0	28.3	27.4
July	19	281.3	27.3	21.7	93.2	11.0	24.9	25.8
August	15	92.9	27.5	20.9	90.1	10.5	24.6	25.5
September	18	275.6	29.6	21.4	81.8	12.1	25.4	26.4
October	10	136.6	30.6	22.4	80.2	27.4	26.4	27.3
November	4	63.5	33.4	23.6	75.7	14.1	27.6	28.4
December	2	42.3	32.1	22.5	76.1	12.2	26.1	29.4

The disappearance and downward movement of imazaquin without cowpea is presented in Figure 1. This figure shows that the disappearance of imazaquin in this tropical alfisol is dependent on rate; by 56 DAT no trace of imazaquin applied at 150g AI/ha was detected at the 0.0-7.5cm soil depth whereas at 300g AI/ha, imazaquin persisted till 70 DAT, two weeks longer

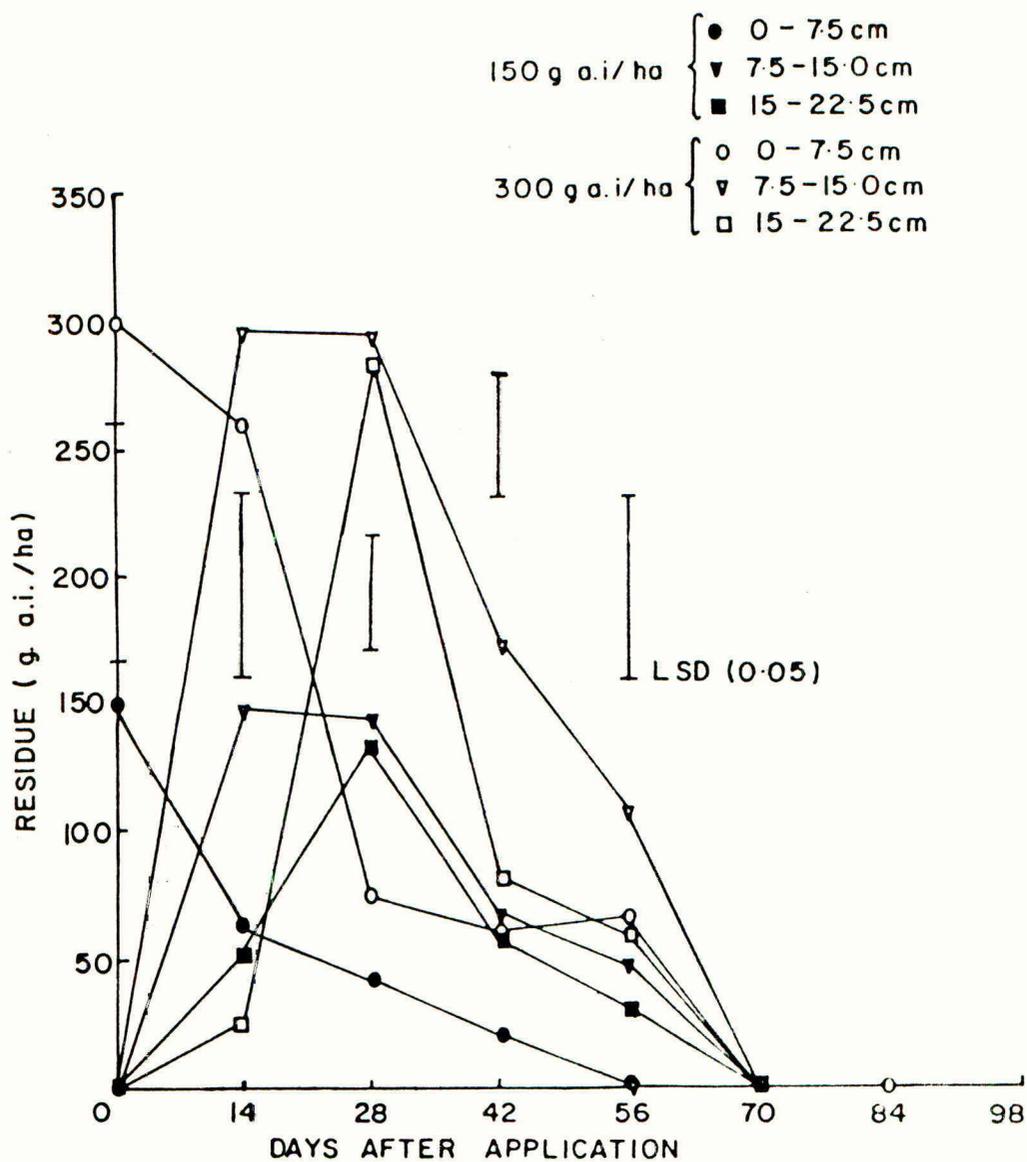


FIG.1: DISAPPEARANCE AND DOWNWARD MOVEMENT OF IMAZAQUIN ON A TROPICAL ALFISOL (WITHOUT COWPEA PLANT).

150 g a.i./ha { ● 0-7.5 cm
 ▼ 7.5-15.0 cm
 ■ 15-22.5 cm

300 g a.i./ha { ○ 0-7.5 cm
 ▼ 7.5-15.0 cm
 □ 15-22.5 cm

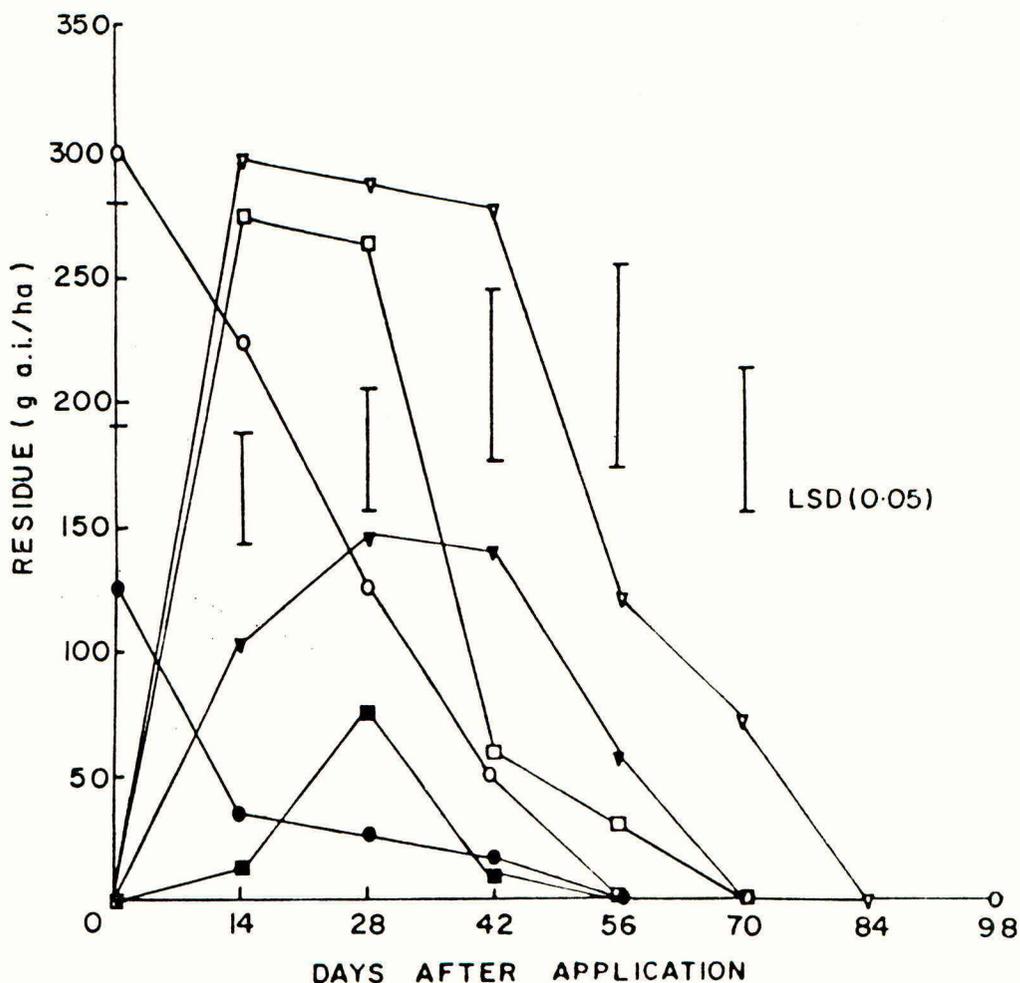


FIG.2: DISAPPEARANCE AND DOWNWARD MOVEMENT OF
 IMAZAQUIN ON A TROPICAL ALFISOL (UNDER COWPEA).

than the lower rate of 150g AI/ha at this soil level. At the sub-soil levels, there was an initial low level as expected, which rose with time after application till a peak at about 28 DAT and declined sharply thereafter till 70 DAT when no residue was detected at both rates and soil depths. Generally, the peak detection of the 150g AI/ha at the two sub-soil levels were lower than the higher rate confirming the fact that the disappearance was dependent on the rate of application. In general this pattern of disappearance conforms to our previous data in this tropical soil (Akinyemiju *et al.*, 1989), but 10-12 weeks shorter than that reported for imazaquin at similar rates by Basham *et al.*, (1987) on three Arkansas soils in U.S.A.

Figure 2 shows that pattern of disappearance and downward movement of imazaquin in the presence of cowpea plants. With imazaquin at the 150g AI/ha, no residue was detected at the soil surface (0.0-7.5cm) 56 DAT in both the cowpea and non crop treatments. However, the amount of residue at each time of sampling was less where cowpea was planted compared to the no cowpea situation. At 300g AI/ha, imazaquin persistence was shorter by 2 weeks and residue was less at each sampling time where cowpea was planted compared with the non-crop situation.

Specifically, in most cases where cowpea was planted, the amount of imazaquin detected at each sampling time was smaller than where cowpea was not planted. For example at 14, 28 and 42 DAT at the surface soil 85%, 42% and 20% of initial rate were detected respectively where 300g AI/ha was applied without cowpea in comparison with 66%, 42% and 16% where cowpea was planted. Similarly, at the 150g AI/ha rate at the surface soil 40%, 27% and 13% were detected where no cowpea was planted but 28%, 20% and 12% respectively where cowpea was planted. This data indicated that in addition to other factors that may account for the disappearance of imazaquin in the soil, cowpea plants contribute by possible absorption of the herbicide molecule making it further unavailable in the soil.

In order to achieve a season long control of weeds where imazaquin has been applied therefore, it is imperative that canopy closes in time to augment the control of weeds by the herbicide. This can be achieved either by maintaining cowpea optimum plant population, or planting a leafy variety, or both.

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PESTICIDE CONTAMINATION OF WATER SOURCES: CURRENT POLICIES
FOR PROTECTION AND A MULTIDISCIPLINARY PROPOSAL TO AID
FUTURE PLANNING

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ABSTRACT

Restricted usage, water protection zones, or even revocation of pesticide approvals, are some of the actions taken by regulators and water protection agencies in response to the detection of several commonly used herbicides in surface and groundwaters. The actions and policies being taken or developed by several countries, including the UK, is reviewed. An expert system which predicts the potential for a pesticide to contaminate surface or groundwater sources is proposed for the UK, whereby usage patterns, land use, soil and geological conditions are integrated, using the most advanced information systems currently available in the UK. The system is seen as satisfying the need for a unified national approach to the initial screening of pesticides and also as a practical tool for local catchment and source management. The system is unique, in that it draws together a multidisciplinary team which will allow a better understanding of the factors and processes controlling the contamination of water sources.

INTRODUCTION

The preservation of water quality in the UK is controlled by several legislative Acts, but it is the EC directive on drinking water quality (EEC 1980) which generates most concern regarding the protection of ground and surface water sources from pesticide contamination. The maximum admissible concentration (MAC) of any single pesticide is $0.1 \mu\text{g l}^{-1}$ and the MAC for total pesticide residues is $0.5 \mu\text{g l}^{-1}$. The directive originated in the 1970s when there was concern regarding the use of organochlorine pesticides such as aldrin, dieldrin and DDT (MAFF 1991). The MAC represented a political zero since the $0.1 \mu\text{g l}^{-1}$ was the limit of detection in 1980. These water quality objectives refer to drinking water from the tap itself and not the source. It is, however, essential that the potential for contamination is minimised in order to comply with the directive and avoid the expensive costs of pesticide removal, mixing of waters or closure of a source.

The potential for any pesticide to contaminate ground or surface waters following application is now the subject of much research in order to satisfy regulatory authorities,

whether it be for a new product or for a compound under review. Data submissions have traditionally included laboratory leaching column studies and degradation in a range of soil types and temperature/moisture conditions in order to assess a pesticide's likely fate and behaviour. The detection of several commonly used herbicides, e.g. atrazine, isoproturon, mecoprop and 2,4,D in some water bodies (HMSO 1991) has led to a recognition that pesticide fate is controlled by a wider range of factors including usage pattern, land use, climate, soil and geological conditions.

Studies carried out in individual fields or in small catchments are ideal but very expensive and require a wide range of experimental conditions over several years before an assessment can be made. The use of predictive models, such as PRZM, the Pesticide Root Zone Model, (Carsel *et al.* 1984) and SESOIL, the seasonal soil compartment model (Bonazountas and Wagner 1984) is required by the German registration authority (BBA) if the physico-chemical properties of a pesticide trigger guidelines based on adsorption and persistence. Lysimeter experiments designed to study pesticides in a semi-controlled environment are a compromise situation providing some valuable information concerning degradation and leaching potential from a 1 m deep soil core.

The concern is not, however, necessarily for the concentration of a pesticide in leachate at 1 m depth from a soil column or at point of entry to a drainage ditch, but for the implications of that concentration to the water quality of a catchment area. Until there is a radical change in pesticide physico-chemical properties there will always be the possibility of water contamination. Blanket revocation or refusal of approvals for pesticides likely to exceed EC limits only under certain land use conditions are not appropriate or necessary. This paper aims to assist the regulatory concern for pesticide safety by considering the spatial impact of a product and the implications for catchment water quality in all areas of potential usage.

POLICIES FOR WATER PROTECTION

No protection or buffer zones currently exist to control the potential contamination of water sources by pesticides in the UK. The current development of a Groundwater Protection Policy will enable the National Rivers Authority (NRA) to define vulnerable aquifer zones for controlling point source pollution, e.g. production, storage or disposal activities likely to present a risk to groundwater. Control of diffuse applications of pesticides by spraying can be covered by the establishment of protection zones empowered by the Water Act (HMSO 1989). At present only Nitrate Sensitive Areas have been established and 10 sensitive aquifer outcrop areas are being monitored to assess the impact of voluntary reductions in nitrogen applications. The NRA is required to take action against known sources of pesticide pollution entering controlled waters unless a discharge consent has been granted. Voluntary agreements to reduce usage of certain herbicides like atrazine and simazine in the non-agricultural sector have already taken place. There is, however, cause for concern with regard to the alternatives being chosen which in some cases have greater potentials to contaminate water sources and have worse toxicological profiles. At present there is no comprehensive advice available to agricultural or non-agricultural users concerning pesticide choice and the preservation of water quality. Certificates of competence for pesticide application are now required but the health and safety of operatives are the main focus in the training programme.

No statutory protection or buffer zone policies exist for the United States. There are, however, examples of negotiated agreements with regard to the use of certain chemicals in sensitive areas. Runoff and soil erosion are common sources of pesticide contamination to surface water bodies and grass strips at field margins have been commonly employed to intercept water and particulate matter. Their total effectiveness

is questionable since unless the pesticide is strongly adsorbed it will continue to move by infiltration and throughflow to surface waters. Flashy events giving peak concentrations will, however, be avoided. The PRZM model has been used to calculate 'well set back' zones for the insecticide aldicarb, the size of protection zone varying according to soil and hydrological conditions. Product labelling restricts the use of the compound in designated areas. Labelling is also used to restrict ground or aerial spraying of pyrethroids within 8 or 30 m respectively of surface waters. The Soil Conservation Service employs local experts supported by extensive data information systems and modelling capability to advise pesticide users of best farming practices.

The use of pesticides in Canada is comparatively small to the other countries discussed in this paper, only 0.1% of the land area receives at least one pesticide application in a year and water contamination problems are perhaps less significant. Regulations concerning the use of pesticides are imposed primarily by the Federal State and then additionally by the Provincial States. Pesticides are categorized in Ontario according to their toxicity and persistence in the environment and from April 1992 only licensed operators will be able to apply the very toxic and/or persistent compounds, following a health, safety and environmental training programme. Buffer zones adjacent to surface waters are statutory and vary from state to state from 15 to 30 m. The distances are applicable to all compounds regardless of their physico-chemical properties. Two mile buffer zones are enforced for aerial spraying of forestry when 4-5 tons of pesticide may be applied by a DC8! Canadian users of pesticides are advised in a similar way to the United States.

Pesticide usage in Israel has reduced dramatically from 140 kg per irrigated hectare in the 1960s to approximately 40 kg in the 1980s. Environmental awareness, improved pesticides, cropping practice, cost and integrated pest management have all contributed to the reduction. Drinking water is derived mainly from two major aquifers, one of which is thought to be free of any contaminant since the outcrop area is unpopulated. Information concerning the extent of contamination in the Coastal Plain aquifer is not yet available. Water source protection regulations vary from zone to zone but careful use of pesticides is encouraged in all areas by the routine monitoring of residues in agricultural and horticultural produce and the possible imposition of fines. Regulatory conditions are similar to Canada and those pesticides with greater pollution potentials are not encouraged.

The majority of drinking water in the Netherlands derives from groundwater and information on soil and hydrogeology (Hodgson 1991) is used to identify vulnerable sources. Protection zones were established around wells in 1975, but their size has been found to be inadequate with a variety of organic chemicals being found in excess of $0.5 \mu\text{g l}^{-1}$. Modelling exercises have shown that current pesticide applications will continue in many situations to contaminate shallow water sources and it could take several decades of prohibition before the EC water quality standard is met. Extensive sophisticated water treatment such as ozonation, active carbon and chlorination are employed in order to meet the guidelines.

The entire area of Denmark is considered to be protected since very few locations are not potential water catchment areas. Usage is controlled through labelling rather than by the designation of protection zones, e.g. products toxic to aquatic life cannot be used within 10 m of surface waters. Other compounds which are known to leach are still registered but usage is carefully controlled by timing and quantity of application. At present pesticide registration is approved when up to $5 \text{ g ha}^{-1} \text{ yr}^{-1}$ of compound leaches from a field or lysimeter test, but a future proposal advocates the maximum quantity of $0.2 \text{ g ha}^{-1} \text{ yr}^{-1}$ so that drinking water quality guidelines are met by leachate just below the root zone.

Intensive use of herbicides on soils derived from gravel and sand has resulted in widespread contamination of shallow water-tables in northern Italy. Barrier zones protect water supply service constructions and prohibit the use of any pesticide within 10 m distance. Protection zones have a radius of at least 200 m of the water collection point and prohibit all activities with potential for contamination. Buffer zones regulate all types of land use including agriculture; they extend over catchment areas and are enforced by the regional authority. Since 1989 regional authorities have controlled or prohibited the use of individual pesticides. Schemes to provide advice with regard to the choice and application rate of alternative products, particularly for maize and rice have been launched.

At present those pesticides which may be considered to be mobile or persistent are prohibited from protection areas designated by the German State authorities until a regulatory decision is made concerning their status. Any product giving an average lysimeter leachate concentration over a 2 year period of $0.1 \mu\text{g l}^{-1}$ or greater for an active ingredient or toxicologically active metabolite will be automatically refused registration. Buffer zones for surface water vary according to type of crop, mode of application and risk to the aquatic environment.

AN EXPERT SYSTEM TO PREDICT HERBICIDE CONTAMINATION OF WATER SOURCES

Agricultural practice over the last two decades has been market led by the Common Agricultural Policy and its interpretation in the EEC. The suitability of land to support farming practice or the pollution potential has been of secondary consideration in determining land use. The parallel trends of intensification and specialisation have led to instances of water contamination, not only by pesticides but also by nutrients and farm wastes. Catchment management for water quality protection needs to integrate a wide range of spatial information concerned with the likelihood of a particular active ingredient appearing in a water resource. The following factors are relevant:

- the extent and pattern (temporal and geographic) of its application
- certain of its chemical properties
- land management practices
- the nature of the underlying soil
- the hydrogeology of the unsaturated zone and aquifer (in the case of groundwater and spring-fed rivers)

Information on each topic area is held by different organisations in the UK and it is proposed that all relevant data from a given area be compiled and integrated by a Geographical Information System (GIS) that will, by the use of simple models, be capable of predicting the presence and concentration of pesticides in water resources. Spatial, lateral and vertical zones of interest are represented which highlight the main pathways of pesticide movement. The conceptual methodology is given in Figure 1.

Climatic zone

Agro-climatic information at various levels of detail would be required by the expert system. Average rainfall, temperature data and duration of the field capacity period can be interpolated for any grid point in England and Wales (Jones and Thomasson 1985). Real time daily or even hourly data is recorded by the Meteorological Office and water agencies for many locations.

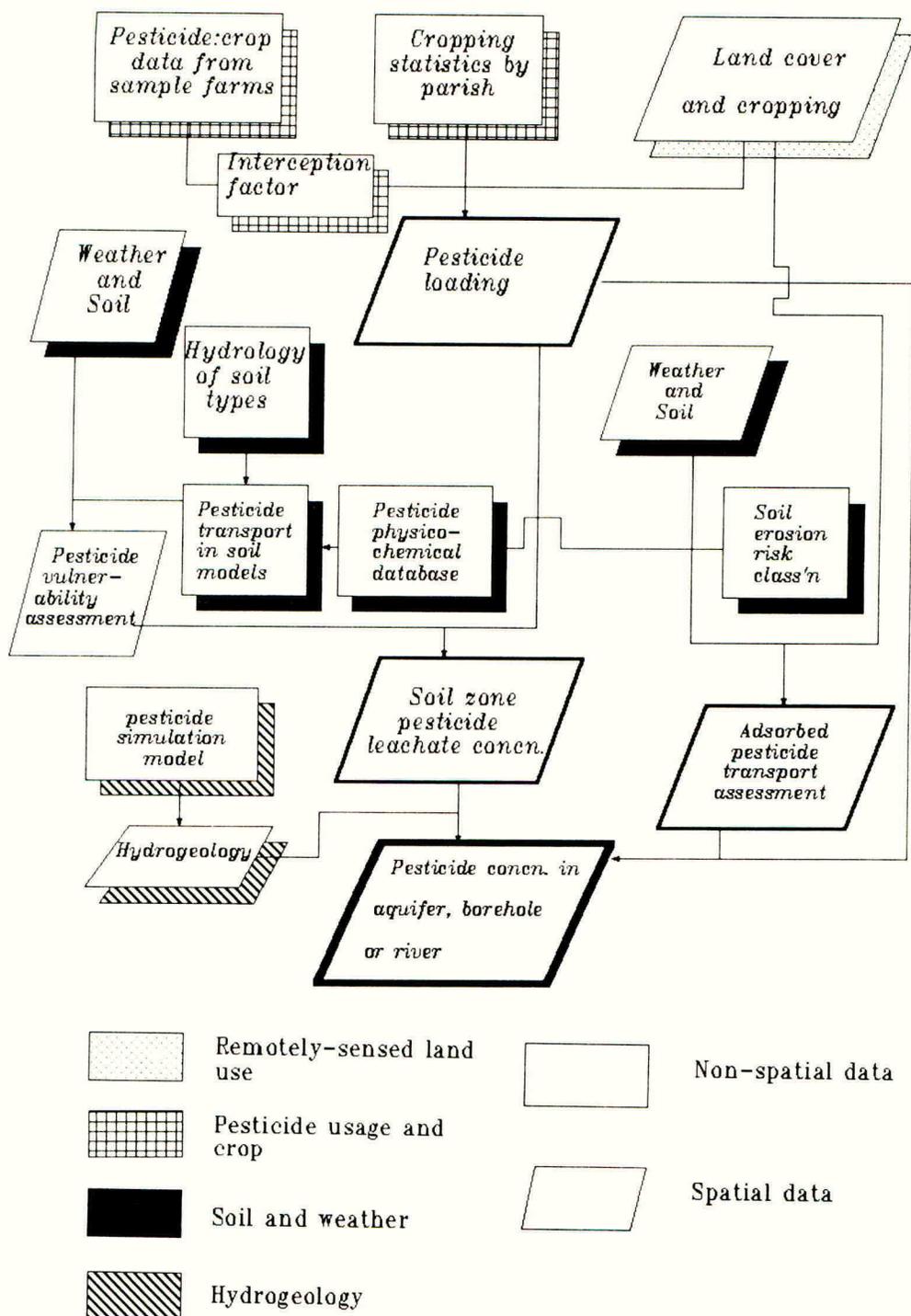


Figure 1 Prediction of pesticides in water sources

Usage zone

Pesticide usage surveys have been conducted by Farmstat Ltd since 1979. The primary function of the survey is to determine behaviour and changes in the regional and sectorial use of agricultural pesticides. Two thousand farms, statistically distributed throughout the UK are monitored on a field by field basis resulting in data from some 40,000 fields. Comprehensive details of every product application are recorded, including date of application and rate, crop growth stage and field location. When compiling the database the active ingredients of each commercial product are identified to determine the total weight or loading of each chemical applied within the confines of any defined geographical boundary on a month by month basis. The historical land use and rotational crop data for each area enables predictions of future pesticide usage. Extrapolation of farm data to the surrounding area would be aided by Parish cropping statistics in addition to land and crop cover information from remotely sensed data.

Soil zone

Soil databases and the use of a GIS to predict aquifer and surface water vulnerability to pesticide contamination have been described by Carter (1989) and Hollis (1991). A user friendly Spatial Environmental Information System for Modelling the Impact of Chemicals (SEISMIC) is currently being developed to provide a stand alone system for interrogation on soil and related subjects in addition to providing some of the input data for the expert system proposed here. Spatial information on the distribution of soil types can be digitised and each soil unit allocated to a soil hydrological class (Hollis 1991) to identify the potential flow pathways of a pesticide in soil. Simple physico-chemical data can be assessed to identify the volatility, mobility and persistence of the chemical. This information and the pesticide loadings serve as input data to pesticide transport models - the most appropriate model being chosen for the circumstances. Several leaching and run-off models are being evaluated and validated with UK data, e.g. Williamson and Carter (1991). Model choice depends on the amount and quality of information available for the catchment area. The products of classification and modelling are: vulnerability assessments; a predicted soil zone leachate concentration; a prediction of maximum pesticide concentration in rapid runoff response to surface waters and a prediction of the quantity of pesticide adsorbed to particulate matter and transported to surface waters.

Unsaturated/saturated zone

A distributive model to predict nitrate leaching (DoE 1986 and Oakes 1987) has been modified to predict pesticide fate in the aquifer zone and ultimately to boreholes or springs. Simulation proceeds in three stages by taking soil leaching losses on a grid basis, for example, at 250 m nodes through to the unsaturated zone and then to the saturated zone. Fissure flow and molecular diffusion processes can be simulated according to hydrogeological conditions. Pesticide degradation is assumed to follow first order kinetics and can be expressed as a half life, though aquifer conditions may necessitate the use of a more complex decay constant. Given available or interpolated spatial data concerning the hydrogeological characteristics of an area, a final prediction of pesticide concentration in the aquifer or borehole source can be made.

RISK FORECASTING AND SOURCE PROTECTION

The expert system will provide a comprehensive assessment of the likely fate and behaviour of a chemical being considered for approval by a registration authority and will highlight the potential risk areas. Restricted usage via an appropriate product label

will ensure the continued applications of a pesticide which might have otherwise been withdrawn or abandoned during product development because of its potential to contaminate a water source. The system will reinforce the proactive attitude to water quality protection by water agencies and Figure 2 summarises the decision making processes envisaged.

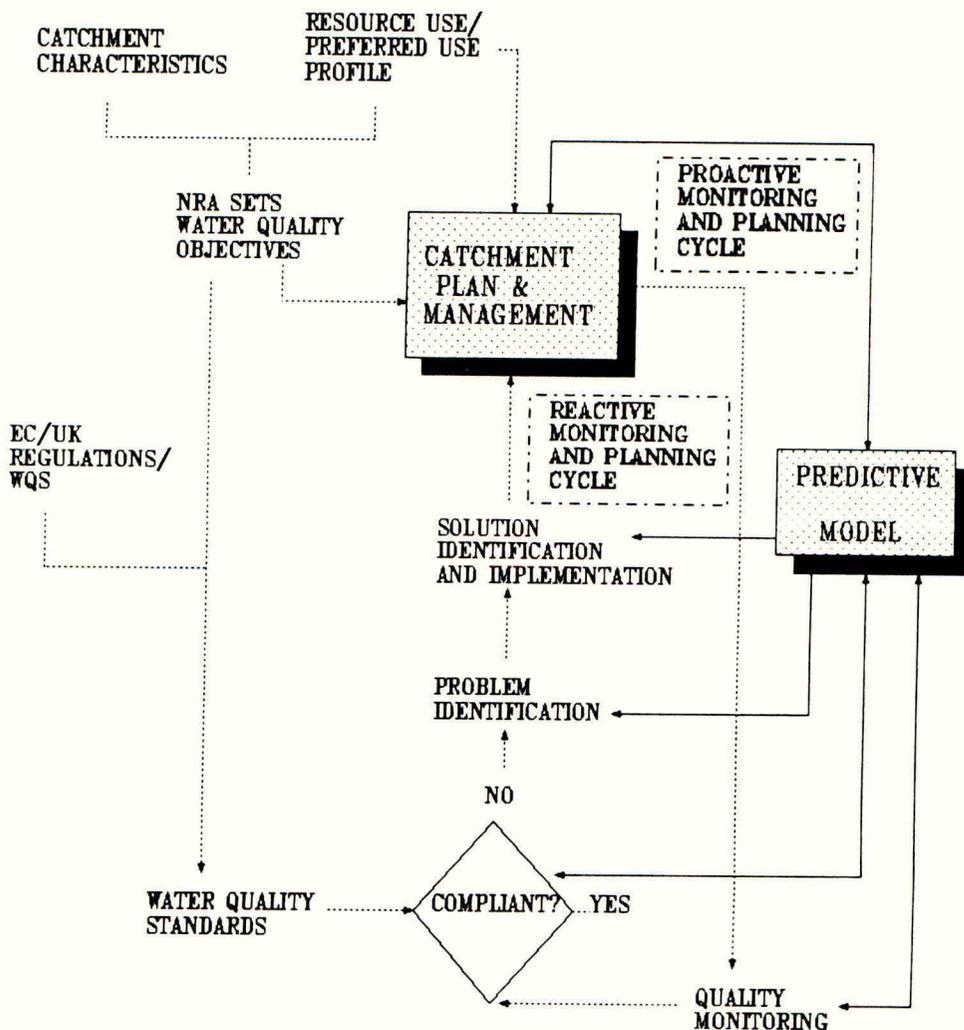


Figure 2 Catchment risk forecasting and protection system

Contamination problems can be avoided by careful catchment management and monitoring whereas analytical resources can be targetted towards specific areas. The facility can be applied to both surface and groundwater catchments of varying sizes and will support real-time resource management (particularly for surface waters). Future problems can be identified from land use trend data, enabling source protection policies to be enforced rather than incurring expensive water treatment costs.

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THE DEGRADATION AND MOBILITY OF ALACHLOR IN A SANDY LOAM SOIL

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ABSTRACT

Alachlor degradation in a sandy loam soil followed first-order reaction kinetics and the rate of loss was strongly influenced by soil temperature and soil moisture content. Half-lives in moist soil varied from 17 days at 25°C to 119 days at 5°C, and at 15°C varied from 46 days at 12% soil moisture to 238 days at 3.8%. Degradation rates in laboratory incubations with fluctuating temperatures were predicted with reasonable accuracy from the constant temperature data. In a field study prepared in autumn with undisturbed soil columns (30 cm x 11 cm diameter) in a mini-lysimeter system, alachlor residues were largely confined to the top 10-12 cm soil over a 6-month period although trace amounts were detected in the leachate on occasions. About 25% of the initial amount remained in the soil 168 days after application in early November, and the total amount recovered from the leachates represented less than 0.4% of the initial dose. The persistence and movement of residues in the columns were predicted accurately by some computer models of herbicide behaviour, although the models did not give accurate predictions of leachate concentrations.

INTRODUCTION

Alachlor (2-chloro-N-2,6-diethyl-N-(methoxymethyl)acetanilide) is widely used in many countries for the control of annual grasses and several broad-leaved weeds in soybeans, maize, cotton and peanuts. It can also be used in temperate crops such as oilseed rape and other brassicas. It is primarily applied pre-emergence and hence its behaviour in soil is of particular importance. It has been reported that alachlor is degraded by microorganisms in the soil (Sun *et al.*, 1990), and the rate of degradation is influenced by temperature and soil moisture content (Walker & Brown, 1985). In the experiments of Walker & Brown (1985), for example, first-order half-lives in a sandy loam soil at 12% soil moisture varied from 7.5 days at 25°C to 39 days at 5°C, and at 25°C varied from 6 days at 15% soil moisture to 23 days at 6%. In a field study to investigate persistence and mobility, Bowman (1990) observed that alachlor did not move beyond the top 10 cm during a 21-week period in spring and summer and that the time to 50% loss was about 10 days. A detailed review of the environmental behaviour of alachlor was presented by Chesters *et al.* (1989). The present experiments were made to gain further information on the persistence and mobility of alachlor in soil under UK conditions. Detailed studies were made of the effects of temperature and soil moisture on rates of loss in laboratory incubations, and the persistence and movement of residues in soil following autumn application were measured under natural conditions using a mini-lysimeter system. The data were evaluated using computer models of herbicide behaviour.

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MATERIALS AND METHODS

Soil and herbicide

The soil used was from Hunts Mill field at Horticulture Research International (HRI), Wellesbourne. It was collected from the 0-20 cm horizon and was classified as a sandy loam. It contained 1.91 % organic matter (loss on ignition) and had a pH of 5.97 in soil : distilled water (1 : 1). Soil moisture contents at applied pressures of 5, 33, 200, 500 and 1500 kPa were 13.41, 8.50, 5.97, 5.01 and 4.17 % respectively. The herbicide used was a commercial emulsifiable concentrate formulation of alachlor (48% AI), together with analytical grade alachlor (British Greyhound Ltd, Birkenhead) and a sample of the compound labelled with carbon-14 (0.10 milli Curies/mg; Monsanto Ltd).

Laboratory studies

A freshly-collected sample of soil was passed through a 3-mm mesh sieve and duplicate amounts (50g) were dried overnight in an oven at 110°C to determine soil moisture content. A suspension of the commercial formulation of alachlor in water was added to seven separate 1-kg samples of soil to give an initial concentration of 8.0 mg AI/kg soil. Further water was added to adjust soil moisture content to a nominal value of 8.50% (i.e the 33kPa percentage). Each sample was thoroughly mixed by passing several times through a 3-mm mesh sieve. Samples of soil (500g) were transferred to loosely-capped polypropylene containers (800ml capacity) and duplicate samples were incubated at constant temperatures of 5, 10, 15, 20 and 25°C. Further duplicate samples were incubated with 7-day cycling temperatures of 10/20 and 5/25°C. Soil moisture content was measured, as above, immediately after preparation of the samples, and was maintained throughout the experiment by addition of water followed by shaking as necessary. The soils were sampled at intervals of 7 or 14 days during the subsequent 70 to 112 days, when 45g amounts of soil were removed and frozen until analysed. A second experiment was made as described above with subsamples of the same soil (500g) incubated at 15°C but with soil moisture of duplicate subsamples adjusted to that equivalent to applied pressures of 5, 33, 200, 500 and 1500 kPa.

Herbicide adsorption

Amounts of air-dry soil (5g) were weighed into 50ml conical flasks and mixed with solutions of analytical grade alachlor in 0.02 M calcium chloride (20ml). There were duplicate samples with initial concentrations of 0.5, 1, 2 and 4 $\mu\text{g/ml}$ and all solutions contained carbon-14 labelled alachlor (5000 disintegrations per minute/ml). The samples were shaken on a wrist-action shaker for 8 h, allowed to stand overnight, and then shaken for a further 1 h. Herbicide adsorption was calculated by determining the difference between the initial herbicide concentration and the concentration present in the equilibrium solution by liquid scintillation counting as described by Walker and Zimdahl (1981).

Field experiment

The outdoor study was made using a mini-lysimeter system and was part of a larger experiment involving several soil-applied herbicides. The lysimeter system comprised a number of PVC tubes (11cm dia; 30 cm long) containing undisturbed soil from the Hunts Mill site. The columns of soil were collected

in early July 1990 by driving the tubes into the soil until the soil surface was approximately 1 cm below the top of the tube. The columns of soil were removed from the field by excavating the tubes and carefully cutting across the bottom. The bottom of each column was then held in place by 0.25 mm mesh nylon gauze fixed to the tube with waterproof sealing tape. A rigid polypropylene funnel (11.5 cm diameter) was sealed to the bottom of each column with waterproof sealing tape and the columns then mounted in a large wooden box (2 x 1.5 m x 30 cm deep). The end tubes of the funnels protruded through holes in the base of the box. The columns were held in position by a layer of soil (5cm) at the base, a layer of perlite (20 cm) in the middle and a final layer of soil (5cm) at the surface so that the soil surface inside the columns was level with that outside. Conical flasks (250 ml) were mounted under the columns beneath the box for collection of leachate. Alachlor was applied to the surface of seven replicate soil columns on 5 November 1990. A suspension of the commercial formulation in water (1 ml) was pipetted dropwise to the surface of each column to give a nominal dose of 8 kg AI/ha. One whole column of soil was removed immediately after application of the herbicide and single columns were removed at intervals of approximately 28 days during the subsequent 168 d. The columns of soil were divided into successive 2-cm segments from the surface downwards using a sectioning apparatus similar in design to that described by Walker *et al.* (1976). Each soil sample was mixed thoroughly and then frozen until analysed. Leachate from the columns was collected after significant rainfall (or snow melt) events when the volume of leachate and its alachlor content were measured.

Herbicide analysis

To extract alachlor residues, single amounts of soil (40g) from the laboratory samples and duplicate amounts of soil (50g) from the field samples were shaken with acetone (50 ml) for 1h on a wrist-action shaker. The soil was allowed to settle, and the concentrations of herbicide in the clear supernatant were measured by glc.

Leachate (25-150 ml) was transferred to a 250-ml separating funnel and 5% sodium chloride solution (40 ml), and dichloromethane (40 ml) added. The mixture was shaken and the dichloromethane removed. The aqueous residue was extracted with a second portion of dichloromethane and the dichloromethane extracts combined and evaporated to dryness. The residue was dissolved in acetone (1 or 2ml) and the concentration of alachlor measured by glc.

All samples were analysed using an Analytical Instruments model 93 gas liquid chromatograph with a nitrogen flame ionisation detector. A glass column (1.5m x 3mm i.d.) packed with 5% OV-1 was used and the operating temperatures of injection port, column and detector were 225, 220 and 235°C respectively.

RESULTS AND DISCUSSION

Laboratory experiments

The results from the incubation studies at constant temperature are summarised in Figure 1. They are presented as residual concentrations on a logarithmic scale against time of incubation. The straight line relationships obtained indicate close correspondence to first-order degradation kinetics and the rate constants and half-lives derived from the

TABLE 1. First-order rate constants (K deg) and half-lives (HL) for alachlor degradation at different temperatures and soil moisture contents.

Temperature effects at 7.94 % moisture content			Moisture effects at 15°C			
Temperature (°C)	K deg (day ⁻¹)	HL (days)	Moisture content		K deg (day ⁻¹)	HL (days)
			kPa	%		
5	0.00581	119.1	1500*	3.82**	0.00291	238.2
10	0.00905	76.6	500	4.25	0.00346	200.3
15	0.01746	39.7	200	5.52	0.00860	80.6
20	0.02696	25.7	33	7.34	0.01125	61.6
25	0.04009	17.3	5	12.05	0.01518	45.7

* nominal values; ** measured values

data are listed in Table 1. There was a marked effect of temperature on degradation rate with a variation in half-life from 17.3 days at 25°C to 119.1 days at 5°C. Temperature effects on degradation of herbicides can often be characterised using the Arrhenius equation (Hurlle & Walker, 1980). The fit of the present data to this relationship was determined by regression analysis of the logarithm of the half-lives against the reciprocal of the absolute temperature. The regression coefficient was 0.99 ($P < 0.001$) and the activation energy derived from the slope of the line was 70.6 kJ/molecule, somewhat higher than the value of 57.0 kJ/molecule derived in the earlier studies of Walker & Brown (1985).

The results from the incubation experiments with 7-day cycling temperatures of 10° to 20°C and 5° to 25°C are shown in Figure 2. The lines drawn on these diagrams are those calculated using the appropriate first-order rate constants listed in Table 1. The predicted residues were in reasonable agreement with those observed, although there was some variation between the two replicates.

The results from the incubations with varying soil moisture levels also gave good approximations to first-order reaction kinetics and the rate constants and half-lives derived from the data are listed in Table 1. The half-lives varied from 45.7 days at 12.05% moisture (5 kPa; field capacity) to 238 days at 3.82% moisture (1500 kPa; permanent wilting point). In previous experiments, the effect of soil moisture on herbicide degradation rates was characterised using an empirical equation:

$$H = AM^B$$

in which H is the half-life at moisture content M, and A and B are constants. The values of A and B derived from the present data were 1418.2 and 1.47 respectively. The slope of the line (B) gives a measure of the moisture dependence of degradation and the value of 1.47 compares favourably with that of 1.42 reported previously for alachlor by Walker & Brown (1985).

The results in Table 1 show a difference in rate of degradation under similar conditions in the two samples of the same soil. In the constant

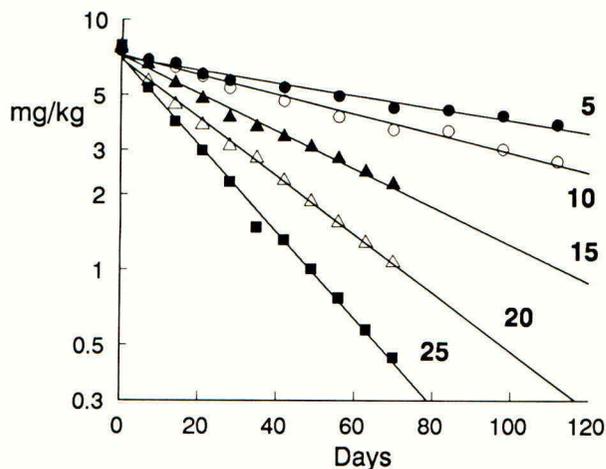


Figure 1. Influence of temperature on the rate of alachlor degradation.

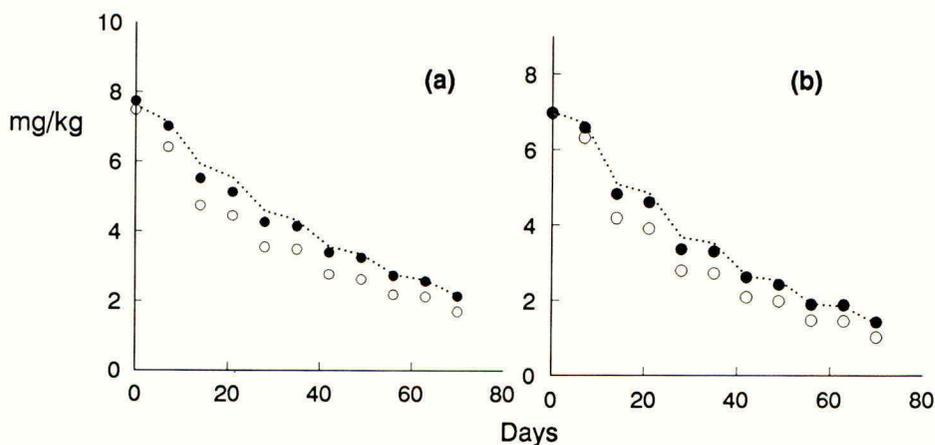


Figure 2. Degradation of alachlor with 7-day cycling temperatures of (a) 10/20°C or (b) 5/25°C. Observed data (●, ○); calculated data (.....).

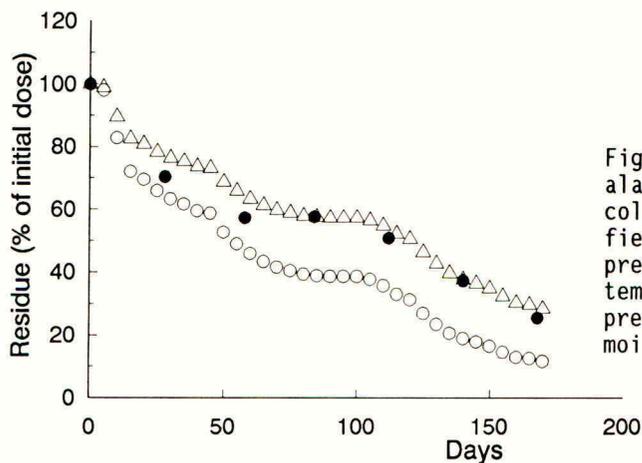


Figure 3. Total residues of alachlor recovered from columns of soil in the field. Observed data (●); predicted using data from temperature study (○); predicted using data from moisture study (△).

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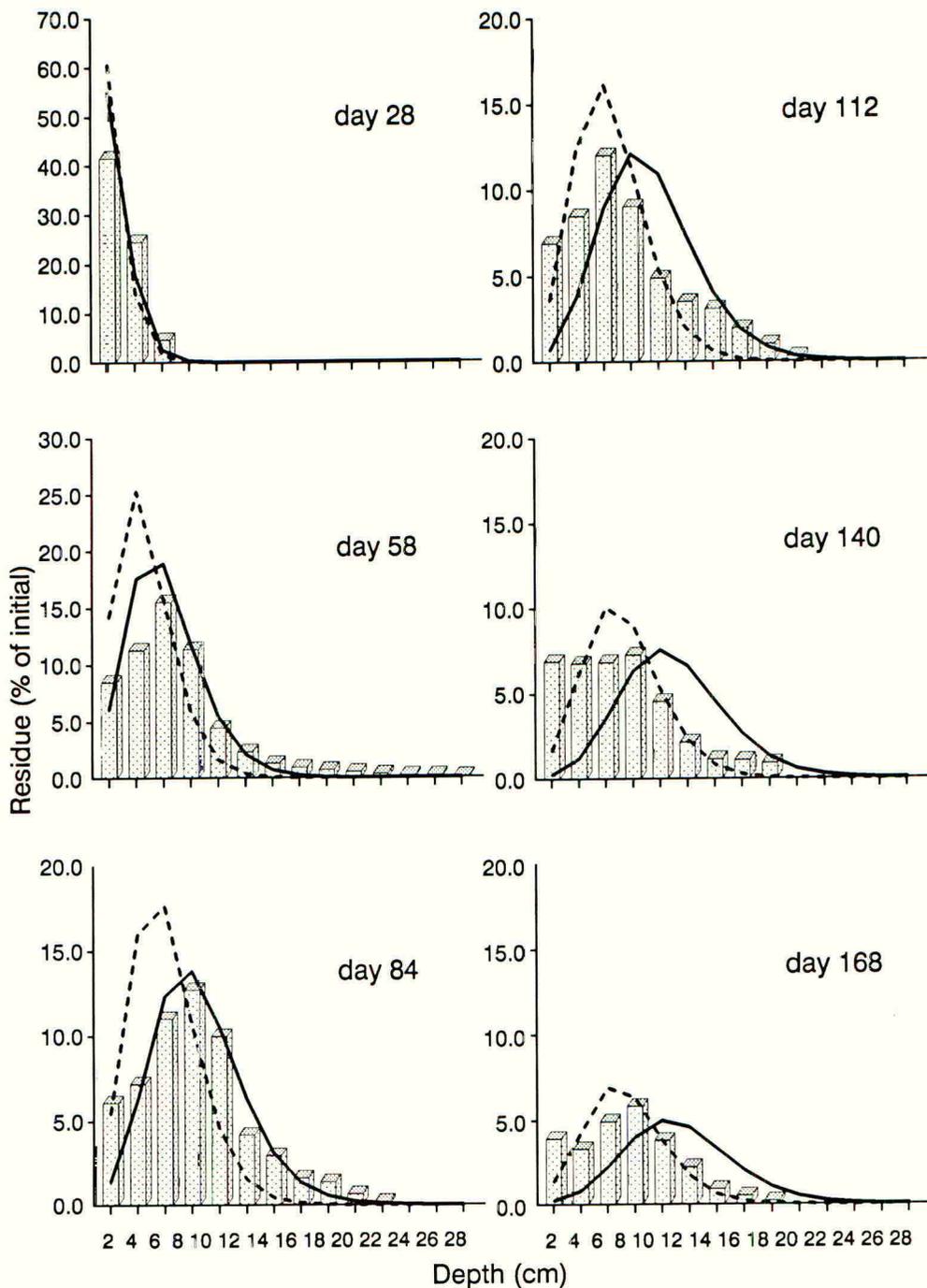


Figure 4. Vertical distribution of alachlor residues in soil. Measured data (histograms); predicted with constant adsorption (—); predicted with adsorption increasing with time (----).

temperature incubations, the half-life at 15°C and 7.9% soil moisture was 39.7 days, whereas in the constant moisture incubations, the half-life at the same temperature and 7.34% moisture was 61.7 days. This difference is unlikely to have resulted from the small difference in soil moisture level but must reflect differences in the microbiological properties of the soil when sampled on different occasions.

The adsorption isotherm for alachlor in the Hunts Mill soil was defined by linear regression analysis of the logarithm of the amount adsorbed ($\mu\text{g/g}$) against the logarithm of the equilibrium solution concentration ($\mu\text{g/ml}$). The correlation coefficient was 0.993 ($P < 0.001$) and the adsorption distribution coefficient (K_d) was 1.07. Peter & Weber (1985) reported that alachlor adsorption, in common with that of many other soil-applied pesticides, was positively correlated with soil organic matter content and they reported a K_d value of 1.02 in a sandy loam soil with 1.7 % organic matter, which agrees well with the value found in the present experiments.

Field experiment

Results from the field experiment are summarised in Figures 3 and 4. Total residues declined progressively throughout the experiment (Figure 3), with approximately 25% of the initial dose remaining at the final sampling time. The data in Figure 4 show that at the first sampling time (28 days after application) residues of alachlor were restricted to the top 6 cm of the columns with over 40% of the initial dose remaining in the 0-2cm layer. At day 58, trace residues were detected at 26-28 cm with a peak concentration in the 4-6 cm layer. Even after 168 days, the peak concentration was still present at 6-8 cm and most of the residues were located in the top 10 cm soil. Leachate from the columns was collected on 12 occasions during the 168-day period of the experiment. Volumes collected were highly variable between columns. Trace quantities of alachlor were measured in the leachate on some occasions. The highest concentration recorded was 0.13 mg/L (130 $\mu\text{g/L}$) in a sample collected in January (77 days after application), but concentrations were generally less than 20 $\mu\text{g/L}$. The total amount of herbicide collected in the leachate over the whole 168 day period of the experiment represented approximately 0.4 % the amount applied to the surface initially.

Prediction of mobility and persistence

The various constants derived from the laboratory experiments were used in conjunction with the appropriate weather data and soil properties in the models of pesticide behaviour described by Walker & Barnes (1981) and Nicholls *et al.* (1982). The results from the simple persistence model of Walker & Barnes (1981) are shown in Figure 3. Two predicted curves are shown, one using the degradation rates derived from the constant temperature incubation data, the second using the detailed data from the constant moisture incubations (Table 1). The somewhat slower rates of loss measured in the second of these experiments gave a much better prediction of the observed soil residues than did the data from the laboratory incubations at constant temperature.

The persistence model of Walker & Barnes (1981) is an integral part of the pesticide leaching model of Nicholls *et al.* (1982) as modified by Walker (1987). The "best fit" degradation constants (Figure 3) were used in this model together with the measured adsorption distribution coefficient with the results shown in Figure 4. Again two predicted lines are shown for each set

of observed data. One assumes a simple and constant equilibrium between adsorbed and solution phase herbicide; the second assumes that the herbicide becomes more strongly bound with increasing residence time in the soil. This modification to the model was discussed in detail by Walker (1987), and the present results (Figure 4) give a clear indication of the need to incorporate this function in the program, particularly at extended times after application. The trace residues that leached from the columns were not predicted accurately by the leaching model which may be a reflection of errors in the model or it may indicate that this movement was not through the soil matrix but by a form of preferential flow between the soil and the column walls. Further experimentation is required to investigate this possibility. The results indicate that alachlor is a moderately persistent herbicide and is slightly mobile in the soil following autumn application in the UK. The results also demonstrate the usefulness of computer modelling techniques to evaluate persistence and mobility data. A valid model of behaviour would permit predictions to be made in a wider range of soils and weather conditions than could be examined in detail experimentally.

ACKNOWLEDGEMENTS

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MEASUREMENT AND MODELLING OF PESTICIDE RESIDUES AT ROSEMAUND FARM

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ABSTRACT

Instruments have been sited in a catchment at Rosemaund in Herefordshire to study the fate and behaviour of agricultural pesticides. The overall objective of the study is to test and develop hydrodynamic models of pesticide movement on the field and catchment scale. The choice of an experimental farm for the catchment ensures that detailed and accurate knowledge of pesticide applications is available. Furthermore, the underlying geology is shallow and impermeable and the hydrology is surface water dominated thus the catchment allows a 'worst case' assessment of pesticide transport to surface waters. Data have been collected on the residues of a number of pesticides in various of the environmental compartments. These include the soil, soil water, soil biota, drainage water, receiving stream water and stream fauna. This paper presents data for the herbicides mecoprop, lindane and isoproturon. Results of modelling these data using the level 2 Mackay fugacity model are presented and its usefulness as a tool for pesticide registration purposes is assessed.

INTRODUCTION

There is a need to assess the environmental fate of new chemicals before they are released to the environment in significant quantities. This is especially true for pesticides, which are released directly through their use. Of particular concern is the extent to which pesticides reach rivers and lakes by leaching and surface runoff. Hence the prediction of possible levels in water will be more important due to the adoption of the EC Drinking Water Directive (Anon., 1975) limit of 0.1 µg/l of any single pesticide in potable waters.

Environmental models may be able to assist in addressing these problems. For new chemicals, models which require only the limited data available for the chemicals to give order of magnitude predictions of their

concentration in the environment would be of obvious use. From a wider viewpoint, models which use factors such as farm practice, crop types, weather and soil type to predict the runoff potential of pesticides would assist decisions about environmentally sound pesticide usage in particular catchments.

A wide range of models of differing complexity have been developed (eg Anon., 1989, Pennell et al., 1990), but few have been tested under UK conditions. The aim of the work at Rosemaund Farm is to generate data to validate such models, and to use the insights gained to develop further and test appropriate model systems. The paper reports results from 1989/90 field experiments, together with modelling studies using a modified Mackay fugacity model (Mackay and Paterson, 1981). This work was funded by MAFF, NRA and the DoE. The field site at Rosemaund is well suited to such experiments for a number of reasons. It lies at the head of a small catchment, where the geology and soil structure maximize chemical transport through surface runoff mechanisms to the outflow stream thus providing a worst case example. As an experimental farm, installation of monitoring equipment is not unusual, good records of chemical applications are kept and technical staff are always on site.

STUDY SITE

The study catchment lies mainly within the boundaries of ADAS Rosemaund 15 km north east of Hereford, UK (Fig. 1).

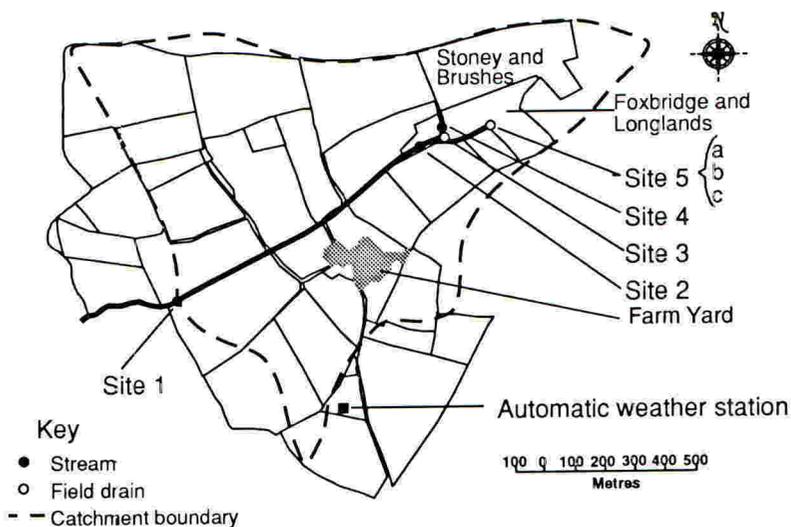


Figure 1. Location of sampling sites within the Rosemaund Catchment

The farm is owned by the Ministry of Agriculture Fisheries and Food (MAFF), operated by ADAS and has been managed as an experimental unit since 1949. The catchment has an area of 1.8 km² with an altitude range of 76 m to 115 m and correspondingly gentle slopes. The soils are from two series, the Bromyard and the Middleton and have been mapped and analyzed by the Soil Survey and Land Research Centre (Hodgeson, 1989). The Bromyard series predominates and is found on the slope areas of the catchment. The wetter Middleton series tends to occur on flatter ground and towards the lower end of the slopes. The soil texture is silt clay loam in the top 60 cm changing to silt loams below this depth, the largest clay fraction being between 25 and 60 cm below the surface. The soil is subject to considerable cracking following periods of low rainfall during the summer months. The organic matter content of the surface 25 cm cultivated layer under long term arable cropping is within the range of 2 - 3 per cent with little organic matter

present below 35 cm. The geology is made up of effectively impermeable siltstones and mudstones which lie between 1 m and 3 m below the surface.

The land within Rosemaund Farm is used for a wide mixture of agricultural enterprises. Of the 176 ha, approximately 30 % of the area is grassland, another 60 % of the farm is in cereals with small areas of oilseed rape, peas and root crops. Finally 10 % is in hops. The average annual catchment rainfall is 664 mm. The catchment is drained by a single stream that continues to flow in all but the driest years. Most of the fields have been under drained using plastic pipes at a depth of 1 m, with permeable backfill to within 300 mm of the surface. The average drain spacing is 20 m.

METHODS

As part of normal husbandry selected pesticides were applied to two fields of winter wheat at the top of the catchment, Foxbridge and Longlands and Stoney and Brushes (Fig 1). Details of the times and rates of application are given in table 1. Pesticide residues were measured in the soil, various drain outfalls and the stream both before and after the application. The monitoring strategy was to concentrate on sampling during rainfall events with manual samples taken between events. Details of are given below. Residues were determined using high performance liquid chromatography or gas chromatography with appropriate detectors, details are given elsewhere (Bird *et al.*, 1991).

Table 1. Details of applications made to fields within the study site.

Pesticide	Rate of active ingredient (kg/ha)	Fields	Application date
Isoproturon	1.0	Foxbridge + Longlands	01/11/89
Isoproturon	0.375	Stoney + Brushes	17/11/89
Lindane	0.5	Foxbridge + Longlands	01/11/89
Mecoprop	0.65	Foxbridge + Longlands Stoney + Brushes	20/03/90 22/03/90

Soil samples

Soil samples were taken from the fields onto which the herbicides had been applied. They were taken from randomly chosen points on the intersects of a 25 m grid superimposed on the fields. Samples were taken to a depth of 1 m using a steel corer. Cores were placed in plastic bags, sealed, and then stored at -20 degrees C until analyzed. The frequency of the sampling was based on the expected lifetimes of the chemicals in the soil as calculated from values given by Matsumura and Krishna (1982). In addition samples were taken as soon as possible following a rainfall event. In all cases samples were taken to give a mean soil pesticide concentration in the top 1 m of the soil.

Water samples

Water samples were taken from the sites 1 to 5 as indicated in fig. 1. Stream sites 1 and 2, and drain outfalls 3 and 5c were equipped with automatic water samplers and structures for measuring flowrate. The automatic samplers were started by the closure of a float switch as the water level rose in the drains and stream. Samples were collected into 24 one litre brown glass bottles. To minimise the risk of contamination and/or loss of active ingredient the sample tubes were made from PTFE and the internal parts of the samplers were almost entirely constructed from stainless steel or coated with PTFE.

RESULTS

The concentrations of the three pesticides in the top 1 m of the soil are presented in tables 2 to 4.

Table 2. Measured and predicted lindane concentrations in the top 1 m of soil for the experimental fields (values based on wet weight).

Time after application (days)	Measured (mg/kg)	Modelled Literature Rate (mg/kg)	Modelled Fitted Rate (mg/kg)
0	-	0.036	0.036
5	0.040	0.035	0.032
21	0.026	0.033	0.022
47	0.015	0.029	0.012
91	<0.002	0.023	0.005

Table 3. Measured and predicted concentrations of isoproturon in the top 1 m of the soil experimental fields following its application (values based on wet weight).

Time after application (days)	Foxbridge + Longlands		Stoney + Brushes	
	Measured (mg/kg)	Modelled (mg/kg)	Measured (mg/kg)	Modelled (mg/kg)
0	-	0.065	-	0.025
5	0.1	0.055	0.03	0.021
21	0.05	0.033	-	-
31	-	-	0.01	0.009
47	0.01	0.014	-	-
75	-	-	<0.01	0.002
91	<0.01	0.004	-	-

Table 4. Measured and predicted concentration of mecoprop in the top 1 m of soil in the experimental fields (values based on wet weight).

Time after application (days)	Measured (mg/kg)	Modelled (mg/kg)
0	-	0.046
5	0.059	0.040
9	0.033	0.024
15	0.020	0.017
22	0.015	0.011
35	0.011	0.005
62	0.002	0.001

The concentration of lindane had fallen to below its detection limit of 0.002 mg/kg, 91 days after application to Foxbridge and Longlands. This decay was more rapid than was expected from the literature, which leads to

implications for the application of the model (see below). For isotroturon, The level measured in the soil in Foxbridge and Longlands was 3 times that measured in Stoney and Brushes, very similar to the ratio of the application rates (table 1).

The concentrations of the pesticides measured at various drain sites and at two stream sites are summarized in tables 5 to 7. The location of the sites can be found by in figure 1.

Table 5. Summary of event data for lindane for sites within the Rosemaund Catchment

Site No	Event Period	Number of samples	Min (ppb)	Max (ppb)	Mean (ppb)	Rain (mm)
5c	0930 08/11/89 to 1930 08/11/89	11	0.03	1.74	0.85	28.5
4	0940 08/11/89 to 0840 09/11/89	12	<0.01	4.46	0.60	28.5
4	0010 10/11/89 to 2210 10/11/89	12	0.06	4.14	0.58	11.5
4	1400 13/12/89 to 1300 14/12/89	10	0.02	0.45	0.15	52.5
2	as above	10	0.04	0.29	0.13	52.5
1	1600 15/12/89 to 2200 18/12/89	11	<0.01	0.75	0.15	57.5
5c	1645 15/12/89 to 0045 19/12/89	11	<0.01	2.55	0.57	57.5
4	1600 19/03/90 to 1500 20/03/90	12	0.001	0.027	0.007	9.0
2	as above	12	0.004	0.03	0.008	9.0

Table 6. Summary of event data for isotroturon for sites within the Rosemaund catchment.

Site No	Event Period	Number of samples	Min (ppb)	Max (ppb)	Mean (ppb)	Rain (mm)
4	0940 08/11/89 to 0840 09/11/89	9	1.2	8.4	2.5	28.5
4	0010 10/11/89 to 2210 10/11/89	11	1.8	13.7	4.6	11.5
4	1400 13/12/89 to 1300 14/12/89	11	1.1	8.8	3.2	52.5
2	as above	10	2.1	5.4	3.8	52.5

Table 7. Summary of event data for mecoprop for sites within the Rosemaund Catchment.

Site No	Event Period	Number of samples	Min (ppb)	Max (ppb)	Mean (ppb)	Rain (mm)
2	1700 15/05/90 to 1600 16/05/90	24	0.1	1.4	0.5	12

The concentrations of lindane at the various sites show a clear pattern with time. At each site the mean concentration of the pesticide is highest in the first event and then falls in each subsequent event. This pattern is

best illustrated at site 4 since this site has provided the most data. The pattern for isoproturon is more difficult to interpret because of the two application dates (1/11/89 and 17/11/89). The mean value for the event starting on 8/11/89 is lower than the following event on the 10/11/89 possibly because the initial two samples were missing from the autosampler sequence; it is these samples that usually held most isoproturon.

MODELLING

Development

The model used here is based on the second level of Mackay's development (Mackay and Paterson, 1981). It uses simple physico-chemical properties of the pesticide to calculate how it partitions between a number of idealised phases or compartments of the environment and hence is appropriate for new pesticides for which limited data are available. Processes which remove the chemical, such as degradation or water flow, are also included. The model has been modified to follow the time pattern of distribution, rather than calculate an equilibrium situation for a constant input. For this particular case, two linked models are used. The first of these is the field itself, and is made up of soil, soil water and air over the field. The dimensions and properties of each phase are derived from measurements at the site. When the chemical is added to the model, it partitions between the three phases. The removal processes then act on the appropriate phase for a set period, usually one hour; the amount of chemical remaining is then repartitioned and new concentrations calculated. Rainfall is used to model the water flow through the field, carry chemical out of the field model and provide the link to the second model (the stream). This consists of five phases: air, water, sediments, suspended sediments and biota. Water from the field model enters the stream carrying the chemical with the input set back in time to allow for the delay in stream rise following rain. Partitioning and removal work as for the field model.

Results

The work reported here concentrates on the applications of pesticides in the 1989/90 experiments. Some previous work at the same site has been reported elsewhere (Brooke and Matthiessen, 1991). The physico-chemical data on the three pesticides were taken from various sources and are shown table 8.

Table 8. Physico-chemical data used in the pesticide model.

Property	Lindane	Isoproturon	Mecoprop
Molecular Weight	206.3	290.85	214.6
Vapour Pressure (mmHg)	2.5×10^{-8}	9.4×10^{-6}	7.5×10^{-7}
Solubility (mg/l)	55.0	17.0	620.0
Log K_{ow}	2.71	3.72	2.3
Log K_{oc}	2.11	-	-
Degradation rate in soil (h^{-1})	1.44×10^{-3}	2.06×10^{-4}	3.0×10^{-3}

These data and the rainfall figures were used to calculate the concentration of the chemical in the field compartments at the intervals of soil sampling. The model gives concentrations in the soil and soil water separately. As the soil measurements are on a wet basis, a composite value was calculated. A comparison of the measured and calculated values is given in tables 2-4.

There are two points to note on these figures. The initial concentrations are in reasonable agreement with the measured levels, but in each case are somewhat lower. The reverse might have been expected, due to

interception of the chemical by the crop or spray drift. In previous work (Brooke and Matthiessen, 1991) the differences were greater, and the amounts added to the field model were adjusted accordingly. In this case as the intention is to develop a tool for use before application, the amounts have not been adjusted. The second point is that the disappearance of lindane was much more rapid than that predicted, while the other chemicals behaved much more in accord with predictions. As it is unlikely that this behaviour was due to the lindane being washed out from the field, then the degradation rate found here appears to be greater than that found in the literature. A higher value for the rate constant was estimated from the measured data, and used to recalculate the concentrations in the field.

The water in the field model carries chemical out of the field, and is thus analogous to the drains. The predicted concentrations in the field water may be compared with those measured in drain water. Data were available only for the isoproturon and the lindane cases. Measured values for isoproturon ranged from 1.1 to 8.8 $\mu\text{g/l}$ with modelled levels of 4.4 to 4.7 $\mu\text{g/l}$; while measured values for lindane range from 0.02 to 0.45 $\mu\text{g/l}$ compared to modelled values of approximately 0.4 $\mu\text{g/l}$ over the rainfall event.

The amounts carried out of the field model were used as inputs to the stream model. From a comparison of the rainfall times and stream flow rates, a delay of 6 hours was used for the isoproturon and lindane data. For mecoprop, a shorter delay of 3 hours was used. Results from the model calculations together with the measured levels are shown in Fig. 2.

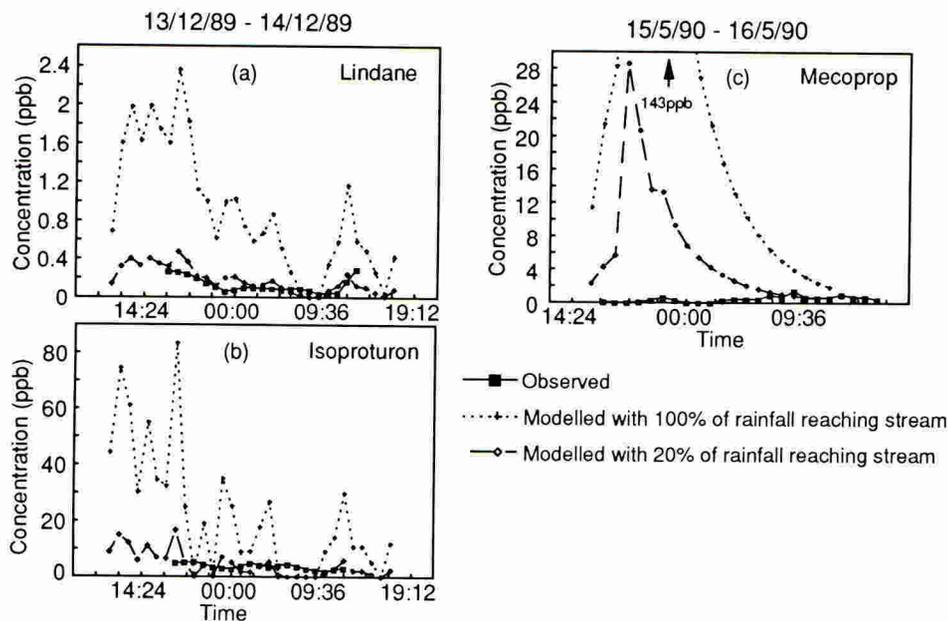


Figure 2. Observed and modelled concentrations of (a) lindane, (b) isoproturon and (c) mecoprop in the Rosemaund Stream at site 2.

The levels predicted in the stream are consistently higher than those measured. This was also noted in the previous work (Brooke and Matthiessen, 1991). Other studies at Rosemaund have looked into the possibility that pesticides move below drain level and thus do not appear in the stream at the top of the catchment and there is some evidence for significant

concentrations of chemical at levels below the drains (Bird *et al.*, 1991). Any pesticide carrying water by-passing the drain will be trapped by the geology no more than a few metres below the surface and the magnitude of this movement is currently being assessed. The initial modelling assumed that all the rainfall appeared in the stream during a storm event. Examination of the rainfall and stream flow records shows that a runoff coefficient of 0.2 is appropriate for this catchment for an individual storm. The stream model was therefore re run with only 20% of the chemical from the field model entering the stream. For isoproturon and lindane, the results are much closer to the measured values (Fig 2.), and approach the order of magnitude requirement of the system, while erring on the side of higher concentrations. This leaves aside the question of where the rest of the chemical goes, although as only a small quantity is removed from the field by water flow (0.8 and 0.1 % respectively of isoproturon and lindane applied, up to the end of the rainfall events modelled) the levels in the field model would not be greatly affected if it were to remain in the field. For mecoprop agreement is not as close, with the maximum calculated level being 20 times the highest measured concentration. A preliminary look at previous data suggests that applying the same procedure would bring model and measured levels closer together, but only to the level of mecoprop in this work. Further applications of other pesticide have been carried out or are planned, to expand the range of chemical types and provide further information on the reliability of the assumptions made in the model.

CONCLUSIONS

Rosemaund is an excellent site for the study of the processes of pesticide runoff to surface waters. A detailed data base of pesticide residues, hydrological variables and crop husbandry has been established. The order of magnitude agreement required between the model and measured concentrations was obtained for lindane and isoproturon, but not for mecoprop. To investigate the reasons for the differences, further work should be carried out applying the model described here and perhaps other models to more pesticide groups.

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BENSULFURON AND QUINCLORAC DETECTION IN SOILS AND WATER

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ABSTRACT

Phytotoxicity in vegetables grown in rice areas near Valencia (Spain) has been attributed to contamination by bensulfuron and/or quinclorac. A Lycopersicon esculentum root bioassay can measure both chemicals in soils and water.

The method only needs 30 ml of affected water or 150 g of affected soil, and is able to detect the herbicides at the levels of ppb in water and ten times these rates in soils. The test is more sensitive to the presence of bensulfuron than quinclorac or other sulfonylureas.

INTRODUCTION

The rice area in Valencia (Spain), is located around the Albufera lake that serves as reservoir for irrigation, thanks to a complex network of canals and pumping stations. Between the Albufera lake and the Mediterranean sea there is a narrow piece of land, where vegetables are grown, mainly for local consumption.

Phytotoxicity in comercial tomato crops recorded in 1990 was attributed to irrigation with water from the lake that contained the herbicides bensulfuron and quinclorac used in the rice fields. The damage was so important that restrictive regulations prohibiting the use of quinclorac and limiting the use of bensulfuron to 3000 ha have been introduced in a law passed by local authorities.

The use of plant root bioassays for chlorsulfuron have been reported by many authors (Groves & Foster, 1985; Hsiao & Smith, 1983; Morishita *et al.*, 1985; Smith & Hsiao, 1985) with corn the main test plant employed. Gomez de Barreda *et al.* (Weed Research in press) have shown that a Lycopersicon esculentum root bioassay was able to detect bensulfuron and quinclorac in water at concentrations of ppb. The purpose of this paper is to describe the biotest mentioned above and show that it can also be used to detect the herbicides in soils at higher concentrations.

MATERIAL AND METHODS

Several plant species including corn and peas were tested in the root bioassay methods used for sulfonylureas, but the results were erratic where bensulfuron and quinclorac were present at ppb levels. The evident damage to commercial crops suggested that Lycopersicon

esculentum was particularly sensitive and this was confirmed by a preliminary test. The species was therefore chosen for this work.

Herbicides in water

Ten pre-germinated (48 h in a chamber at $30\pm 2^{\circ}\text{C}$) tomato seeds were sown on a 9 mm Petri dish. To this either 10 ml of either a standard herbicide solution or the water under test were added. The Petri dish was immediately wrapped with laboratory film paper and placed in a growth chamber a 30°C , 16/8 h light/dark and $100 \mu\text{E m}^{-2} \text{s}^{-1}$ PAR (microeinteins per square meter, per second of photosyntetic active radiation). Each treatment was replicated three times. Table 1 shows the analysis of two different water sources used.

After a period of 6-9 days the main root was measured to the nearest mm and the average root length of the ten seedlings in each Petri dish was calculated.

A more precise description of this method will appear in Gomez de Barreda et al. (Weed Research in press).

TABLE 1. Water analysis from the two sources used

	Albufera	Moncada Tap
E.C. dS/m-1 at 25°C (*)	1.81	1.47
pH	7.85	7.20
	me/l	me/l
Cations: Ca ⁺⁺	3.35	7.35
Mg ⁺⁺	11.52	4.16
Na ⁺	5.39	3.22
K ⁺	0.19	0.04
Anions: Cl ⁻	8.6	3.41
SO ₄ ⁼	7.6	7.60
CO ₃ H ⁻	4.4	4.40
CO ₃ ⁼	-	-

(*) Electrical conductivity in decisiemens per meter at 25°C .

Herbicides in soil

The method in this case, is very similar to the above for water. A shallow layer of soil is first placed in a petri dish. Ten germinated tomato seeds are sown on the surface and covered with more soil to give a total of 50 g of soil in the dish. The dish is then irrigated with a pipette using either 20 ml of water or 10 ml of water plus 10 ml of herbicide solution depending on whether a suspect soil sample or a standard herbicide concentration is under test.

RESULTS

Bensulfuron was more phytotoxic than quinclorac to tomato roots. But in Table 2, even the least aggressive treatment of quinclorac at 0.05 ppm was statistically different ($P=0.01$) to the untreated.

TABLE 2. Tomato root bioassay for bensulfuron and quinclorac.

	Average length of main root in mm.	
	0.5 ppm	0.05 ppm
bensulfuron	10.9 ± 2.1	12.2 ± 1.6
quinclorac	20.8 ± 2.0	29.3 ± 4.7
untreated	39.7 ± 8.1	

In this proposed bioassay, the test plant appears to be very sensitive to environmental growth conditions. Table 3 shows that three tomato varieties performed differently depending on the water source (see Table 1) and chamber periode (5 days versus 8 days). The effect of growth conditions is shown again in Tables 4 and 5 where the Rio Grande variety was treated with bensulfuron in different types of water and grown under a variety of growth chamber environments. Those conditions which encourage the greatest development of roots in the untreated seedlings would appear to be most suitable for the test because they also produced the greatest differences between the untreated and the standard herbicide treatments. Also, those varieties which have the greatest root growth are likely to be more sensitive.

TABLE 3. Response of three tomato varieties to two sources of water and growth periods.

Average length of main root in mm.				
WATER SOURCES				
Varieties	A L B U F E R A		T A P	
	Length of the growth period in the chamber			
	5 days	8 days	5 days	8 days
Pomodoro	58.8±10.6	84.7±30.1	49.8±10.4	83.5± 8.3
Robin	101.9±10.2	142.5±3.2	96.9± 4.4	112.0± 7.3
Rio Grande	99.7±21.8	119.1±13.4	87.7±15.9	90.8±21.2

TABLE 4. Tomato bioassay response to bensulfuron in different growth chamber conditions.

Average (n=3) length of main root in mm			
Growth chamber conditions			
Herbicide concentr.	under a filter paper	under aluminum foil	without covering foil
10 ppb	9.4 ± 1.8	11.1 ± 0.9	11.6 ± 2.3
1 ppb	17.0 ± 3.8	17.0 ± 5.9	18.7 ± 4.1
untreated	84.5 ± 7.1	45.4 ± 6.4	68.5 ±21.1

TABLE 5. Tomato bioassay response to bensulfuron in two types of water.

Average (n=3) length of main root in mm		
Types of water		
	DEIONIZED	TAP
10 ppb	15.1 ± 2.3	16.0 ± 2.2
1 ppb	17.1 ± 0.6	29.5 ± 8.2
0.1 ppb	21.0 ± 1.9	38.5 ± 10.6
untreated	31.7 ± 6.8	61.2 ± 14.3

The results of the soil procedure are shown in Tables 6,7 and 8. In Table 6 quinclorac was less phytotoxic to the test plant than bensulfuron, but even at 1 ppm of quinclorac, the data are significantly ($P=0.05$) different from the untreated.

Table 8 shows the responses of several sulfonylureas. The apparent decreasing order of phytotoxicity is as follows: bensulfuron, chlorsulfuron, cinosulfuron and primisulfuron.

TABLE 6. Bioassay in loam soil for bensulfuron and quinclorac.

	Average length of main root in mm	
	rates in ppm	
	10	1
quinclorac	17.0 ± 0.15	42.5 ± 2.80
bensulfuron	5.9 ± 1.7	7.9 ± 1.30
untreated	53.9 ± 7.6	

TABLE 7. Bioassay in sandy soil for quinclorac

	Average length of main root in mm	
	Periods of the Petri dish in the growth chamber	
quinclorac 4 ppm	4.60 ± 0.47	5.0 ± 0.2
quinclorac 0.4 ppm	11.20 ± 0.47	11.0 ± 0.8
quinclorac 40 ppb	24.30 ± 5.76	27.6 ± 2.4
quinclorac 4 ppb	-	55.9 ± 1.1
untreated	37.57 ± 3.00	60.4 ± 7.1

TABLE 8. Tomato root bioassay for different sulfonylureas.

Average length of main root in mm.		
Periods of the Petri dish in the growth chamber		
	eight days	twelve days
bensulfuron	25.1 ± 3.0	30.0 ± 2.4
cinosulfuron	53.9 ± 6.6	chlorsulfuron 77.8 ± 11.3
primisulfuron	72.4 ± 2.8	110.4 ± 3.4
untreated	89.4 ± 20.2	112.0 ± 11.9
	seven days	eight days
bensulfuron	19.5 ± 2.6	17.7 ± 6.9
chlorsulfuron	18.5 ± 3.8	21.5 ± 3.2
untreated	81.4 ± 14.2	94.7 ± 28.0

The biotest proposed is quite simple, sensitive and only uses 30 ml of suspect water or 150 g of suspect soil (10 ml and 50 g respectively for each of the three replications). It is not a method which specifically detects bensulfuron and quinclorac, but it appears to be more sensitive to bensulfuron than quinclorac or other sulfonylureas.

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THE EFFECT OF A RANGE OF ENVIRONMENTAL FACTORS ON THE DEGRADATION RATE OF CLOPYRALID IN SOIL UNDER AEROBIC CONDITIONS

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ABSTRACT

The degradation of the herbicide clopyralid was investigated in a laboratory study in 5 soils with a range of initial microbial biomasses. DT50 and DT90 values (disappearance time for 50% and 90% of the initial concentration) determined showed that clopyralid was quickly degraded in soil under these conditions to give CO₂ as the sole observed metabolite. The rate of degradation of the herbicide could be roughly correlated to the microbial biomass of the soils. Soils with higher biomass degraded clopyralid faster than those with lower microbial biomass. The effect of temperature, soil moisture and initial clopyralid concentration on the rate of degradation of the herbicide were also investigated in 3 agricultural soils. Overall, higher temperatures and soil moistures led to more rapid degradation of clopyralid. Lower DT50 and DT90 values were obtained at lower initial clopyralid concentrations indicating that residues disappear from the soil sooner at lower concentrations.

INTRODUCTION

3,6-dichloropyridine-2-carboxylic acid, common name clopyralid, is the active ingredient of the herbicide LONTREL 100. Clopyralid is a systemic herbicide with exceptional activity against the creeping thistle (*Cirsium arvense*) and is very selective in a number of broad leaved crops (Worthing & Hance, 1991).

The degradation of clopyralid was investigated in a laboratory study in five different soils with a range of initial microbial biomass values (Table 1). Two standard German soils, as designated by the German regulatory authority, The Biologische Bundesanstalt (BBA), (2.1, sand and 2.2, loamy sand) and three agricultural soils (German Parabraunerde, silt loam; UK Marcham soil, sandy clay loam and UK Castle Rising soil, organic sandy loam) were used in the experiment. For the major part of the experiment clopyralid was incubated with the different soils at a concentration of 0.3 mg/kg soil (field rate) with the moisture content of the soils set at 40% maximum moisture holding capacity (MHC) and the temperature at 20°C.

In addition, the effect of incubation temperature and soil moisture on the rate of clopyralid degradation and metabolism was

* LONTREL 100 Trademark of DowElanco Ltd.

investigated in the 3 agricultural soils. Incubations were carried out at two different temperatures 10°C and 20°C and 3 different soil moisture contents, 10%, 40% and 60% MHC. The effect of different initial clopyralid concentrations on the rate of degradation was also studied by incubating soil with 3 different concentrations of the herbicide - 0.05mg/kg, 0.3mg/kg and 1.0mg/kg.

MATERIALS AND METHODS

50g oven dry equivalent of soil was weighed out into one side of a biometer flask. The moisture content of the soils was adjusted to that required (40, 10 or 60% MHC) with the addition of distilled water. [2,6-¹⁴C pyridine] clopyralid, formulated as the monoethanolamine salt, was added to the soil to give the appropriate concentration (0.05, 0.3 or 1mg/kg) and well mixed. In the other side of the biometer flask was added 100 mlitres 0.1M NaOH solution which served as a CO₂ trap. The biometer flasks were then incubated at either 10°C or 20°C. The CO₂ traps were changed at regular intervals and monitored using scintillation counting. Biometer flasks were removed from the incubators 0, 7, 14 and 28 days and 3 and 6 months after application. For the incubations at 20°C, 40% MHC and 0.3 mg/kg clopyralid concentration, additional sampling times of 1 and 3 days, and 9 and 12 months after application were also included. The microbial biomass was determined at the start of the study.

The soil samples were extracted sequentially with 0.01M CaCl₂, followed by acidified acetone and finally with 0.5M NaOH. The radioactivity extracted was determined by scintillation counting and those extracts with greater than 10% of the applied radioactivity were analysed by thin layer chromatography (TLC).

RESULTS AND DISUSSION

The monitoring of the CO₂ traps throughout the experiment showed that ¹⁴C-clopyralid was readily degraded and extensively mineralised to ¹⁴CO₂ in all 5 soils studied. Analysis of all the extractable radioactivity by TLC showed only clopyralid to be present. As no other metabolite apart from CO₂ was observed it can be assumed that the rate of mineralisation can give an indication of the rate of clopyralid degradation. The rate of mineralisation was dramatically reduced after about 92 days for all soils. This decrease in the rate of degradation is possibly due to depletion of nutrients in the soil and thereby a reduction in microbial biomass or an increased binding of clopyralid to soil particles and soil organic matter (Frehse & Anderson, 1983).

By day 92 the majority of the radioactivity was mineralised to CO₂ and only a small amount was readily extractable into CaCl₂ in all of the soils studied. In Parabraunerde soil about 11% of the ¹⁴C applied radioactivity remained bound to the soil particles and organic matter. This fraction is unlikely to be available for movement in the soil or for biological activity.

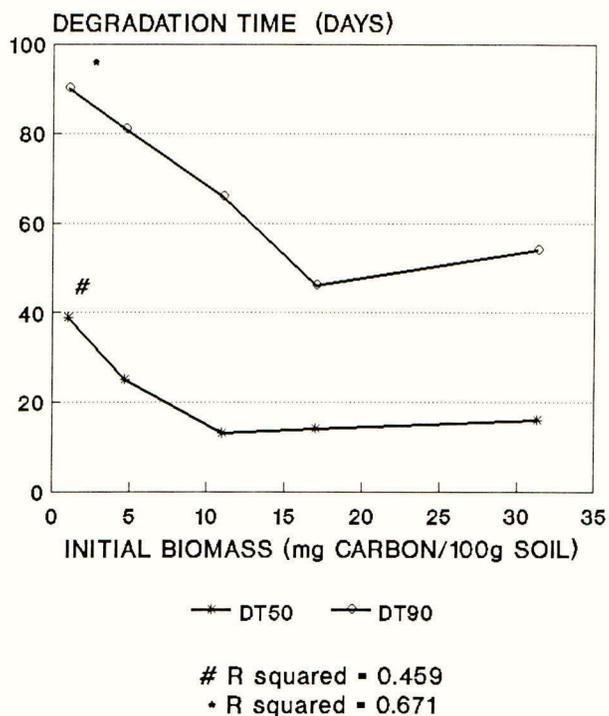


Figure 1. Relationship of DT50 and DT90 values with initial microbial biomass

TABLE 1. DT50 AND DT90 values for 5 soils using data from 3 months with 20°C, 40% CaCl₂ extractable samples

Soil	Microbial Biomass (mg Carbon/100g)	DT50 (Days)	DT90 (days)
Parabraunerde	4.7	25	82
Marcham	17.0	14	46
Castle Rising	31.3	16	54
2.1 Standard	<1.0	39	90
2.2 Standard	11.0	13	66

The rate of clopyralid degradation in all the soils was calculated as DT50 and DT90 values (disappearance time for 50% and 90% of the initial concentration) using the Timme-Frehse programme (Timme & Frehse, 1980; Timme *et al.*, 1986). The results obtained using the readily extractable data for the first 3 months showed that in all soils clopyralid has DT50 and DT90 values of less than 100 days (Table 1).

Figure one shows that the rate at which clopyralid degrades in soil can be roughly correlated to the microbial biomass of the soil. Marcham soil had a relatively high biomass value at the start of the study (17.0mg Carbon/100g) reflecting the rapid rate of clopyralid degradation while 2.1 standard soil had a biomass of <1mg Carbon/100g soil corresponding to a slow degradation rate. Castle rising soil had the highest microbial biomass of 31.3mg Carbon/100g soil but the rate of clopyralid degradation was not the fastest under these conditions. This would indicate that although microbial biomass is important for microbial degradation it is not the only factor affecting the rate of clopyralid degradation.

Effect of temperature on clopyralid degradation rate

To study the effect of temperature on the rate of clopyralid degradation the three agricultural soils were incubated at 10°C and 20°C for 6 months. Table 2 shows the DT50 and DT90 values at the two temperatures studied.

TABLE 2. DT50 AND DT90 values in days showing the effect of temperature on clopyralid degradation

Soil	20°C		10°C	
	DT50	DT90	DT50	DT90
Parabraunerde	25	82	177	>200
Marcham	14	46	69	>200
Castle Rising	16	54	66	>200

In all 3 soils the rate of degradation of the herbicide was found to be markedly slower at 10°C than at 20°C. As clopyralid degradation is microbial in nature (Swann & Unger, 1980) then increases in temperature would be expected to increase the rate of degradation until an optimum is reached dependent on the temperature optimum of the soil micro-organisms involved in the degradation process (Lynch, 1983).

Effect of soil moisture on clopyralid degradation rate

As well as the incubations set up at 40% MHC, additional incubations were set up where the soil moisture was set at 10% and 60% MHC. Table 3 compares the DT50 and DT90 values obtained with the 3 different moisture contents. At 10% MHC degradation and metabolism of clopyralid was not observed at all in any of the soils. There was no mineralisation and even the bound fraction was small. Close to 100% of the applied radioactivity could be readily extracted and on analysis was found to be clopyralid. This result suggests that at 10% MHC the soil is too dry to sustain the activity of the micro-organisms involved in clopyralid degradation (Paul & Clark, 1989).

TABLE 3. DT50 AND DT90 value in days showing effect of soil moisture on clopyralid degradation

Soil	40% MHC		10% MHC		60% MHC	
	DT50	DT90	DT50	DT90	DT50	DT90
Parabraunerde	25	82	>200	>200	24	79
Marcham	14	46	>200	>200	14	46
Castle Rising	16	54	>200	>200	1	15

For Parabraunerde and Marcham soils the DT50 and DT90 values obtained at 60% MHC were almost the same as at 40% MHC. However, with Castle Rising soil the DT50 value was dramatically reduced from 16 days (40% MHC) to 1 day (60% MHC). It would appear that at around 40% MHC and above, the moisture content of the Parabraunerde and Marcham soils is sufficient to ensure that clopyralid is available to the micro-organisms for degradation and that microbial activity is not limited by lack of water. It is likely that moisture could be increased in these two soils and rate of degradation will stay the same until the soil becomes flooded and oxygen becomes limiting (Paul & Clark, 1989).

In the case of Castle Rising soil it is likely that at 40% MHC the moisture content of the soil is too low to allow sufficient clopyralid to be available in solution for optimal microbial activity. This was confirmed by the soil moisture curve for Castle Rising soil which indicated that the moisture content of the soil at 40% MHC is close to the "wilting point" of the soil. Castle Rising soil has a high organic matter content, 27.6% compared to Marcham and Parabraunerde soils of 3.19% and 1.74% respectively. As such a much larger quantity of clopyralid is likely to be associated with the soil organic matter and more water is required to bring it into

solution so that it becomes available for microbial activity (Bartha et al., 1983). When DT50 and DT90 values from the 3 agricultural soils were plotted against initial microbial biomass the correlation obtained was very good ($R^2 = 0.999$, DT50 and 0.996 , DT90). This demonstrates that it is not just the microbial biomass of the soil which is important for optimum rate of degradation but also the availability of the compound. It would seem that at 40% MHC soil moisture was the limiting factor in Castle Rising soil and could explain why despite having the highest microbial biomass value the fastest rate of degradation was not observed in this soil at 40% MHC.

Effect of initial clopyralid concentration on clopyralid degradation rate

In addition to the field rate concentration (0.3mg/kg) incubations, two other concentrations, 0.05mg/kg and 1.0mg/kg were incubated with the 3 agricultural soils. The DT50 and DT90 values are shown in Table 4. In general the results show that the lower the initial clopyralid concentrations the lower the DT50 and DT90 values obtained. This suggests that, clopyralid residues disappear from the soil sooner at lower concentrations.

TABLE 4. DT50 AND DT90 values in days showing the effect of different initial clopyralid concentration on disappearance time from soil

Soil	0.3mg/kg		1mg/kg		0.05mg/kg	
	DT50	DT90	DT50	DT90	DT50	DT90
Parabraunerde	25	82	177	>200	13	42
Marcham	14	46	83	>200	9*	26*
Castle Rising	16	54	46	>200	17	57

* Data does not correlate to 95% significance

If the rate of mineralisation is considered in terms of disintegrations per minute (dpm)/day and this is plotted against time (Figure 2), it is observed that the amount of radioactivity released as $^{14}\text{CO}_2$ increases for the first few days at the about same rate for all three concentrations. After this, for the two lower concentrations of clopyralid, 0.05mg/kg and 0.3mg/kg, the expected decline curve is obtained. One possible explanation for this shape of curve is to consider that the first part of the curve is due to a "lag" phase during which time the microbial population responsible for clopyralid degradation is being established. This population is established at the time a normal decline curve is observed which is then just concentration dependent.

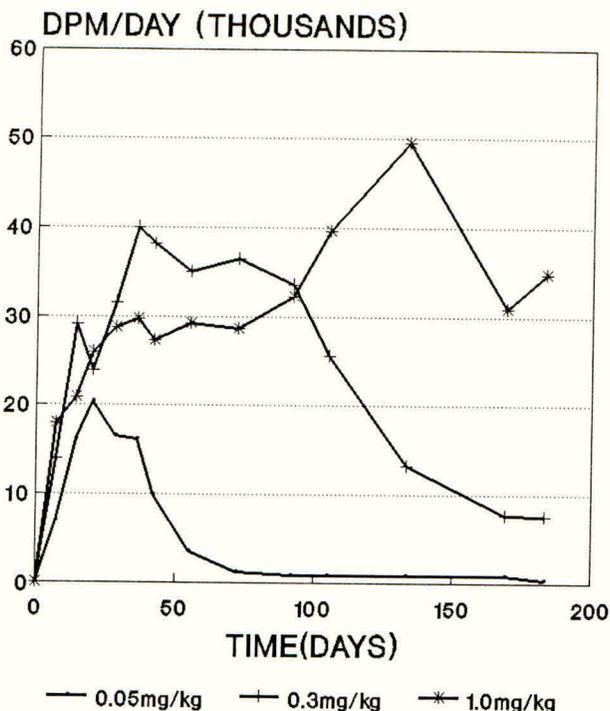


Figure 2. Effect of initial clopyralid concentration on the rate of degradation in parabraunerde soil

With 1mg/kg however it was observed that after the initial phase, which appears to be the same for all three concentrations, instead of the normal decline curve, a plateau is observed; after about 90 days the amount of $^{14}\text{CO}_2$ again starts to increase. This observation can possibly be explained by considering the presence of a second population. It can be envisaged that two different populations of micro-organisms are involved in degrading clopyralid. The first population establishes quickly (15-20 days) and is able to metabolise clopyralid to a certain concentration. The second population requires more time to establish and it is the combined effect of the two populations, the first which is declining in activity and the second which is establishing which causes the plateau effect with the 1mg/kg initial concentration curve.

CONCLUSION

Clopyralid is metabolised in soil to give only CO_2 as a metabolite. Providing the moisture content of the soil is not limiting, the degradation rate of clopyralid could be correlated to

initial microbial biomass of the soil. In general, the results show that soils with higher microbial biomass degraded clopyralid faster than those with lower microbial biomass.

Temperature and soil moisture both influenced rate of clopyralid degradation. Overall, higher temperature and higher moisture led to a more rapid degradation of clopyralid.

The lower the initial clopyralid concentration the lower the DT50 and DT90 values obtained. This suggests that residues disappear from the soil sooner at lower concentrations.

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FIELD PERSISTENCE OF ALACHLOR IN SOIL AND ITS RESIDUES IN MAIZE

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ABSTRACT

To assess the persistence of alachlor in soil and its potential residues in maize, three field experiments were carried out under typical Italian conditions. The alachlor persistence was studied for over 150 days at three different depths (0-10, 20-30 and 45-60 cm) while alachlor residues as metabolites DEA and HEEA, were also detected in grains, stovers, cobs and leaves of the maize plant. All analyses were done by **hplc** and **glc**. Alachlor residues in soil have shown a dependence on climatic and soil conditions with an apparent half-life of 8-22 days. Alachlor metabolites in plants were found mainly in the leaves but also in the stovers in one field. Grains and cobs were always free from alachlor and its metabolites DEA and HEEA.

INTRODUCTION

Alachlor movement in soils has received increased attention in Italy in recent years because of its potential effects on ground-water quality. Alachlor has been widely used in maize and soyabean crops, but since 1990, these uses have been restricted by Italian law. It has been completely banned on soyabean and can only be used at reduced doses on maize. Residues of alachlor have occasionally been found in ground water and several authors found positive samples in 9 wells of 1285 monitored (Funari *et al.*, 1989; Frascini *et al.*, 1990; Trevisan & Del Re, 1988; Camoni *et al.*, 1989; Vietti *et al.*, 1988). On the other hand considerable research has been carried out in other countries of the environmental behaviour of this herbicide and recently a complete review has been published (Chester *et al.*, 1989).

Leaching and microbial degradation are the most important factors influencing alachlor dissipation in the field. Leaching is affected by water solubility (240 mg/l) and adsorption; alachlor adsorption is moderate and an adsorption coefficient from 0.5 to 13 has been demonstrated for various soils and conditions (Chester *et al.*, 1989). Microbial degradation is the principal degradation pathway and it is affected by soil moisture and temperature (Walker and Brown, 1985). Volatilization is low but can be important in the presence of high soil moisture, under windy conditions or where there are cycles of drying and rewetting of the soil (Strek and Weber, 1982). However, the relative importance of these factors for alachlor persistence in the field depends on meteorological factors, soil properties, crop management (e.g., time of application and irrigation). Dissipation rates in the field have been reported to result in an average half-life of 4-24 days (Chester *et al.*, 1989).

In tolerant plants alachlor is detoxified by rapid conjugation with glutathione and mainly converted into two metabolites 2,6-diethylaniline (DEA) and 2-hydroxyethyl-6-ethylaniline (HEEA). The most important metabolites found in plants contain sulphur linkages in the 2-position; this indicates that one of the major detoxification pathways of alachlor is initial conjugation with glutathione, with further metabolic transformations (Leavitt & Penner, 1979). The formation of HEEA metabolites shows that alachlor is oxidised by substitution of one ethyl group with a phenyl ring. Recently Scarponi *et al.* (1990) have demonstrated that alachlor conjugation with glutathione and homogluthathione is the main detoxification pathway in the plant.

The aim of the present studies was to assess the persistence of alachlor in soil and its potential residues in maize under typical Italian conditions. The translocation of alachlor and some of its metabolites was examined in grains, leaves, stovers and cobs of maize.

METHODS

Field experimentation

The purpose of these trials was to study the persistence and uptake of alachlor by plants in different soils and climates. The fields were located in the north of Italy (Po Valley) where maize is the main spring/summer crop. Maize in an experimental field in Lardera farm (South Milano area - 45.07 N; 9.48 E), was in continuous culture for more than ten years. Maize in an experimental field in Cassinassa farm (North Milano area - 45.30 N; 9.22 E), was in rotation with barley, mixture of grasses, alfalfa and other cereals. Maize in an experimental field in Castel San Giorgio farm (Pavia area - 45.09 N; 8.42 E), was in rotation with soyabean and rice crops. The trial locations were selected to ensure different agronomic conditions as well as other characteristics (Table 1). Conventional agricultural practices were used in all fields (e.g., irrigation). After emergence of the maize crop the soil was tilled twice, to a depth of 10 cm, to incorporate the fertilizer and to help infiltration of irrigation water.

TABLE 1 Soil properties of the experimental fields*.

Farm/field depth (cm)	Sand (%)	Clay (%)	Silt (%)	Texture type	Organic matter (%)	pH	C.E.C. [‡] (meq/100g) [§]
<u>Lardera</u>							
0-20	20.5	18.5	61.0	Silt loam	2.9	5.9	17.5
30-50	14.0	24.4	61.6	Silt loam	1.4	6.2	13.4
<u>Cassinassa</u>							
0-20	44.0	11.4	44.6	Loam	2.0	6.0	10.3
30-50	44.5	13.8	41.7	Loam	1.5	6.2	9.3
<u>C. San Giorgio</u>							
0-20	46.5	11.1	42.5	Loam	1.7	5.1	9.7
30-50	43.7	10.0	46.3	Loam	1.1	5.7	9.1

*mean of three replicates

‡: C.E.C. = cationic exchange capacity; §: meq = milliequivalent

Each field was chosen for intrinsic homogeneity of soil properties and for ease of experimentation. The experimental plot, in each field, was the length of the field times the width of farm's tractor sprayer (9-10.2 m). The plot length was aligned along the direction of the tillage and irrigation. Each plot was divided into three sub-plots of about 10x20 m. The plots were treated in April/May 1988 with alachlor formulation (Lasso 48 % e.c.) at different doses and mixed with other herbicides as appropriate (Table 2). Herbicide was applied pre-emergence of the crop to the soil surface with a tractor mounted sprayer calibrated to give 400 L/ha of water. Daily values of air temperature and rainfall were recorded in each experimental field.

Sampling and analysis

Soil samples were taken at different times after herbicide application (Table 2) using a motor-driven core sampler. Five or seven cores per plot were taken from different depths: 0-10, 20-30 and 45-60 cm. In the laboratory soil samples were mixed, sieved through a 5 mm mesh

sieve and immediately frozen at -20°C until analysis. Moisture contents of the samples were determined before analysis.

TABLE 2. Field details.

		FARM		
		Lardera	Cassinassa	C. San Giorgio
Dose of AI	(kg/ha)	2.83	2.4	2.4
Date treatment		27/04	23/04	20/04
Date sowing		27/04	23/04	20/04
Hybrid		Luana	Crono	Lorena
Date soil sampling*	(days)	1; 8; 29; 71; 97; 194	1; 10; 23; 60; 161	1; 13; 33; 77; 97; 192
Date plant sampling*	(days)	154	154	199
Date harvest		28/09	24/09	14/11
Crop yield**	(t/ha)	14,2	9,1	13,7
Irrigation	(number of times)	2	2	3

*days from treatment

**t/ha yield at 15.5 % moisture (wt/wt)

Plant samples were collected at crop harvest when whole plants were removed from each plot. In the laboratory the plants were divided into leaves, stovers and cobs; each part was mixed and stored separately. Grain samples were also collected during mechanical harvest directly from the harvester. All samples were immediately frozen at -20°C until analysis.

Soil samples collected one month before treatment, were sieved at 2 mm after air-drying at room temperature, were characterized for physical and chemical properties following normal analytical methods (SISS, 1988; SSSA, 1962). Alachlor residues in soil were measured by gas chromatography following the Del Re extraction procedure (Del Re *et al.*, 1991); the residues of DEA, HEEA and alachlor in different plant parts were measured by liquid chromatography as reported by Fleschar (1989).

Gas chromatography

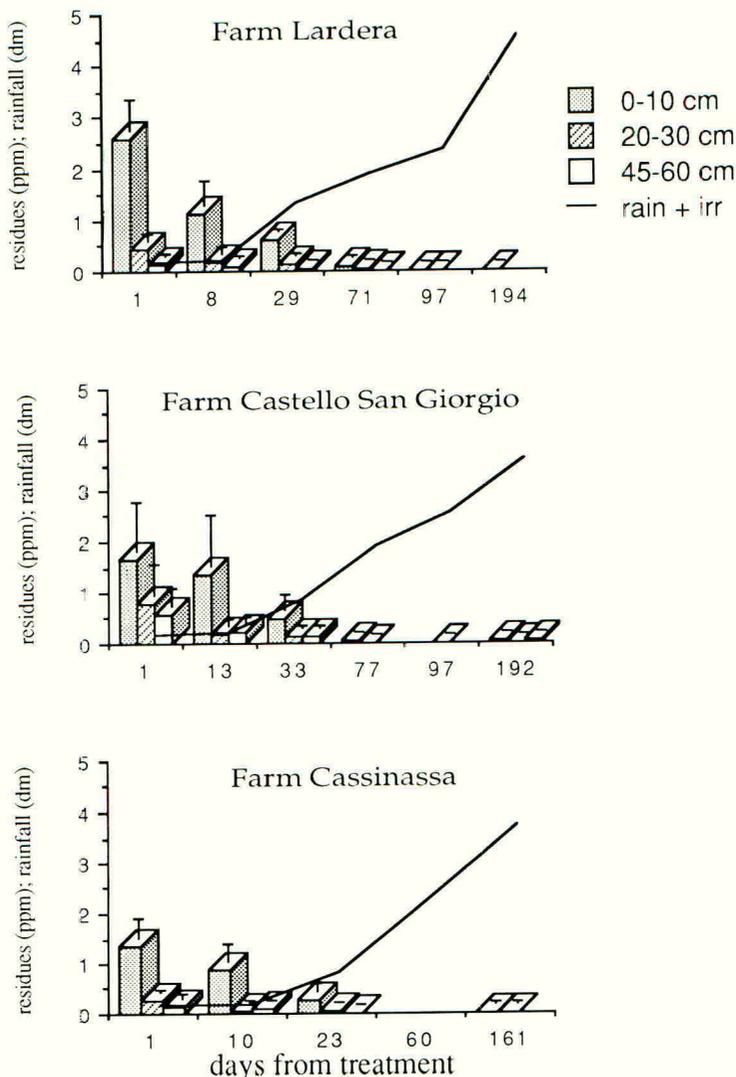
A Dani model 3800 gas chromatograph, equipped with NPD detector and a PTV injector, was used with an autosampler set to inject 2 μl . A Supelco (cat. N° 2-5322) Sup-Herb wide bore capillary column, 15 m x 0,53 mm ID 0.5 μm film, was used with the temperature programme of 60°C for 1 min, then to 280°C at $16^{\circ}\text{C}/\text{min}$ and hold for 2 min. The carrier gas was helium with a flow rate of 5 ml/min. Alachlor detection was carried out at different times for each trial: limits were 0.02 ng for Lardera, 0.013 ng for both Castello San Giorgio and Cassinassa farms; mean recovery determined by the extraction of un treated soil fortified at 50 and 200 $\mu\text{g}/\text{kg}$ was 95 %.

Liquid chromatography

This analytical method (Fleschar, 1989) determines residues of alachlor and its DEA and HEEA metabolites (Figure 2) in leaves, stovers, cobs and grain of maize crop samples. The HEEA yielding metabolites are converted to 2-(1-methoxyethyl)-6-ethylaniline (MEEA) for analysis. Samples are extracted with acetonitrile, filtered and evaporated. The residue is hydrolyzed with base and the resulting hydrolysis products are steam distilled into acid. The distillate is made basic and partitioned against methylene chloride to extract DEA and MEEA. Then the methylene chloride is extracted with an aqueous-methanolic-acid solution. Following

separation from the methylene chloride layer, additional methanol is added to the aqueous layer and allowed to stand for approximately 12 hours, during which all HEEA is converted to MEEA. After this conversion the pH of the aqueous-methanolic-HCl solution is adjusted between 5-7. The analytes are separated and quantitated by reverse phase HPLC with Oxidative Coulometric Electrochemical Detection (HPLC-OCED). Alachlor residues levels for each metabolite class are expressed as the equivalent amount of alachlor. HPLC-OCED operating conditions are reported in table 3. The quantification limit was 1.51 $\mu\text{g}/\text{kg}$ as alachlor equivalent.

Figure 1. Alachlor dissipation following the application in the field. The residues shown are means of three replicates and the bars are the standard deviations. Cumulative rainfall for all sampling times includes irrigations (assume to be 30 mm each).

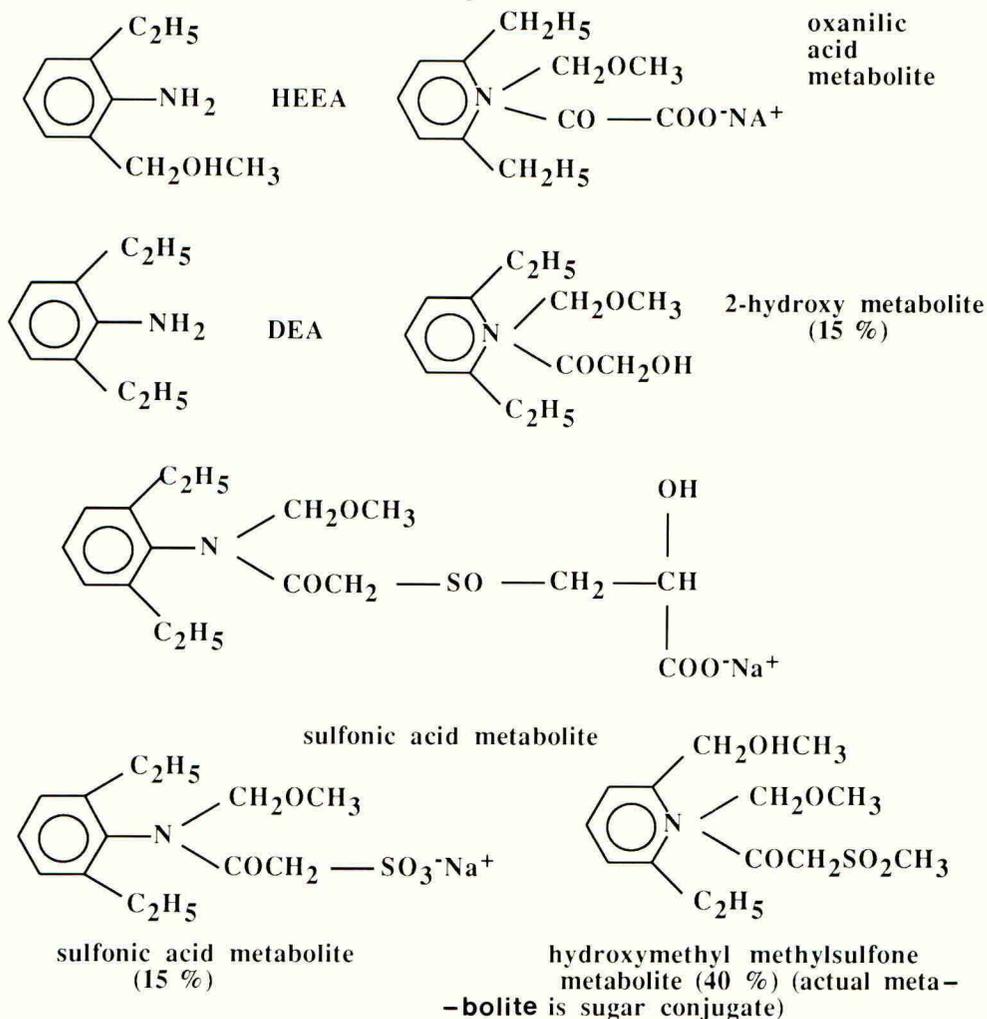


RESULTS AND DISCUSSION

Persistence and mobility of residues in soil

After application alachlor residues were detected down to 45 cm but the higher concentration was always located in the upper layer in all experiments. It is possible that some contamination of the deeper soil occurred during the first sampling. However, there is evidence that the mobility downwards was greater in the sandy Cassinassa soil and C. San Giorgio than in the loamy soil from Lardera. In the top layer the residues (Table 4) were greatest at Lardera (2.57 ppm) as influenced by the higher application rate and adsorption capacity of the soil (C.E.C. 17.3 in the top layer) (Table 1).

Figure 2. Main metabolite of alachlor in soil, plants and water.



Patterns of loss in the different fields can be broadly correlated with weather conditions: the rainfall in the first month was relatively high, in particular during the first 10 days (60-100

mm). In fact the most consistent loss was restricted to this time. Following the initial losses, persistence was similar in all fields and after 160 days from treatment residues were still detectable [0.57 ± 0.02 % (11 ppb) in the top layer of Lardera farm; 1.23 ± 0.86 % and 0.87 ± 0.76 % (18 and 13 ppb) for 0-30 cm and 20-30 cm respectively in Cassinassa farm; 1.47 ± 0.33 , 1.03 ± 0.13 and 2.68 ± 1.0 % (22, 16 and 40 ppb) respectively at 0-10, 20-30 and 45-60 cm in Castel San Giorgio farm (Figure 1)].

TABLE 3. HPLC-OCED operating conditions.

Flow rate	1.0 ml/min		
Mobile phase	50% acetate buffer, about 4.8 pH/50% methanol (V/V)		
Column	Lichrospher 100 RP-8 Merck (125x4 mm i.d., 5 μ m)		
Temperature	ambient		
Detection operate	screen mode with	+0.85 volts guard cell potential	+0.50 volts detector 1 potential
			+0.75 volts detector 2 potential
Gain	2000		
Sample size	50 μ L		

Dissipation rate in soil

The rate of alachlor dissipation from soil in two fields was assessed on the assumption that first-order reaction kinetics would apply. Apparent first-order rate constants (Table 4) were derived from the slopes of the lines of best fit calculated by linear regression analysis of the logarithm of residue concentrations. The data after 100 days were excluded from the calculations because residue levels were very low and variable. All linear regression gave good fits with correlation coefficients between 0.86 and 0.97.

In each site dissipation rate was slow in the deepest layer, but the deepest layer did not always give a rate constant different from the 20-30 cm layer. Alachlor dissipation rate was not very different between fields, the soil with more fine texture the higher dissipation rate and the general order was Cassinassa > C. San Giorgio > Lardera (Table 4).

TABLE 4. Different first order degradation rate constants (K), dissipation time (DT) and statistical test of the correlation coefficients (R) and of regression slope (t), for alachlor residues in soil. DT is calculated from the apparent first order constant divided by 0.693.

Farm/field	Depth (cm)	K (day ⁻¹)	DT (days)	R	t	p#
Lardera	0-10	0.0515	13.5	0.97	- 7.8	****
	20-30	0.364	19.0	0.94	- 11.8	****
	45-60	0.389	17.8	0.94	- 6.5	****
Cassinassa	0-10	0.0843	8.2	0.98	- 4.7	****
	20-30	0.0449	15.4	0.87	- 3.2	***
	45-60	0.0308	22.8	0.86	- 3.7	***
C. San Giorgio	0-10	0.0523	13.3	0.97	- 5.5	****
	20-30	0.0326	21.3	0.87	- 4.0	***
	45-60	0.0323	21.5	0.90	- 3.3	**

the test for significance at $p < 0.001$, < 0.01 and < 0.05 is expressed by the symbol ****, *** and ** respectively.

Residues in plant

Nadeau (1982) reported that alachlor uptake by maize plants was 3.9 % of the total amount soil applied; 3.49, 0.09, 0.49 and 0.03 % was found in foliage, grain, stovers and cobs respectively. Alachlor was degraded by nucleophile attack at the carbon-chlorine bond, and the intermediate metabolites were conjugated by sugars. Further modification of some of these metabolites by hydroxylation at the benzyl position was observed.

Lauer (1982) reported alachlor residues in maize forage in range of 0.11 to 0.30 ppm after 4.4 kg/ha of alachlor AI applied; in maize stovers alachlor residues were 0.05-0.27 ppm.

Arras and Graham (1984) have reported HEEA residues in maize forage and grain of 0.05 ppm at 4.4 kg/ha rate applied on soil; in maize stover residues were 0.14 ppm. DEA residues in maize grain were <0.03 ppm in maize forage 0.06 ppm and in maize stover 0.11 ppm.

In accordance with the cited literature, in this experiment residues of alachlor were found in leaves at levels of 16-54 ppb. Residues of HEEA and DEA were detected in leaves from all fields. HEEA residue levels were always 3-4 times higher than other metabolites; this suggests hydroxylation as the main metabolic pathway of alachlor in the maize plant. In maize stovers from Lardera we have found unexplained quantities of DEA. As the standard deviation is greater than the mean we have to be careful about this value. Cobs and grains were always free from alachlor metabolite residues (Table 5).

TABLE 5. Residues of alachlor expressed as metabolites and alachlor parent total (see text). The values of Lardera and Cassinassa are means \pm standard deviation of the variable.

Farm/field	sample	MEEA (ppb)	DEA (ppb)	alachlor (ppb)
<u>Lardera</u>	leaves	41.2 \pm 28.5	12.6 \pm 10.0	53.8 \pm 37.1
	stovers	1.1 \pm 2.0	3.0 \pm 3.3	4.2 \pm 3.6
	cobs	NQ	NQ	NQ
	grains	NQ	NQ	NQ
<u>Cassinassa</u>	leaves	12.2 \pm 11.9	3.9 \pm 2.1	16.1 \pm 14.0
	stovers	NQ	NQ	NQ
	cobs	NQ	NQ	NQ
	grains	NQ	NQ	NQ
<u>C. San Giorgio</u>	leaves	22.6	4.9	27.5
	stovers	NQ	NQ	NQ
	cobs	NQ	NQ	NQ
	grains	NQ	NQ	NQ

NQ = under the quantification limit of 1.51 ppb.

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INVESTIGATIONS INTO THE FATE OF BENFURESATE IN RICE AND SOIL

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ABSTRACT

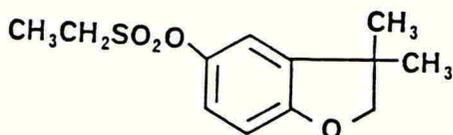
The fate of benfuresate in 2 soil types and 2 rice varieties was investigated. [^{14}C]-Radio-labelled benfuresate was used in a series of glasshouse and laboratory studies.

The half-life of benfuresate in both soil types was less than 3 weeks. After 1 year 55% to 60% of activity had been mineralised to $^{14}\text{CO}_2$ and less than 5% was available to solvent extraction.

Benfuresate was rapidly metabolised in rice. The majority of extractable radioactivity in mature plants was in the form of conjugates. The residue in mature grain was less than 0.3mg/kg of which 9% was identified as parent compound.

INTRODUCTION

Benfuresate (2,3-dihydro-3,3-dimethyl-5-benzofuranylethanesulphonate) (1) is a selective herbicide with activity against a broad spectrum of weeds. It is presently marketed as a pre-planting incorporated herbicide for cotton. It is also an effective post-emergent herbicide in rice, and is especially effective in the control of *Echinochloa oryzicola* and *Eleocharis kuroguwai*, both serious weeds of rice in Eastern Asia.



1

Rice paddies are flooded one to two weeks prior to transplantation of seedlings. Flooding gives rise to reducing conditions necessary for rice growth (Rowell 1988). A mean water depth of 5-7.5cm is typical.

Benfuresate is applied to the rice crop a minimum of 5 days after transplantation. It is applied in the form of 2% granules at a rate of 0.6kg AI/ha (1.2mg/l assuming 5cm depth of water). The paddy is not drained for a minimum of 3 days after benfuresate application.

As part of a programme of work designed to investigate the fate of the compound in the environment, studies into the fate of benfuresate in rice and in soil have been conducted. This work has been focused on quantifying and characterising residues and determining the metabolic pathways involved in benfuresate degradation.

MATERIALS AND METHODS

Degradation in soil

Two soils, a sandy loam and a silty clay loam, were collected from field sites which have been kept free of pesticides for a minimum of 5 years. The soils were air dried and sieved (2mm mesh). Aliquots (100g dry weight equivalents) of each soil were dispensed into 250ml Erlenmeyer flasks and water was added to increase the soil moisture content to 50% water holding capacity. This moisture content was maintained throughout the study.

Twenty six flasks of each soil type were treated with 0.442mg [^{14}C]-benfuresate (11.7 $\mu\text{Ci}/\text{mg}$) (1 μCi = 37kBq) uniformly labelled in the benzene ring, in 100 μl benzene/acetone (1:3). The application was equivalent to 1kg AI/ha. The flasks were shaken to incorporate the herbicide into the soil.

Samples were incubated in the dark at $20^\circ\text{C} \pm 2^\circ\text{C}$. A gentle stream ($\leq 10\text{ml}/\text{min}$) of moist CO_2 free air was passed over the soil surface and bubbled through a sequence of solutions (ethanediol, 0.1M sulphuric acid and ethanolamine) to trap evolved degradation products including $^{14}\text{CO}_2$. The trapping solutions were changed regularly. After 42 days no activity had been detected in either the ethanediol or the sulphuric acid traps so they were removed and a second set of ethanolamine traps were added.

Duplicate soil samples were collected for analysis at various time points up to one year after treatment. Samples were Soxhlet extracted with dichloromethane followed by acetonitrile/water (4:1) for 18 hours each. The activity in each extract was gauged by liquid scintillation counting (LSC) in triplicate. Soil bound residues were assessed by combustion of dried and finely ground soil with D-glucose (added as an aid to combustion) in a Packard 306 or 307 sample oxidiser. The released $^{14}\text{CO}_2$ was collected into 'Carbosorb' (Canberra-Packard Instruments Ltd), mixed with scintillant and quantified by LSC.

To characterise the activity in the ethanolamine trapping solutions 4M HCl was added to the ethanolamine, releasing trapped volatiles which were collected in 1M NaOH. 1M BaCl_2 was added in excess and the product was centrifuged. Activity remaining in the supernatant was determined by LSC. Trapped $^{14}\text{CO}_2$ forms a precipitate ($\text{Ba}^{14}\text{CO}_3$) which is lost from the solution.

The activity in extracts was characterised by hplc and tlc. Reference standards of possible degradation products were included in all

chromatographic systems to aid identification. Radio-gas chromatography-mass spectrometry was used to confirm the identity of major products.

Metabolism in rice

Two rice varieties, Sasanishiki and Kohishikari, were grown in flooded soil (sandy loam) in 5 litre beakers. Each beaker was treated with 2.84mg (equivalent to 1kg AI/ha) [^{14}C]-benfuresate (10.2 $\mu\text{Ci}/\text{mg}$). The treatment was applied 15 days after transplantation to rice which was then grown to maturity, and 45 days after transplantation to rice which was harvested before reaching maturity. The rice was grown under glasshouse conditions.

Rice was harvested by excision at the soil surface, either as immature plants (59 days after transplantation), or at maturity (112 days after transplantation). The immature rice was separated into lower stem (15-20cm) and upper foliage. The mature rice was separated into lower stem, upper foliage and mature grain.

A total [^{14}C]-residue for each tissue type was determined by combustion of a sample after milling in dry ice. Duplicate samples of each tissue type were extracted by blending with acetonitrile followed by acetonitrile/water (3:1). The activity of each sample was quantified by LSC and the fibre bound residue was determined by combustion.

The activity in extracts was characterised by hplc and tlc. Those extracts which were found to contain very polar metabolites were hydrolysed at 100°C in 2M HCl to cleave conjugates. The hydrolysed samples were back extracted with diethylether and the products of hydrolysis were characterised by hplc and tlc.

Fibre bound residue was extracted by heating the fibre at reflux overnight with 1M NaOH (foliage) and 2M NaOH (mature grain). After filtration the solution was acid hydrolysed with 2M HCl before being back extracted with diethylether. Radioactivity was characterised by hplc and tlc.

RESULTS AND DISCUSSION

Degradation in soil

Benfuresate was readily degraded in both soil types with DT_{50} values (time for disappearance for 50% of the compound) of 18 days (sandy loam) and 20 days (silty clay loam). All radioactivity trapped by ethanolamine was identified as $^{14}\text{CO}_2$. Degradation proceeded via mineralisation of the radio-labelled carbon to carbon dioxide. By the end of the study 55-60% of the radio-label had been evolved as carbon dioxide, 33-36% of the activity was bound to the soil and less than 5% of the residue could be extracted (Figure 1 and 2).

Benfuresate was the major species in all the extracts. One minor degradation product (<3%) was observed which did not accumulate. Very small quantities (<0.5%) of other transient products were also observed.

Figure 1 The distribution of radioactivity in a silty clay loam after treatment with [^{14}C]-benfuresate

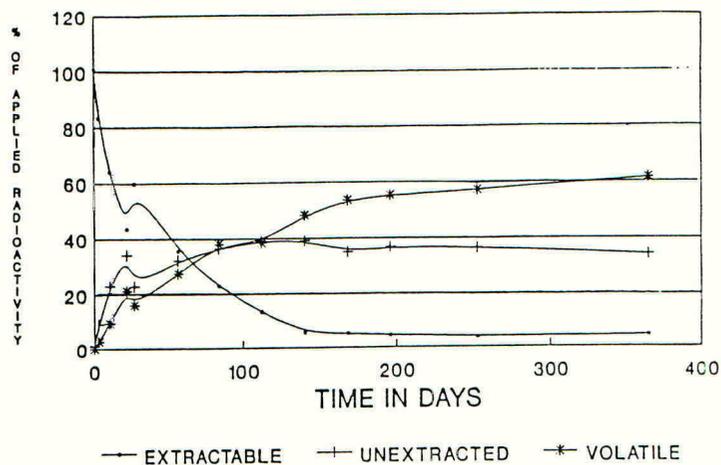
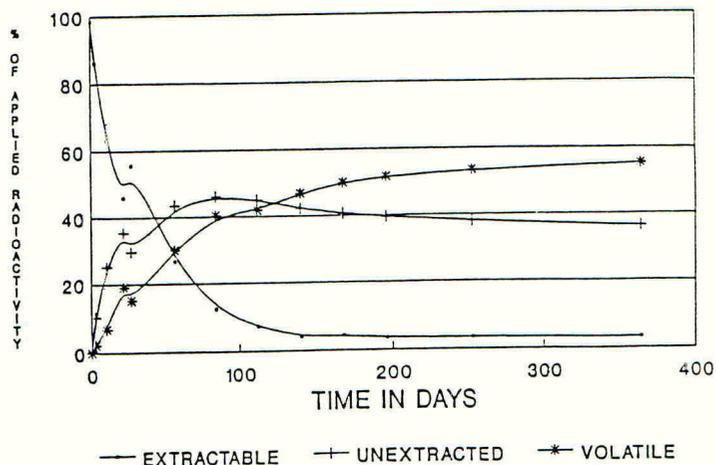


Figure 2 The distribution of radioactivity in a sandy loam after treatment with [^{14}C]-benfuresate.



Metabolism in rice

Residue levels above 10mg/kg were not detected in any of the treated rice tissues (Table 1). Field conditions would be expected to generate considerably lower residues. The maximum residues were found in immature top growth and these levels dropped as the plants matured. Mature grain, of the Sasanishiki variety, exhibited the lowest residues (<0.3mg/kg). The amount of mature grain produced by the Kohishikari variety was too small to allow analysis.

Table 1 Summary of activity in harvested tissues and the distribution after solvent extraction

TISSUE	TOTAL RESIDUE (mg/kg)	SOLVENT EXTRACT % total residue	FIBRE BOUND RESIDUE % total residue
Immature top foliage (S)	9.48	69	31
Immature bottom foliage (S)	2.10	NA	NA
Mature top (S) growth	7.09	59	41
(K)	6.30	61	39
Mature grain (S)	0.27	34	66

K = Kohishikari S = Sasanishiki NA = Not analysed

Benfuresate was rapidly metabolised in rice. Approximately 10% of total residue was characterised as benfuresate in the immature top growth (Table 2) and this decline to less than 5% in the mature top growth. The mature grain had very low residue levels.

Table 2 The distribution of activity in solvent extracts

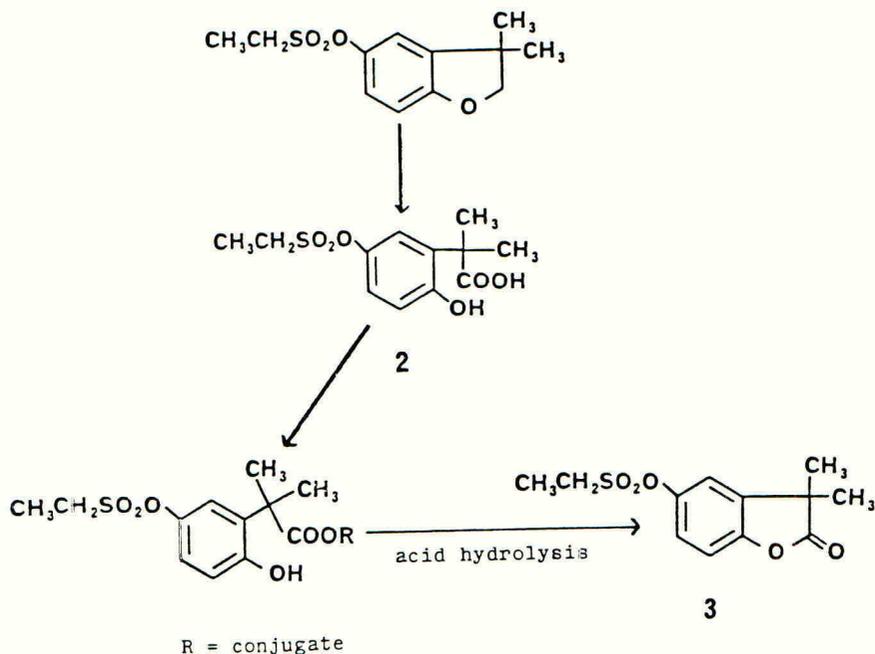
TISSUE	BENFURESATE (%)	RING OPEN NC 20696 (%)	CONJUGATES (%)
Immature top foliage (S)	20	51	29
Mature top foliage (S)	8	ND	92
Mature top foliage (K)	2	ND	98
Mature grain (S)	26	ND	74

K = Kohishikari S = Sasanishiki ND = Not detected

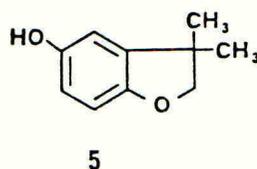
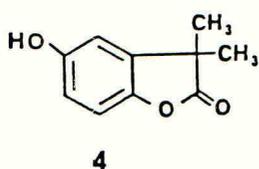
The major component of the residue in immature rice was 2-(5-ethylsulphoxy-2-hydroxyphenyl)-2-methylpropionic acid (ring open NC 20696) (**2**) (Table 2). In mature tissues no ring open NC 20696 was detected and the majority of activity was characterised as polar conjugates. On acid hydrolysis the conjugates were cleaved and the low pH caused ring closure to form 2,3-dihydro-3,3-dimethyl-2-oxobenfuran-5-yl (NC 20696) (**3**). The postulated route of metabolism is given in Figure 3.

Between 85% and 95% of the fibre bound radioactivity in both foliage and grain was liberated into base. Analysis of the extracts identified 5-hydroxy-3,3-dimethyl benzofuran-2(3H)-one (4) and 2,3-dihydro-3,3-dimethyl benzofuran-5-ol (5). The loss of the ethsulphonate group from both of these compounds may be a result of base hydrolysis.

Figure 3 The proposed route of degradation for benfuresate in rice



Products released from fibre



CONCLUSION

Benfuresate is readily degraded in soil to soil bound residues and CO_2 . The compound is readily metabolised in rice, via cleavage of the furan ring, to conjugates and to fibre bound residues.

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DEGRADATION BEHAVIOUR OF TRIASULFURON IN THE SOIL. RESULTS OF REPLANTING STUDIES AND BIOASSAYS.

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ABSTRACT

A total of 307 trials were carried out in the U.K. between the 1985/6 and 1989/90 seasons to examine the degradation of triasulfuron in the soil. All of these trials have involved the planting of a broad-leaved crop after a cereal crop treated with triasulfuron at up to 5 times the recommended rate.

The potential of triasulfuron applications to affect sensitive following crops is compared with applications of other sulfonyl urea herbicides. The effect of triasulfuron application timing and of the cultivation type prior to establishment of the following crop is discussed and recommendations are made which allow the safe use of triasulfuron in a commercial rotation.

INTRODUCTION

Triasulfuron is a sulfonyl urea herbicide under development for the control of broad-leaved weeds in cereal crops. Although the use rate of triasulfuron is extremely low (7.5 gAI/ha) it was realised early in the development of this herbicide that the extreme sensitivity of certain broad-leaved crops such as sugarbeet and oilseed rape to this group of chemistry meant that extensive investigations into the soil behaviour of triasulfuron under a wide range of environmental conditions would be required to ensure the safe use of the compound.

Rotational studies have therefore been carried out with triasulfuron in the U.K. since the 1985/86 season. These have included assessing trial sites treated with triasulfuron which have been subsequently planted with broad-leaved crops as part of a normal commercial rotation. Specifically sown trials where short recropping intervals and differing cultivation techniques were examined have also been carried out.

One of the main factors influencing the persistence of sulfonyl urea herbicides is the potential for leaching into areas of the soil profile where low biological activity reduces the rate of degradation (Nicholls *et al.*, 1987). Studies to determine the fate of triasulfuron in the soil have been carried out by taking soil samples at intervals after application and using the bioassay technique developed by Iwanzik *et al.* (1988) in conjunction with chemical analysis to locate and quantify any triasulfuron residues.

This paper presents a summary of five years data taken from trials carried out across the U.K. where triasulfuron application has been followed by the planting of a broad-leaved crop as well as results from bioassays carried out on two different soil types in East Anglia. Data is presented which compares triasulfuron with the herbicides

chlorsulfuron and metsulfuron-methyl and which examines the effect of cultivation type on triasulfuron residues.

MATERIALS AND METHODS

Field trials were carried out in either commercial crops or on experimental farms at Whittlesford, Cambridgeshire or Elmdon, Essex. There was some variation in the trials design over the five years of testing but most trials were of a randomised complete block design with three or four replicates. However due to the inherent difficulties of soil residue trials it was felt that experience of triasulfuron application across a large number of sites, where a wide range of soil and environmental conditions would be encountered, was required before firm recommendations could be made. For this reason some trials were of single replicate design which could be carried out at a large number of sites. At these sites up to 12 test compounds (not all reported here) were applied to large plots in a layout including several untreated plots. The site was carefully marked to ensure correct location after sowing of the following crop, which was drilled across the plots. Careful seedbed preparation was carried out to ensure an even crop stand and at sites located on the experimental farms irrigation was used in very dry conditions. Visual evaluations of % phytotoxicity were made in comparison to untreated plots on at least 5 occasions after the sowing of the following crop in all trials. Where phytotoxicity occurred it was either as a purple discolouration and/or in the more severe cases, reduced biomass (either as a loss of plants or stunting). Treatment layout was not known by the trials officer when the evaluations were being carried out. Plot sizes were normally 3 x 12 m or 3 x 8 m except for the single replicate trials where plot size was 3 x 40m or 6 x 24m.

All applications were made using a precision plot sprayer fitted with Lurmark 02-F110 nozzles and calibrated to deliver 200 l/ha at a pressure of 207 kPa and a forward speed of 1 ms⁻¹. Applications were made pre- or post-emergence to winter or spring wheat or barley or to bare soil where short recropping intervals were used.

The results presented are taken from a database of 307 trials carried out between the 1985/86 and 1989/90 seasons where treatments were applied in the spring (post January 1st). The trials were carried out in many areas of the U.K. and across a wide range of soil types and conditions. The results are presented as the maximum level of phytotoxicity observed but in most cases good recovery took place before harvest. It has been suggested that yield loss may occur in the absence of foliar symptoms but work carried out by Upstone (1991) has demonstrated that yield loss due to sulfonyl urea residues will only occur when foliar symptoms are observed.

In the results tables the cultivation descriptions minimal (M) and ploughing (P) are used. The equipment and methods used by farmers at the trial sites varied considerably. However in all cases minimal cultivation refers to a tillage method where the soil was mixed to a depth of less than 10cm and where ploughing was used the soil was turned through approximately 120° to a depth of 25 - 30cm.

The soil bioassay was carried out according to the technique described by Iwanzik *et al.* (1988) on 10cm diameter soil cores which were taken to a depth of 75cm using a Humax earth borer. 15 gAl/ha of triasulfuron was applied on 21st February 1989 at two sites. Samples were taken at intervals after application and were split into 0-12cm, 12-25cm, 25-50cm and 50-75cm horizons. The test species *Nasturtium officinale* was grown in

samples from these horizons and the amount of growth was then assessed visually against plants grown in previously untreated soil infused with known concentrations of triasulfuron. The limit of detection for this method is 0.1 - 0.5 gAI/ha and results have been shown to be consistent with chemical analysis (Iwanzik and Egli, 1989).

RESULTS AND DISCUSSION

Comparison with other sulfonyl urea herbicides

Trials where triasulfuron was compared to chlorsulfuron or metsulfuron-methyl are presented in tables 1 and 2 where the following crops were sugarbeet and winter oilseed rape respectively. From these results it can clearly be seen that on a rate for rate basis triasulfuron presents much less hazard to subsequent crops of sugarbeet and oilseed rape than chlorsulfuron. The use rate of triasulfuron (7.5 gAI/ha) is lower than the use rates of chlorsulfuron implicated in residue damage and therefore an even greater safety margin is evident. At most sites where triasulfuron was compared to metsulfuron-methyl there was no visual phytotoxicity (35 of 39 sites), even at double rates. Where damage did occur minimal cultivations were used and double rates of either triasulfuron or metsulfuron-methyl caused similar levels of phytotoxicity. Ploughing however makes a considerable difference to the potential persistence of triasulfuron. Tables 3 and 4 show the results of trials carried out during 1986, 1988 and 1989 to specifically examine the effect of cultivation type on the potential for triasulfuron damage to subsequent sugarbeet and oilseed rape respectively. Only sites where damage occurred have been included. The results clearly show that where minimal cultivations were used there was a risk of residue damage from double rate or above applications of triasulfuron. Where ploughing was used however, rates of up to 40 gAI/ha (>5 times (n) the efficacy rate) caused no residue damage in both sugarbeet and oilseed rape, even with the artificially short interval between application and recropping of three months for oilseed rape and ten months for sugarbeet.

Table 1. Potential of triasulfuron to damage subsequent sugarbeet compared with chlorsulfuron and metsulfuron-methyl

Cultivation Type	Months after Soil applic to Type sowing	triasulfuron		chlorsulfuron		metsulfuron-methyl	
		gAI/ha	% visual phytotoxicity	gAI/ha	% visual phytotoxicity	gAI/ha	% visual phytotoxicity
minimal	ZL 11	15	20			12	18
minimal	SL 11	15	8			12	10
minimal	SCL 11	30	0	30	30		
minimal	CL 11	30	0	30	90		
minimal	CL 12	30	0	30	90		
plough	CL 11	30	0	30	10		
minimal	SL 13	30	0	30	30		
plough	CL 14	30	0	30	15		
minimal	CL 14	40	15	30	30		
minimal	CL 14	40	15	30	60		

42 other trials produced no visual symptoms. 16 metsulfuron-methyl, 26 chlorsulfuron.

Table 2. Potential of triasulfuron to damage subsequent oilseed rape compared with chlorsulfuron and metsulfuron-methyl

Cultivation Type	Soil Type	Months after sowing	triasulfuron		chlorsulfuron		metsulfuron-methyl	
			gAl/ha	% visual phytotoxicity	gAl/ha	% visual phytotoxicity	gAl/ha	% visual phytotoxicity
minimal	CL	2	15	37			12	40
minimal	CL	3	15	0	30	80		
minimal	SL	3	15	15	30	40		
plough	CL	3	15	0	30	80		
plough	SL	3	20	0	30	30		
minimal	ZCL	4	15	25			12	35
minimal	SL	5	40	0	30	10		
minimal	CL	5	40	0	30	60		
minimal	SL	6	20	0	30	30		
plough	SL	6	30	0	30	10		
minimal	SL	8	40	0	30	10		
minimal	CL	8	40	0	30	30		
plough	SL	8	40	0	30	10		
plough	CL	8	40	0	30	20		
minimal	CL	10	40	0	30	50		
minimal	SL	10	40	0	30	10		
plough	CL	10	40	0	30	50		
plough	SL	10	40	0	30	15		

48 other trials produced no visual symptoms. 19 metsulfuron-methyl, 29 chlorsulfuron.

Table 3. Comparison of the effects of minimal cultivation (M) and ploughing (P) on the potential of triasulfuron to damage subsequent sugarbeet.

Rate gAl/ha	Applic. date	Re-crop date	Interval (months)	Location	Soil type	pH	Organic matter (%)	Cumulative rainfall (mm)	% visual phytotox. Cultivation	
									M	P
40	24/4/86	30/4/87	12	Whittlesford	SL	8.2	2.0	607	20	0
20	12/6/86	30/4/87	10	Whittlesford	SL	8.2	2.0	521	10	0
15	12/6/86	30/4/87	10	Elmdon	CL	8.0	3.2	521	15	0
40	25/2/87	13/4/88	14	Elmdon	CL	8.0	3.2	829	10	0
30	1/5/87	13/4/88	11	Elmdon	CL	8.0	3.2	724	10	0

Table 4. Comparison of the effects of minimal cultivation (M) and ploughing (P) on the potential of triasulfuron to damage subsequent oilseed rape.

Rate gAl/ha	Applic. date	Re-crop date	Interval (months)	Location	Soil type	pH	Organic matter (%)	Cumul- ative rainfall (mm)	% visual phytotox. Cultivation	
									M	P
30	25/2/87	6/8/87	6	Whittlesford	SL	8.2	2.0	421	10	0
30	1/5/87	6/8/87	3	Whittlesford	SL	8.2	2.0	316	15	0
15	9/5/86	18/8/86	3	Elmdon	CL	8.5	2.7	243	15	0
15	24/4/86	19/8/86	4	Elmdon	CL	8.0	3.2	307	10	0
20	24/4/86	19/8/89	4	Whittlesford	SL	8.2	2.0	307	17	0
40	28/4/88	1/8/88	3	Whittlesford	SL	7.9	2.0	175	20	0
15	28/4/88	1/8/88	3	Elmdon	CL	8.0	3.2	175	20	0

Use rate and recropping interval

The rate of triasulfuron used and the recropping interval also have an impact on the potential for damage from residues to occur and in this respect does not differ from other residual herbicides. Table 5 shows that when following crops of sugarbeet or oilseed rape are sown after ploughing at least 40 gAl/ha triasulfuron is required to cause damage from a January or February application, at least 30 gAl/ha is required from a March or May application and from a June application at least 20 gAl/ha is required. A safety margin of at least 2n is seen from June applications of the recommended rate (7.5 gAl/ha) and as June application of triasulfuron in a commercial situation is extremely unlikely due to a GS33 (Tottman and Makepeace, 1979) label restriction, a more realistic safety margin of at least 3n is seen from March and May applications rising to at least 4n when applied in January or February.

Soil type and pH influence on potential soil residues

The trials were carried out across a wide range of soil types, including soils with high organic matter content, and a pH range of 6.8 to 8.6. No relationship with soil type or pH and soil residues was observed, although previous work (Nicholls *et al.*, 1987) has indicated that damage to subsequent sensitive crops on soil types such as alluvial gleys, where the pH is high, may be more severe. Work presented by Ryan *et al.* (1991) where triasulfuron was applied to such soils has however demonstrated that even on these soils the rate of triasulfuron degradation was rapid and that leaching was low.

Other broadleaved crops

Trials where beans, peas, linseed or potatoes were planted as following crops where triasulfuron had been used in the previous cereal crop (table 6) demonstrate that high rates of triasulfuron do not cause damage in these crops even with minimal cultivations.

Table 5. Summary of triasulfuron trials (spring applications)

Results expressed as the number of occasions the dosage indicated caused visual phytotoxicity in the following crop. Figures in parenthesis indicate the number of occasions tested.

Application period Cultivation method Crop	gAl/ha	Number of trials where visual phytotoxicity occurred (occasions tested)					
		Jan/Feb		Mar/May		June	
		P	M	P	M	P	M
Oilseed Rape (Autumn sown)	>40	5 (5)	4 (4)	3 (3)	3 (3)		
	40	1 (6)	0 (4)	3 (10)	2 (13)		
	30	0 (2)	1 (4)	4 (15)	3 (21)		
	20	0 (3)	0 (3)	0 (7)	1 (10)		
	15	0 (2)	0 (2)	0 (13)	6 (21)		
	10	0 (3)	0 (3)	0 (6)	3 (15)		
Sugarbeet (Spring sown)	>40	2 (2)	1 (1)	5 (5)	1 (1)	1 (1)	
	40	0 (2)	0 (2)	1 (6)	1 (6)	0 (3)	0 (3)
	30	0 (2)	0 (2)	2 (5)	1 (6)	1 (3)	1 (3)
	20	0 (2)	0 (2)	0 (8)	2 (5)	1 (3)	0 (3)
	15	0 (2)	0 (2)	0 (8)	0 (6)	0 (3)	1 (3)
	10	0 (2)	1 (2)	0 (8)	1 (5)	0 (3)	1 (3)

Table 6. Summary of sites where a triasulfuron application has been followed by the planting of a broad-leaved crop other than sugarbeet or oilseed rape

Crop	Number of sites	Rate (gAl/ha)	Cultivation Type	Maximum Visual Phytotoxicity (%)
Beans	3	33 - 120	Ploughed	0
Beans	1	40	Minimal	0
Peas	7	20 - 120	Ploughed	0
Peas	3	40	Minimal	0
Potatoes	6	20 - 40	Ploughed	0
Potatoes	5	20 - 40	Minimal	0
Linseed	3	20 - 40	Minimal	0

Bioassays

Results from the bioassays carried out are presented in figures 1 and 2. These showed a rapid rate of triasulfuron degradation and virtually no detectable leaching. These results support those from the re-cropping trials and those presented by Ryan *et al.* (1991) in showing that triasulfuron degrades rapidly in the soil, with the majority of any remaining residue staying in the upper levels of the soil profile. In this soil layer triasulfuron remains

available for microbial degradation and it can be further dispersed by ploughing. Rainfall patterns during these studies were slightly below the 30 year mean (Smith and Trafford, 1975) at Whittlesford and were slightly above the 30 year mean at Elmdon.

Figure 1. Bioassay results - Hill Farm site.

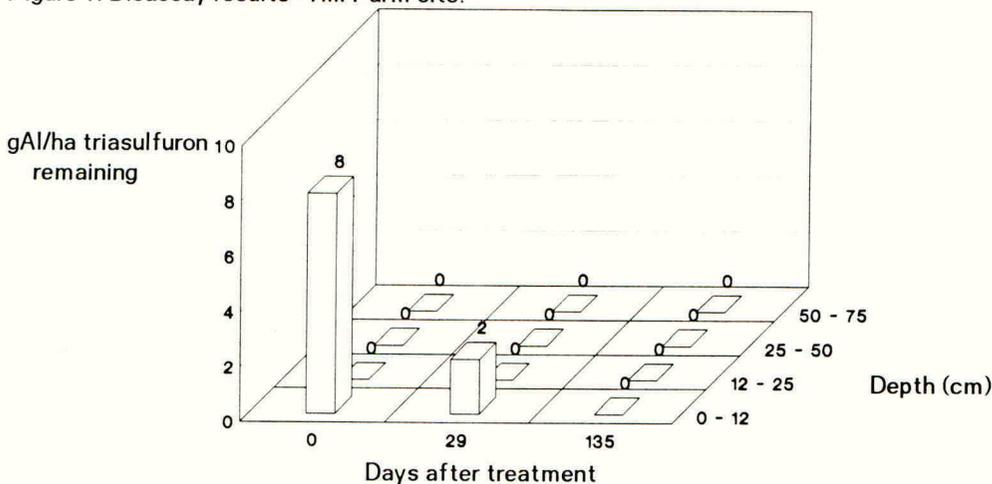
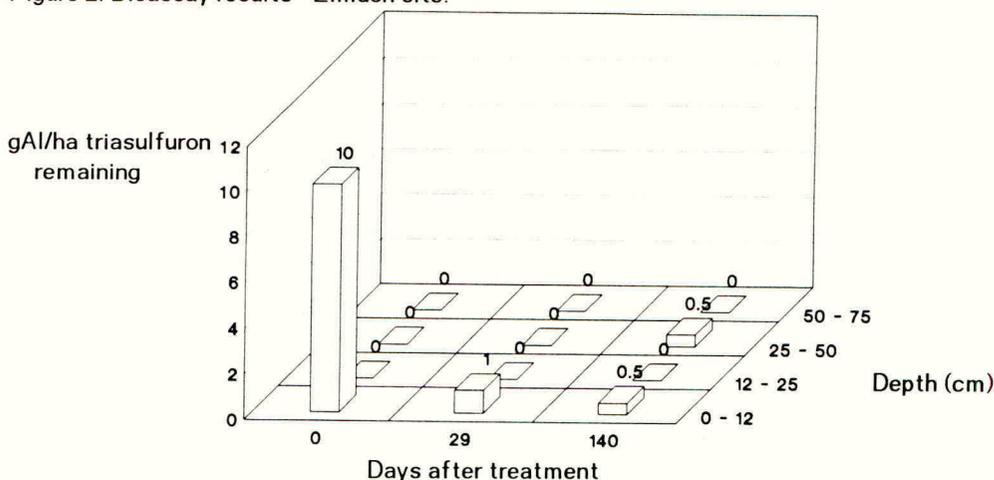


Figure 2. Bioassay results - Elmdon site.



CONCLUSIONS

Triasulfuron will be recommended for spring applications (post January 1st) up to GS33 of the crop, at a rate of 7.5 gAI/ha or less. The label will carry a positive list indicating which crops may be sown safely following triasulfuron use in the previous crop. This list will include all the major arable crops with ploughing being recommended before crops such as oilseed rape and sugarbeet may be safely sown. When used according to these label recommendations triasulfuron degradation is good leaving no significant residues and gives

an excellent safety margin which allows the planting of extremely sensitive crops such as sugarbeet and oilseed rape after its use in the previous cereal crop, on all soil types.

Other broad-leaved crops such as beans, peas, linseed and potatoes appear to be less sensitive to sulfonyl urea herbicides with trials data showing that these crops can be safely planted following a cereal crop treated with triasulfuron, regardless of cultivation type.

Bioassays (Iwanzik *et al.*, 1988 and 1989. Rahman and James, 1989), chemical analysis (Iwanzik and Egli, 1989) and computer models (Walker and Welch, 1989) show that triasulfuron applied in the spring remains in the upper layers of the soil allowing rapid degradation and dispersion by ploughing. This is supported by trials data which shows that where ploughing is used before the establishment of a sensitive crop, spring applied treatments of at least double rate triasulfuron are completely safe when applied at normal application timings. Where only minimal cultivations are employed however damage to following crops of sugarbeet or oilseed rape is possible. The margin of safety for triasulfuron applications where ploughing has been used appears to be at least three times the recommended used rate of 7.5 gAl/ha, which has been established following five very different seasons of trials use.

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