

EVALUATION OF PESTICIDE LEACHING MODELS USING THREE ITALIAN DATA-SETS

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ABSTRACT

An evaluation of four pesticide leaching models (VARLEACH, PRZM-2, LEACHP and PESTLA) with three different data-sets is reported. Experimental data on residues of metamitron in soil after application to sugar beet were collected at Piacenza (51 m above sea level, 45° N, silty clay loam soil), Perugia (155 m above sea level, 43° N, silt loam soil) and Tor Mancina (Rome) (105 m above sea level, 42° N, clay loam soil). The models were evaluated using standard indices to evaluate overall goodness-of-fit, mass balance and distribution down the soil profile. The results show differences in predictive ability for the three data-sets and confirm the necessity of more work on model validation.

INTRODUCTION

The environmental fate of pesticides applied in the environment is governed by many processes such as leaching, degradation, crop growth, meteorological conditions and soil hydrologic behaviour. Simulation models provide a means to evaluate the interaction between these processes and to predict potential pesticide fate, mainly in non-target environments (e.g. surface and ground waters). Many models are available, but few are tested for use under Mediterranean conditions. The aim of this work is to test and compare four models using three Italian data-sets. The quality of the data-sets is an important factor in evaluation exercises. The data were obtained using the same protocols for all field and laboratory procedures.

We have chosen four models used widely in Europe: VARLEACH (Walker, 1987), PRZM-2 (Mullins *et al.*, 1992), PESTLA (Boesten, 1993) and LEACHP (Hutson & Wagenet, 1993). Metamitron is the reference pesticide and sugar beet the reference crop. Experimental sites were located in areas with very different pedoclimatic conditions, in the Po valley, in Umbria and near Rome.

MATERIALS AND METHODS

Experimental tests

Experiments were carried out at three farms located in Piacenza (51 m above sea level, 45° N, silty clay loam soil), Perugia (155 m above sea level, 43° N, silt loam soil) and Tor Mancina (Rome) (105 m above sea level, 42° N, clay loam soil) with nine 4-m² sampling plots identified within large experimental fields at each (2, 1, 0.3 ha, respectively). Sugar beet was cultivated following the standard agronomic practices used on the farm. Metamitron was applied pre-emergence using a tractor-mounted sprayer calibrated to distribute approximately 400 l/ha. Application rates, treatment dates and soil properties are given in Table 1.

TABLE 1. Field information

Agronomic information								
Site	Treatment date		Rate of application of Metamitron (kg/ha)					
Perugia	10 March 1994		1.61					
Piacenza	03 March 1994		1.54					
Rome	23 March 1994		2.45					
Soil properties								
	Depth cm	pH	O.M. (%)	Clay (%)	Silt (%)	Sand (%)	Bulk density (kg/l)	CaCO ₃ (%)
Perugia	0-30	8.2	1.78	26.4	55.2	18.4	1.35	28.0
	30-50	8.2	1.77	27.6	54.3	18.1	1.35	27.7
Piacenza	0-20	7.8	2.21	35.7	47.2	17.0	1.60	9.6
	20-40	7.8	2.14	33.8	49.5	16.7	1.40	10.0
Rome	0-30	7.4	1.44	38.3	20.0	41.7	1.40	6.4
	30-50	7.4	1.50	38.0	21.0	41.0	1.35	6.1

Analyses were carried out according to ASA-SSSA methods (Page, 1982; Klute, 1986).

TABLE 2. Climatic conditions during the experimental trials from application to 60 days after treatment.

Site	Mean min. temp (°C)	Mean max. temp (°C)	Rainfall (mm)	Absolute min. temp (°C)	Absolute max. temp (°C)
Perugia	4.5	19.0	83.4	-2.9	25.2
Piacenza	2.1	15.2	61.1	-3.0	28.9
Rome	5.8	21.4	114.6	3.0	31.8

Soil samples were taken from each plot from fixed positions and at different times. Soil core lengths ranged from 30 to 100 cm.

Herbicide analysis was carried out following the method of Ghebbioni & Trevisan (1992). Evapotranspiration values were calculated for all models using the Linacre equation. Table 2 reports air temperatures and rainfall for the three experiments.

The models

PRZM-2 1.02, VARLEACH 2.0, PESTLA 2.3 and LEACHP 3.1 differ mainly in their description of water flow. The first is a capacity model, based upon field capacity, whilst the second is also a capacity model but defines two regions for mobile and immobile water; LEACHP and PESTLA describe water flow using Richards' equation. All the models use the convection-dispersion equation to describe pesticide transport apart from VARLEACH which uses solute displacement. Pesticide degradation is described using first-order kinetics, with LEACHP, PESTLA and VARLEACH accounting for effects of soil moisture, temperature and depth on degradation. Pesticide sorption is modelled as linear by PRZM-2, linear but variable with time by VARLEACH, using linear or Freundlich isotherms by PESTLA, and using linear or Freundlich isotherm and two site sorption by LEACHP. All the models are one-dimensional and none contain a representation of macropore flow. VARLEACH does not simulate crop growth, only PRZM-2 predicts runoff and erosion, and only PRZM-2 and LEACHP model pesticide volatilization from the soil surface.

TABLE 3. Parameters used for simulations with VARLEACH (VA), PRZM-2 (PR), PESTLA (PE) and LEACHP (LE) for each site.

Site/Model	VA/PR	VA	PR	PE	LE/PE	PE/VA	LE/PR
Parameter	FC (%)	WC2 (%)	WP (%)	WCs (%)	Ks (cm/d)	HL (d)	Kdeg (d ⁻¹)
Perugia	27.2	16.3	10.4	0.40	229.0	58.2	0.0119
Piacenza	26.0	15.6	15.7	0.40	92.6	39.8	0.0174
Rome	32.6	19.6	17.7	0.51	230.4	20.5	0.0338

Site/Model	LE	LE/PE	PE	VA/PR	VA	VA/PE	VA/PE
Parameter	Kfoc (l/kg)	1/n	Kom (l/kg)	Kd (l/kg)	A	B	E (J/mol)
Perugia	302.9	0.635	216.3	3.85			
Piacenza	121.9	0.865	70.9	1.56	1463	-1.23	61112
Rome	866.6	0.700	500.5	7.28			

FC=field capacity; WC2=water content at 2 bar; WP=wilting point; WCs=saturated moisture content; Ks=saturated hydraulic conductivity; HL=half life; Kdeg=degradation rate; Kf=Freundlich sorption coefficient; 1/n=Freundlich exponent; Kom=organic matter sorption coefficient; Kd=sorption coefficient; A,B,E=constant for degradation rate

Hydrologic properties, sorption and degradation measurements have been carried out according to Cavazza (1981), OECD Guidelines No 106 (1981) and Walker (1987), respectively

Table 3 reports the parameter values used for testing the four models. The following parameters were kept constant for all sites: pesticide incorporation depth (1 cm), lower boundary condition (free-draining profile), pan factor (0.90), pesticide plant uptake factor (0.5), crop cover (0.95), maximum root depth (40 cm), total profile depth (100 cm), layer thickness (5 cm), dispersivity (5 cm), water solubility of metamitron (1820 mg/l), vapour density (8.6×10^{-8} mg/l), Henry constant (5.9×10^{-7}).

Model performance assessment

The approach used for this study was that described by Boesten *et al.* (1994), so that water flow was tested to obtain a fit between observed and predicted values for soil moisture content before testing pesticide behaviour. For this reason, all models were calibrated using experimental soil moisture data. The more sensitive input parameters, such as degradation rate or sorption coefficient, were not varied to take into account the intrinsic variability inherent in such parameters but we use only mean data determined experimentally.

Assessment of model performance was carried out using three different sets of indices to evaluate prediction of the movement of pesticide through soil, the mass balance (degradation) and overall goodness-of-fit, as reported by Melacini & Gunther (1994). The assessment is carried out at a specified time interval (60 days after treatment) to obtain an evaluation of the perfect fit (overall evaluation), perfect residual amounts prediction (mass balance evaluation) and perfect distribution simulation (movement evaluation).

Perfect fit is obtained when all predicted data are equal to observed data. Perfect residual amounts prediction is obtained when the total amount of pesticide predicted is equal to that observed in the field. Perfect distribution simulation is obtained by a condition of proportionality between the predicted and observed pattern of residues down the soil profile.

The indices used for the evaluation were total scaled error (TSE), scaled root mean squared error (SRMSE) and model efficiency (ME) for the overall evaluation; coefficient of residual mass (CRM) and degradation load (DL) for the mass balance evaluation; coefficient of determination (CD), cumulative value test (CVT) and mean depth (MD) ratio for the leaching transport evaluation. The best result (i.e. predicted data equal to observed data) is zero for TSE, SRMSE and unity for ME; when ME becomes negative the fit is remarkably poor. For CRM and DL, the best result is also zero; when the index is less than zero, the model tends to underpredict observed data and vice versa. The best result for CD and MD is unity, whereas for CVT it is zero.

RESULTS AND DISCUSSION

Table 4 gives experimental and predicted data for all combinations of site and model. To allow easy comparison, results for residues of metamitron in soil are always reported as a proportion of that applied. The experimental data show that metamitron leaches slowly and is degraded more rapidly where temperature are higher (Rome). Model predictions are different for the three data-sets.

For the Piacenza data-set, all models underpredict concentrations at 0-5 cm and then differ; for Perugia and Rome the opposite occurs and in the first layer the predictions are overestimated by all models. If we consider total recovery, the best fits are VARLEACH for

Perugia (37% against 32% observed), LEACHP for Piacenza (39% against 56%) and PRZM-2 for Rome (36% against 24%).

TABLE 4. Comparison between observed (obs) concentrations of metamitron in soil (% of that applied) and predicted by the four models [VARLEACH (VA), PRZM-2 (PR), PESTLA (PE) and LEACHP (LE)]

Depth cm	Perugia 61 DAT					Piacenza 63 DAT					Rome 30 DAT				
	obs	VA	PR	PE	LE	obs	VA	PR	PE	LE	obs	VA	PR	PE	LE
0-5	27.43	37.41	49.86	61.23	35.60	50.19	27.80	18.84	40.01	29.64	19.60	63.74	23.66	63.44	43.23
5-10	1.61	0.01	20.96	12.06	8.70	1.27	2.89	10.81	23.25	6.68	2.30	0.01	11.32	7.10	5.38
10-15	1.69	0.00	3.83	0.25	0.29	2.50	0.48	0.01	6.48	2.12	2.57	0.00	0.54	0.12	0.12
15-20	1.34	0.00	0.45	0.01	0.00	2.31	0.00	0.00	1.09	0.22	0.00	0.00	0.02	0.00	0.00
20-25	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.09	0.01	0.00	0.00	0.00	0.00	0.00
25-30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
total	32.07	37.42	75.14	73.55	44.59	56.27	31.17	29.65	70.92	38.67	24.47	63.75	35.54	70.66	48.73

Table 5 shows index results for all models and data-sets. The first three indices are used to assess the overall goodness-of-fit of the model prediction and results from all three indices are similar. It is probably sufficient to have only one index for an overall evaluation (ME). VARLEACH is the best model for the Perugia data-set, LEACHP for Piacenza and PRZM-2 for Rome. The second two indices are used to assess predictions for the mass balance and to evaluate the tendency of prediction (over- when >0 and under- when <0). As can be seen in Table 5, VARLEACH gives the best prediction of the mass balance for the data from Perugia and PESTLA for the data from Piacenza. No single model performed best for the Rome data with the CRM index showing PRZM-2 to give the best results and the DL index showing VARLEACH to be more accurate.

TABLE 5. Index results for the four models [VARLEACH (VA), PRZM-2 (PR), PESTLA (PE) and LEACHP (LE)]. Values in bold are the best for that index and site.

Index	Perugia				Piacenza				Rome			
	PE	VA	LE	PR	PE	VA	LE	PR	PE	VA	LE	PR
TSE	1.446	0.456	0.561	1.397	0.664	0.503	0.505	0.812	2.594	2.389	1.478	0.808
SRMSE	2.209	0.645	0.685	1.853	0.874	0.805	0.759	1.171	4.637	4.634	2.577	1.151
ME	-1.498	0.787	0.760	-0.757	0.653	0.705	0.738	0.376	-7.768	-7.755	-1.708	0.460
CRM	1.293	0.166	0.390	1.342	0.259	-0.446	-0.313	-0.473	2.594	2.242	1.479	0.807
DL	0.882	0.366	0.696	0.960	0.390	-0.886	-0.619	-0.582	1.000	0.939	1.000	1.000
CD	0.169	0.476	0.568	0.252	1.770	2.500	2.756	4.058	0.068	0.067	0.156	0.544
CVT	0.155	0.281	0.187	0.265	0.374	0.111	0.187	0.383	0.029	0.075	0.040	0.275
MD	0.914	0.781	0.943	1.092	1.261	0.910	1.053	1.105	1.027	0.930	1.037	1.256

The final indices are used to assess the distribution profile and the results do not indicate that any single model performed better than the others. The use of indices allows models to be assessed at different stages of the simulation. Weaknesses in simulation can be found for subroutines describing pesticide behaviour, degradation, or transport, and this is facilitated by the earlier calibration using water balance data because water flow effects have been eliminated.

In conclusion, the four models are not generally good at predicting the fate of metolachlor in the three experimental scenarios. Their limitations are demonstrated especially by the distribution indices and this may be due to preferential flow, which has been shown to occur under field conditions, but is not considered by any of the models. As previously reported (Gottesburen *et al.*, 1994), this remains the main problem to solve for the practical use of models. No model has proved to be superior to others. A specific software tool to determine the best routine in each model for describing a specific process may represent a step forward towards improving predictive ability.

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RESULTS OF A LYSIMETER STUDY WITH METHABENZTHIAZURON
COMPARED TO RESULTS OBTAINED BY THE SIMULATION MODELS PELMO
AND WAVE.

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ABSTRACT

Soil water contents, amount of leachate and concentrations of methabenzthiazuron (MBT) residues in soil and leachate were measured in a lysimeter study. Actual evapotranspiration has been estimated from the soil water balance components. The results obtained were compared to simulated values from the models PELMO (capacity model, solute transport: solute displacement, degradation according to first-order kinetics) and WAVE (Richards' equation, solute transport: convection dispersion equation, degradation according to first-order kinetics) in order to test the selected models in their ability to describe the processes affecting the fate of pesticides in soil. Two cylindrical lysimeters containing undisturbed cores of an orthic luvisol, 1 m² in area and 1.10 m deep were used. [Phenyl-U-¹⁴C]MBT was applied at rates of 2.1 to 3 kg MBT/ha pre-emergence to winter wheat. In the course of the lysimeter study the natural precipitation was adjusted to 800 mm/a by applying 222.5 mm of irrigation water. Volumetric water contents of the topsoil ranged from about 10 % in summer to saturation during winter. Whereas WAVE could simulate the drying during summer, PELMO simulated volumetric water contents of more than 25 %. About 24 and 29 % of the applied compound remained in the soil after harvest of the treated crop and this was overpredicted by WAVE (37 %) and underpredicted by PELMO 2.0 (18 %). In leachate, average concentrations of 0.01 and 0.05 µg MBT/l were measured during the first year, respectively. However, neither of the models predicted residues of MBT in leachate.

INTRODUCTION

In Germany, lysimeter studies with undisturbed soil cores are required for regulatory purposes for those pesticides that are expected to have a potential for leaching in soil (BBA, 1990). Lysimeters offer a chance to make up a complete balance sheet of the fate of a

pesticide in soil, including the soil water balance, sorption and degradation, plant uptake of pesticide residues, and transport of pesticide residues in leachate below the soil core (Führ *et al.*, 1991). They may therefore be useful tools to produce data sets for testing and calibrating models simulating the fate of pesticides in the soil/water/plant environment. This study was conducted in order to compare the soil water balance, degradation and translocation of MBT in the soil measured in a lysimeter study with values obtained by two different models. The discussion is focused on the ability of the models to describe the soil water balance with particular respect to the soil moisture and temperature in the upper soil horizon as important factors influencing the microbial degradation of a pesticide in soil.

MATERIAL AND METHODS

Lysimeter study

Two free-draining lysimeters (round type, 1 m² surface area, 1.10 m profile depth) were used (Steffens *et al.*, 1992). They contained undisturbed soil cores of an orthic luvisol (degraded loess soil, plough horizon (A_p): pH 7.2, 1.2 % C_{org}, 78.2 % silt, 15.4 % clay, 6.4 % sand). MBT (1-benzothiazol-2-yl-1,3-dimethyl-urea) is the AI in Tribunil® (WP, 70 % AI), an effective herbicide used on many cereal crops (Hack, 1969). In this study [phenyl-U-¹⁴C]MBT was used as test substance and had a specific radioactivity of 429.2 kBq/mg AI. It was applied pre-emergence to winter wheat on November 10, 1992 at rates of 3.0 kg AI/ha (lys. MBT_3kg) and 2.1 kg AI/ha (lys. MBT_2kg). Crop management was according to agricultural practice and natural precipitation was supplemented to at least 800 mm/a according to the German guideline for lysimeter studies (BBA, 1990). In lys. MBT_2kg, soil moisture content was measured for each horizon using a neutron probe (Berthold Inc.). Water contents of the entire profile were calculated from these values. Leachate was sampled on a 2-3 weekly basis and analyzed for residues of MBT. After wheat harvest, 255 d after application of MBT, soil samples were taken from the upper 25 cm of lys. MBT_3kg and MBT_2kg. Air-dried soil was desorbed with 0.01 M CaCl₂ (22 h) and subsequently extracted with acetone (1 h), ethylacetate (15 h), and chloroform (1 h). Extracts were analysed by radio-TLC with co-chromatography of the non-labelled standard substance.

Models

The model PELMO 2.0 (Klein, 1994) is used for regulatory purposes in Germany. It includes a capacity model for the simulation of water flow and solute transport is calculated as mass movement with a correction for dispersion. Pesticide sorption in soil is described as linear sorption and the initial K_D-value used was 6 ml/g, increasing with time (220 % increase/a). Pesticide degradation is simulated according to first-order kinetics. The influence of soil moisture and temperature on pesticide degradation in soil is calculated as follows (parameters according to Pestemer & Auspurg (1987)):

$$\text{Soil moisture: } DT_{50}(\Theta) = DT_{50}(\Theta_0) \cdot \left(\frac{\Theta}{\Theta_0}\right)^{-0.31} \quad \text{Temperature: } \begin{aligned} DT_{50}(T) &= DT_{50}(20^\circ\text{C}) \cdot 2^{\frac{T-20}{10}} \\ DT_{50}(20^\circ\text{C}, 40\% \text{ WHC}) &= 66 \text{ d} \end{aligned}$$

* Registered trademark of Bayer AG

WAVE (Vanclouster *et al.*, 1993) is a research model using Richards' equation for simulation of water flow and the convection-dispersion equation for solute transport. Sorption is again described as a linear process with a constant K_D -value of 6 ml/g used. Pesticide degradation is simulated according to first-order kinetics assuming the influence of soil moisture and temperature:

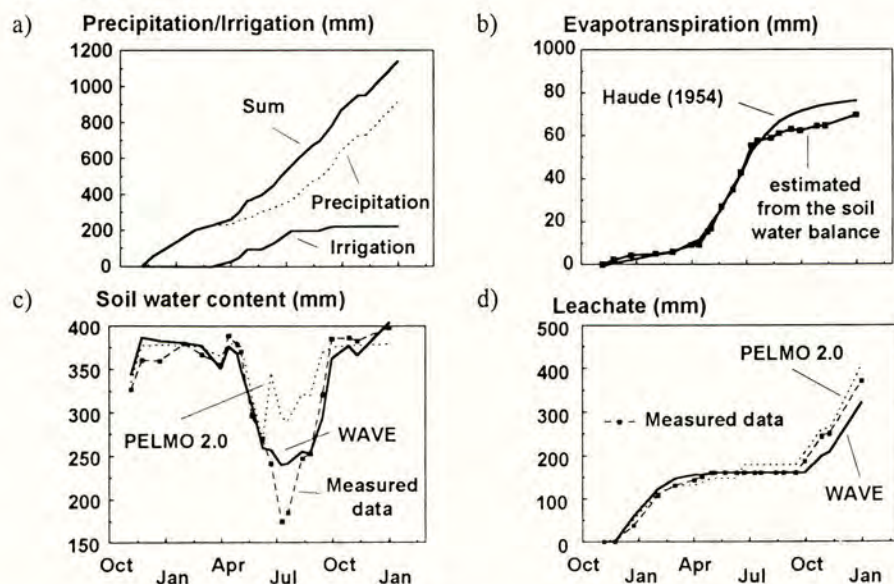
$$\text{Soil moisture: } DT_{50}(20^\circ\text{C}) = 213 \cdot \Theta^{-0.31} \quad \text{Temperature: } DT_{50}(T) = DT_{50}(20^\circ\text{C}) \cdot 2^{\frac{T-20}{10}}$$

The measured evapotranspiration in lys. MBT_2kg was satisfactorily described by the empirical model of Haude (1954) using culture-specific factors for winter wheat (Figure 1b). Therefore in both models daily evapotranspiration (ETR) according to the model of Haude (1954) was used as input.

RESULTS AND DISCUSSION

During the first 14 months of the lysimeter study, a total precipitation of 917.4 mm was recorded (Figure 1a). A total of 222.5 mm were additionally added during the growing period of winter wheat in spring 1993 to a sum of 1139.9 mm. In the course of the growing periode, volumetric water contents (VWC) in the soil's upper horizon were reduced to below 10 % (Figure 2) and the water content in the entire soil profile decreased from 350 to 170 mm (Figure 1c) due to plant transpiration. During the first leaching period (Nov. 1992 - Apr. 1993), 160 mm of leachate were collected. After the harvest of winter wheat, the soil profile was rapidly saturated with water and during the last four months of 1993 another 212 mm of leachate were measured (Figure 1d).

FIGURE 1. Time course of the terms of the soil water balance for lys. MBT_2kg (Nov. 1992 - Jan. 1994).



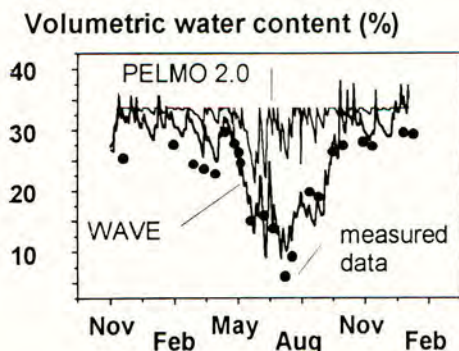
The model WAVE simulated the drying of soil at 20 cm depth in excellent agreement with the measured data (Figure 2). Changes in water content in the entire profile were also satisfactorily described, although the extreme drying at harvest of winter wheat was not simulated (Figure 1c). The total amount of leachate simulated with WAVE was 50 mm less than measured (Figure 1d) probably due to the higher ETR during the second leaching period (Sep 1993 - Jan 1994) calculated by the method of Haude (1954) (Figure 1b).

TABLE 1. Comparison of measured and simulated data for the soil water balance (mm) for lys. MBT_2kg (evaporation calculated by Haude = 768 mm. All data in mm (L/m²).

	Precipitation/ Irrigation	Δ Water content	Leachate	ETR
Measured	1139.9	71.0	372.5	696.4
WAVE	1139.9	60.6	322.0	757.3
PELMO 2.0	1139.9	50.1	407.3	682.5

PELMO 2.0 was not able to simulate drying of soil during summer. The simulated VWC at 20 cm depth was above 20-25 % and the water contents above 250-300 mm (Figures 1c and 2). The intensive irrigation in June 1993 increased the soil water content to about 350 mm in July (Figure 1c) and leaching was simulated by PELMO 2.0 which was not measured. The total amount of leachate, however, was in good agreement with the measured data (Table 1). Whereas the ETR calculated for WAVE from the simple soil water balance was in accordance with the ETR calculated by the method of Haude (1954), the ETR simulated by PELMO and the ETR according to the model of HAUDE (input parameter) differed by 80 mm (Table 1).

FIGURE 2. Time course of volumetric water contents in 20 cm depth. Comparison of measured and simulated data.

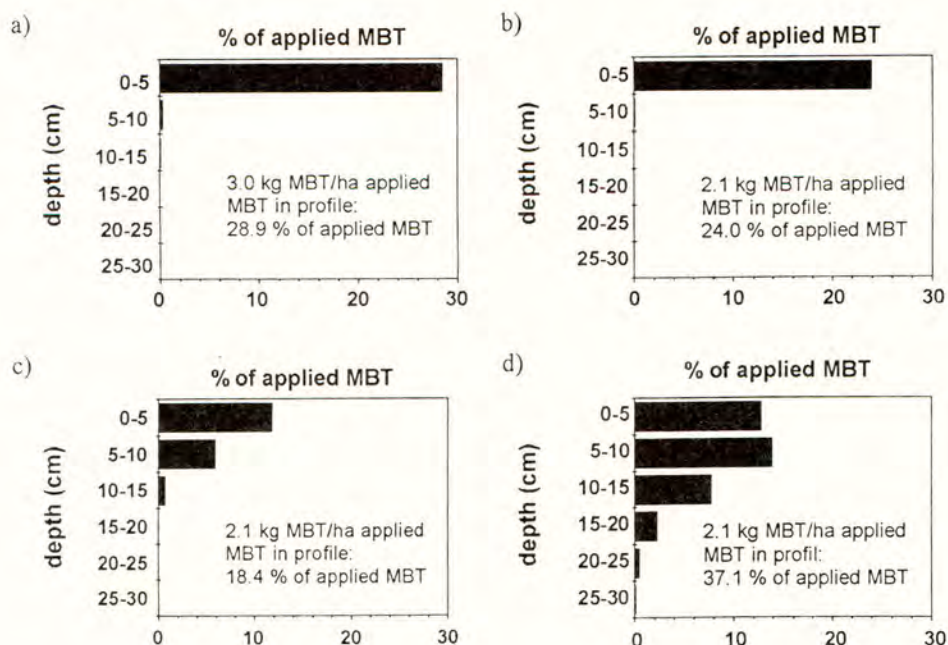


MBT showed a very low leaching potential in soil (Figures 3a and 3b). In both lysimeters almost all of the MBT residues were found in the top 5 cm of the upper horizon 255 days after application. In lys. MBT_3kg 28.9 % and in lys. MBT_2kg 24.0 % of the applied radioactivity could be characterized as the AI, respectively. The WAVE model calculated a herbicide recovery of 37.1 % at day 255 after application for lys. MBT_2kg and simulated a translocation of MBT residues within the top 30 cm of the soil with the highest concentration of MBT in the 5-10 cm layer (Figure 3d).

In the simulation with PELMO 2.0, 18.4% of the applied MBT was recovered. Compared to the WAVE simulation, PELMO 2.0 calculated a more intensive dissipation of MBT from the soil (Figure 3c). This may be due to the large soil moisture content (Figure 2) and the overestimation of soil temperature in the upper horizon (average temperature at 5 cm during the first year: 10.5 °C vs. 8.9 °C measured, WAVE: 9.3 °C) resulting in overprediction of the degradation of MBT in soil. PELMO 2.0, however, simulated less translocation of MBT residues within the upper cm of the soil compared to the WAVE model. This may be explained by the assumption of the increase in the linear sorption coefficient with time for PELMO 2.0, whereas for the WAVE model a constant K_D -value of 6 ml/g was assumed. Compared to the measured data, both models failed to simulate the extremely low leaching potential of MBT in soil.

Neither of the models simulated residues of MBT in leachate collected at a depth of 1.10 m. Leachate from lys. MBT_3kg and lys. MBT_2kg contained average concentrations of 0.05 and < 0.01 µg MBT/l, respectively.

FIGURE 3. Distribution of MBT residues (% of that applied) measured in the upper horizon of a) lys. MBT_3kg, b) lys. MBT_2kg 255 d after application, and simulated with c) PELMO 2.0 and d) WAVE.



CONCLUSIONS

The WAVE model, using Richards' equation, simulated the observed drying of soil (VWC < 10%) during summer very well, whereas the capacity model, PELMO 2.0,

simulated values above 25 %. Compared to WAVE, PELMO 2.0 simulated a more intensive dissipation of MBT in soil which may be due to the unsatisfactory calculation of soil moisture and temperature in the upper horizon of the soil.

The research model WAVE gave a more precise description of the soil water regime than PELMO 2.0, but WAVE still did not describe the loss and translocation of MBT in soil satisfactorily.

This study shows that lysimeter studies on the long-term fate of pesticides can be useful tools for testing models which simulate the fate of pesticides in the soil/water/plant environment. More useful data sets can be obtained by measuring soil moisture content more frequently (daily basis) in order to investigate more closely the soil moisture regime. Additionally, more soil samples should be taken during the time between application and first tillage in order to generate enough data to describe the kinetics of pesticide degradation.

ACKNOWLEDGMENTS

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LIMITS AND POSSIBILITIES OF USING COMPUTER MODELS TO PREDICT FATE AND BEHAVIOUR OF PESTICIDES IN SOIL

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CONCLUSIONS

The models PELMO and VARLEACH were used to simulate the behaviour of pesticides in the unsaturated zone. The simulations showed that it depends mainly on biodegradation and sorption. The calculated pesticide concentrations at the groundwater surface were confirmed by field investigations. Examinations on the efficiency of the computer models used led to the following results:

- On the basis of application time, the quantity applied and the worst-case conditions it was possible to predict the time period the pesticide would require to reach the groundwater and to estimate pesticide concentrations at the groundwater surface.
- By using computer models the behaviour of different pesticides in soil could be well compared if identical application areas were considered.
- The precision of computer simulations decreased with increasing depth.
- Simulation models are also suitable for water resources management to estimate the behaviour of pesticides in soil by using a worst case scenario. So computer models could help to avoid the contamination of groundwater with pesticides.
- A disadvantage of the tested computer models is that they do not consider the preferential flow, e.g. through macropores.
- A spatial and temporal variability of input data could only be considered insufficiently. For an optimal simulation specific data of the examined location are essential. The most important data are the distribution coefficient k_d , values of the decay rate, weather data and information about the water transport in soil.
- A principal weakness of PELMO and VARLEACH is the incomplete and defective description of biodegradation and sorption processes (Gottesbüren *et al.*, 1992). Nevertheless our investigations showed that these restrictions do not influence the simulation results as much as quality and quantity of input data.

INTRODUCTION

In combination with a research project the time course of pesticide concentrations in the groundwater of the catchment area of the water treatment plant MÖNCHENGLADBACH-GATZWEILER has been observed for several years (Overath *et al.*, 1995).

As a part of this project computer models were used in order to get a temporal and quantitative relationship between the pesticide input at the soil surface and the appearance of pesticides in groundwater.

CHARACTERISATION OF THE EXAMINATION AREA

The examination area is situated in the catchment area (3,5 km²) of the waterworks MÖNCHENGLADBACH-GATZWEILER. This area is predominantly in agricultural use. The field chosen for the examinations represents the characteristic soil properties of the catchment area. At this location three core drillings to the groundwater surface (5 m below surface area) were taken in order to get samples for the characterisation of the soil horizons.

The arrangement of the drill holes (named HB 6/1, HB 6/2, HB 6/3) was in form of a triangle. The distance between these holes was 20 m.

These drill holes are located in the groundwater catchment area of the well HB 6. Samples of the water of the groundwater surface in these observation wells have been taken in order to attach pesticide residues of these samples to their origin above. The results of these investigations are shown in FIGURE 1. The german limit for a single pesticide substance in drinking water is 0,1 µg/l. It is obvious that the concentrations for atrazine, isoproturon and metribuzin were higher than this value in most cases. The limit of 0,5 µg/l for the sum of pesticides were also frequently exceeded.

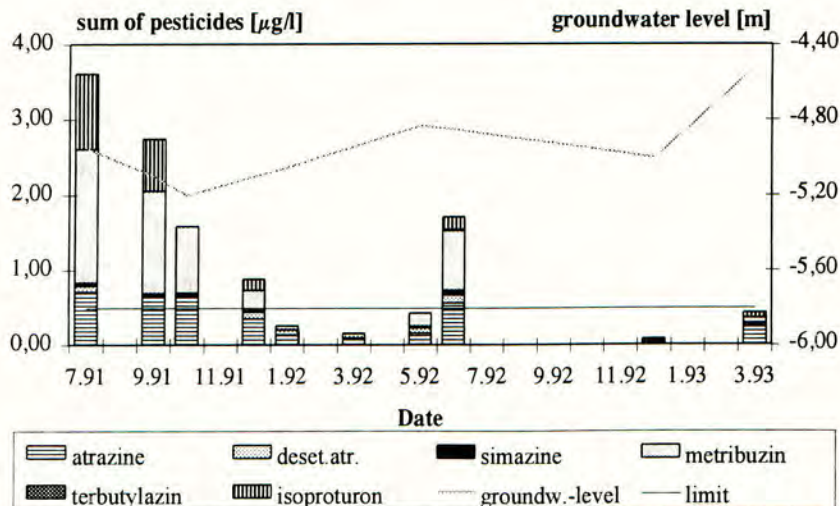


FIGURE 1. Pesticide concentrations of water of the groundwater surface in well HB 6 (July '91 to March '93)

INPUT-DATA FOR PELMO AND VARLEACH

The complete details of model theory, including equations and other applications are presented elsewhere (Klein, 1993; Walker, 1987). The most important parameters of the models are the adsorption partition coefficient (k_d), the overall decay rate (k) based on the half-life of the pesticides, the on-site weather data including daily rainfall and average air temperature, pH, the soil bulk density and the soil field capacity. The models also require data of other soil physical parameters, crop cultural information and pesticide application information.

TABLE 1 and TABLE 2 show the most important data of the three soil cores from the observation wells.

TABLE 1. Characterisation of the examined soil and sediment samples (increment 0,0 - 0,3 m below the surface, mean value of HB 6/1 - HB 6/3)

	C_{org} [%]	sand [%]	silt [%]	clay [%]
mean value	1,11	40,0	37,5	2,2

TABLE 2. k_d -values of the examined soil and sediment samples (increment 0,0 - 0,3 m below the surface, mean value of HB 6/1 - HB 6/3)

	atrazine	isoproturon	metribuzin	metamitron
mean value	0,88	0,95	0,32	0,94

RESULTS OF COMPUTER SIMULATIONS

FIGURE 2 shows a typical concentration-time-diagram of a PELMO-simulation. Concentrations given in this and the following diagrams refer to the pesticide content in the new arisen groundwater.

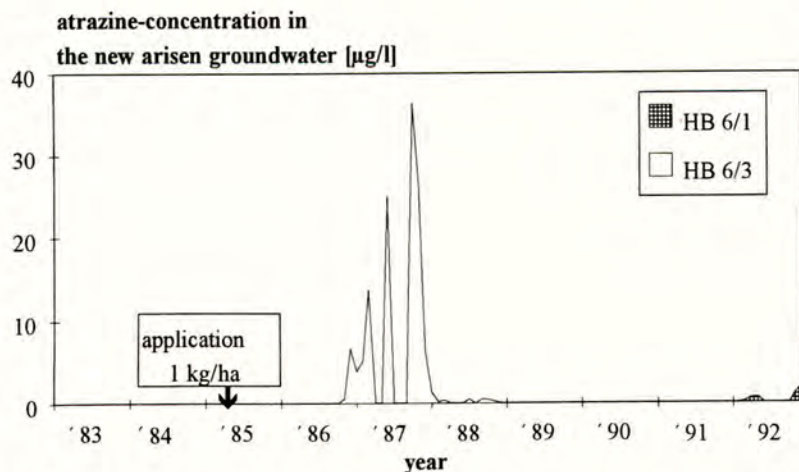


FIGURE 2. Comparison of PELMO-simulations; scenario atrazine, profiles HB 6/1 and HB 6/3, depth 0 - 5 m

FIGURE 2 shows that atrazine reached the groundwater with very high concentrations with a maximum of 38 $\mu\text{g/l}$ 2 years after application. The profile of HB 6/3 seemed to be a "window" in the unsaturated zone. In comparison to HB 6/3, atrazine leached 6,5 years

through the unsaturated (vadose) zone in profile HB 6/1 before it reached groundwater. The difference between the results of the simulations for HB 6/3 and HB 6/1 is due to the different content of organic carbon and of silt.

Altogether PELMO-simulations showed that atrazine needed 5,5 years to percolate through the vadose zone. The calculations for the other examined pesticides yielded different results. Metribuzin leached faster and reached higher concentrations in the vadose zone than atrazine while isoproturon behaved like atrazine. Metamitron needed a long time to reach groundwater, about 7 years and its concentration in the percolate was very low.

In FIGURE 3 a comparison between real pesticide concentrations in well HB 6 and results of PELMO-simulations is demonstrated. The figure shows that there is a relatively good conformity between the two graphs.

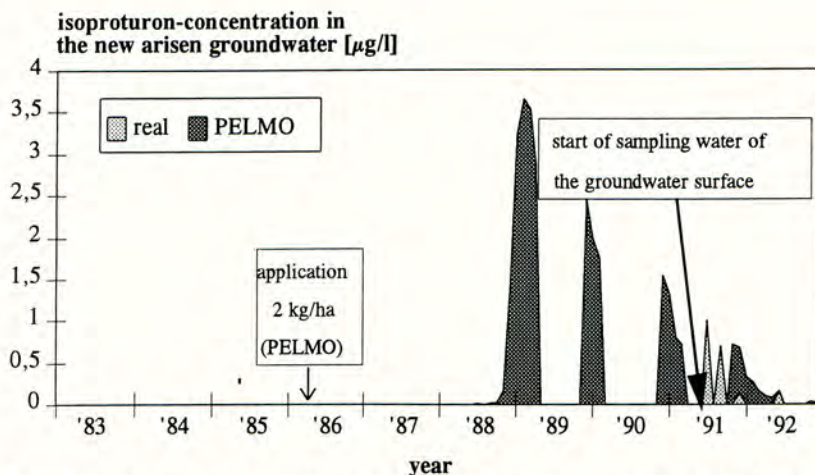


FIGURE 3. Comparison between the result of a PELMO-simulation and real pesticide concentrations in the water of the groundwater surface of well HB 6

SENSITIVITY ANALYSIS OF THE MODELS

To judge the reliability of the simulations with PELMO and VARLEACH we made a sensitivity analysis of the two models. First we compared simulations with different values for the half-life of isoproturon (FIGURE 4).

The decay rate was the only parameter that we could not determine by own experiments. So we had to use values of the literature (Perkow, 1992; Dibbern & Pestemer, 1992; Domsch, 1992), which varied over a wide range. The results of these simulations showed that the decay rate only influenced the concentration of the pesticides in the percolate but not the velocity of pesticide leaching through soils (FIGURE 4).

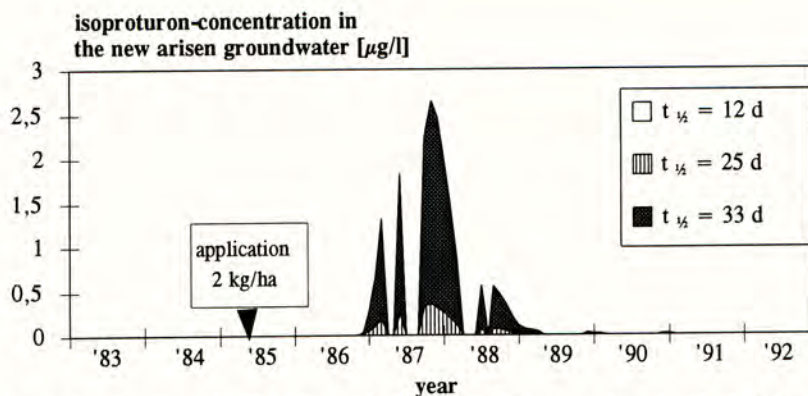


FIGURE 4. Results of PELMO-simulations with different values for the half-life of isotroturon

The k_d value influenced both the velocity and the concentrations of pesticides in the soil. This is shown in FIGURE 2 because the difference in the behaviour of atrazine in the two scenarios HB 6/1 and HB 6/3 is based mainly on the different k_d values. A simulation with k_d values which varied within standard deviation for every increment, showed the same result. This analytical error was very high for increments lower than 2 m depth.

In FIGURE 5 the results of simulations for metamitron and metribuzin are compared.

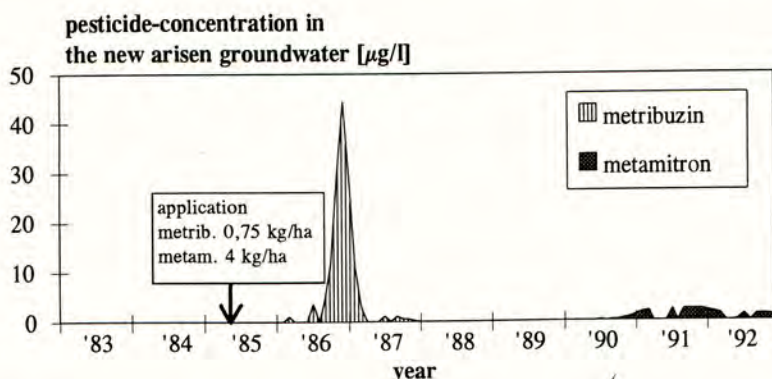


FIGURE 5. Comparison of results of PELMO-simulations for metribuzin and metamitron; worst-case conditions

These calculations using worst-case scenarios show the obvious influence of the k_d value and decay rate on the behaviour of pesticides in soil. Because of its low k_d values metribuzin leaches through the unsaturated zone very fast so that there is only a short time for degradation processes. In contrast metamitron has higher k_d values and there is more time for degradation. These results could be confirmed in the catchment area of Gatzweiler. Metribuzin was often observed in the water of the groundwater surface, but no metamitron. These investigations, field data and simulations, led to the conclusion that in the area of Gatzweiler metribuzin has a higher potential for groundwater contamination than metamitron.

COMPARISON OF RESULTS OF SIMULATIONS WITH PELMO AND VARLEACH

The model VARLEACH allows simulations to a depth of approximately 1,2 m. That is why we could only compare PELMO and VARLEACH simulations from ground surface to the depth of 1,2 m. FIGURE 6 shows the results of these simulations for the profile HB 6/3. Both models calculated that the first appearance of pesticides in the percolating water in a depth of 1,2 m happen 1,5 years after application. The results of the VARLEACH simulation showed lower pesticide concentrations in this water than PELMO-simulations. But it was obvious that VARLEACH does not calculate the water flux in soil correctly. This was shown by the real weather data.

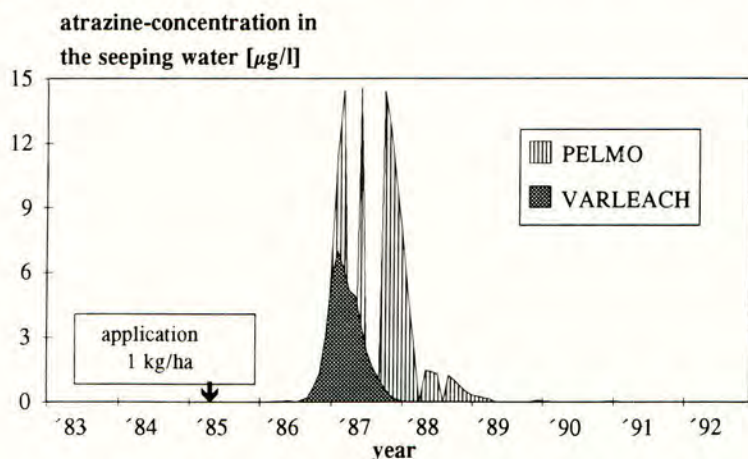


FIGURE 6. Comparison of results of PELMO and VARLEACH-simulations; scenario HB 6/3, atrazine, depth 0 - 1,20 m

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THE FATE OF ISOPROTURON AND DIFLUFENICAN IN AN AGRICULTURAL SANDY LOAM SOIL UNDER LABORATORY AND FIELD CONDITIONS INCLUDING SIMULATION MODELLING

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ABSTRACT

The effects of soil temperature and soil moisture content on the rate of degradation of isoproturon and diflufenican in a sandy loam soil were measured in the laboratory using a flow through soil metabolism system. Both herbicides followed first-order reaction kinetics, with half-life values ranging from 55.5 to 106.3 days for isoproturon and 169 to 365 days for diflufenican at 15°C and 5°C, respectively. In the field following a spring application, residues of both compounds were monitored in 5 cm sections down to a depth of 20 cm. Using similar rainfall conditions to those in the field, simulation experiments were conducted with isoproturon under outdoor conditions using intact soil columns to determine the rate of movement and degradation. Adsorption experiments indicated that the binding of diflufenican to soil was extensive with Kd values ranging from 37.8 to 345.6. The comparative Kd values for isoproturon ranged from 0.26 to 2.18, indicating the higher leaching potential of this compound particularly in the less organic sandy loam subsoil. The fate of diflufenican and isoproturon were predicted with PERSIST and CALF simulation models using field weather records in conjunction with laboratory generated parameters and the predicted results compared with the observed results.

INTRODUCTION

Studies to examine herbicide residue levels are generally conducted in the South of England. In comparison, the West of Scotland has relatively higher precipitation levels and lower air and soil temperatures, both of which can affect the environmental fate of a compound. Research was initiated to assess the fate of selected herbicides in a typical West of Scotland agricultural soil under typical meteorological conditions; it was designed to incorporate the simulation approach of the PERSIST and CALF models. The two herbicides selected for study have different mobility and persistence patterns, providing a useful range of characteristics to study in a Scottish environment. Diflufenican is a very lipophilic (log Kow = 4.55), relatively persistent, non mobile compound whilst isoproturon (log Kow = 2.9) is a relatively non persistent, mobile compound which has been detected in ground water in the South of England (Fisher et al., 1991).

MATERIALS AND METHODS

Soils and herbicides

Pertinent characteristics of the West of Scotland sandy loam soil (Dreghorn series, brown Forest soil) are shown in Table 1. Water retention characteristics of the soils were determined by the Soil Survey and Land Research Centre, Derby. The gravimetric moisture content at 0.33 bar was 16.18 % and 14.62 % for the topsoil and subsoil regions, respectively. The bulk density of the topsoil was 1.2 g cm⁻³. The herbicides used were commercial formulations of diflufenican (N-(2,4-difluorophenyl)-2-[3-trifluoromethylphenoxy] pyridine - 3 - carboxamide), 50 % a.i. (w/v) and isoproturon (3 - (4 - isopropylphenyl) - 1, 1 - dimethylurea), 50 % a.i. (w/v); together with analytical grade samples of the two compounds.

Table 1 Characteristics of the test soil

Depth (cm)	Sand (%)	Clay (%)	Silt (%)	Organic Matter (%)	pH
0-30	70.8	16.0	13.2	3.81	5.4
30-60	78.9	9.6	11.5	1.52	5.6

Field studies

The field site (12.5 m x 12.5 m), situated at the Scottish Agricultural College, Auchincruive, Ayr, was ploughed, rotavated and left to settle in October 1991. On March 9 1992 the area was manually hoed prior to spraying. On April 8 1992 plots (2.8 m x 10 m) were sprayed using a Ciba Geigy knapsack plot sprayer with commercial formulations of isoproturon and diflufenican at application rates of 2.1 and 0.5 kg a.i. ha⁻¹, respectively. Each plot was divided into 3 sub-plots (1.6 m x 1.6 m) for each compound. On the day of application 4 cores (10 cm i.d. by 20 cm depth) were extracted randomly from each plot. and at each sampling date, thereafter, 3 cores were similarly removed. Cores were sectioned into 5 cm segments and corresponding segments within a plot bulked together and thoroughly mixed in plastic bags. Triplicate samples (100 g) were selected from each of the bulked segments and stored at - 20°C until required for analysis. Isoproturon plots were sampled at intervals of 0, 36, 50, 85, 114 and 183 days. Diflufenican was sampled at 0, 37, 65, 119, 183, 253 and 485 days.

Column studies

The persistence and mobility of isoproturon was investigated using intact soil columns to supplement field site data. PVC columns (10 cm i.d. by 45 cm depth) were used to collect intact soil cores (10 cm i.d. by 40 cm depth) from sites adjacent to the field plots. Following removal of the top 5 cm of turf, the columns were driven into the soil to a depth of 40 cm and removed intact. In the laboratory the cores were flooded then left to drain for 24 h before isoproturon was applied in acetone (150 µl) to the top of the column at a rate equivalent to the field application. The columns, situated outdoors, at the University of Strathclyde, Glasgow, were subject to the same simulated rainfall conditions as the field studies, with 2 columns harvested at intervals of 7, 14 and 35 days in the same manner as the field studies.

Laboratory degradation studies

The rates of degradation of both herbicides were determined in the sandy loam topsoil using a flow-through system (Guth, 1980) with an ethanolamine volatiles end trap. ^{14}C pyridine ring labelled diflufenican and technical isoproturon were applied in acetone (150 μl) to < 2mm sieved moist soil (101.5 g dry weight equivalent) at rates equivalent to 0.25 and 2.1 kg a.i. ha^{-1} , respectively. The soil samples were adjusted to 8.07 % and 12.14 % moisture content and incubated at 5°C and 15°C to produce 4 treatments. Replicate flasks (3) were removed for analysis at each sampling point over a period of up to 270 days and 286 days for diflufenican and isoproturon, respectively. Degradation of isoproturon was also examined in the subsoil at 15°C and 10.96 % moisture content (equivalent to 75 % of 0.33 bar).

Sample preparation and analysis

A modified version of the gas liquid chromatography method developed by Rhône-Poulenc (Hill and Sharpe, 1984) for diflufenican was used to extract and clean-up samples of field soil. Soil samples were extracted by shaking for 1 h with acetonitrile (150 ml) followed by filter extraction through a sintered glass funnel. Soil residues were further extracted (twice) with acetonitrile (50 ml) for 15 min. The filtered solvent extract was partitioned with hexane in a separating funnel (3 x 100 ml) and the washed acetonitrile extracts reduced to dryness by rotary evaporation and redissolved in toluene (5 ml). The toluene extract was reduced to dryness and taken up in acetonitrile (5 -100 ml). Radiolabelled diflufenican was used in the laboratory degradation studies and following filtration, radioactivity in the solvent was quantified by liquid scintillation counting (LSC). The clean-up procedure was not required for these samples prior to analysis. Isoproturon residues in soil were extracted and analysed by the method of Byast et al (1977). Soil samples treated with isoproturon were extracted with methanol and filtered in the same way as diflufenican. The filtered extracts were reduced to dryness and redissolved in a known volume of methanol. The concentration of both compounds in solvent was determined by high performance liquid chromatography (HPLC) using a Spherisorb ODS2 column (250 mm x 4.6 mm i.d.). Diflufenican was detected at 282 nm with a acetonitrile/water (65/35 v/v) mobile phase flowing at 1 ml min^{-1} with a retention time of 15.7 min. The isoproturon mobile phase consisted of methanol/water (70/30 v/v) flowing at 1 ml min^{-1} with detection at 240 nm and a retention time of 6.1 min. The concentration of diflufenican in field residues and isoproturon in laboratory and field residues was quantified by reference to the peak area of standard solutions. In the diflufenican laboratory studies, residues were determined by collection of peak fractions with quantification by LSC.

Herbicide adsorption

The adsorption of [^{14}C] diflufenican and [^{14}C] isoproturon (benzene ring labelled) was determined in the sandy loam topsoil and subsoil at 15°C. Triplicate samples of moist soil (4 g dry weight equivalent) were shaken for 24 h on a revolving shaker with solutions (20 ml) containing different concentrations (0.01, 0.2, 1.0, 5 $\mu\text{g ml}^{-1}$) of isoproturon in 0.01 M calcium chloride. Adsorption of diflufenican was measured over 16 h using a single solution concentration (0.05 $\mu\text{g ml}^{-1}$), equivalent to its water solubility. Following centrifugation (2000 rpm x 20 min), the concentration of the radioactive herbicide in solution was determined by LSC and in the soil by combustion and LSC.

The models

The PERSIST model (Walker and Barnes, 1981) was used to predict the persistence of diflufenican and the CALF model (Nicholls, Walker and Baker, 1982) as modified by Walker (1987), Walker and Welch (1989) and Walker and Hollis (1994) was used to predict the persistence and mobility of isoproturon. Both models were run on a PC with a 486 processor. Weather data used in the model was collected daily at the field site.

RESULTS AND DISCUSSION

Laboratory degradation experiments

Results showing the degradation of isoproturon and diflufenican are summarised in Table 2. Diflufenican was less persistent than reported for the same soil by Haynes and Kirkwood (1988), who detected 86.3% of applied diflufenican remaining in soil after 112 days at 30°C. This may be due to the more optimum degradation conditions provided by the flow-through system used in the present study. First order half-life values ($t_{1/2}$ days) and the constants to describe temperature and moisture dependence of degradation (Table 3) were determined in the manner used by Walker (1987). Half-life values for isoproturon were greater by a factor of 2 than those reported by Blair et al., (1990) in a sandy clay loam soil at similar temperatures; $t_{1/2}$ values were 61.2 days at 5°C and 35.5 days at 15°C. Mudd et al., (1983), however, found that in a sandy loam soil, the rate of degradation at 4°C was too slow to calculate a half-life value, but indicated it would have exceeded 70 days; in the same soil at 20°C the half-life value was 20.9 days.

Table 2 First-order half-lives ($t_{1/2}$ days) and determination coefficients (r^2) for the herbicides.

Soil type	Temperature (°C)	Moisture (%)	Isoproturon		Diflufenican	
			r^2	$t_{1/2}$	r^2	$t_{1/2}$
Topsoil	5	8.07	0.913	106.3	0.953	365
	5	12.14	0.936	72.4	0.951	315
	15	8.07	0.96	71.3	0.963	198
	15	12.14	0.899	55.5	0.931	169
Subsoil	15	10.96	0.966	66.3	-	-

Adsorption studies

Soil adsorption of isoproturon was characterised by the standard Freundlich distribution coefficient (k). Adsorption in the topsoil ($k = 2.184$, $1/n = 0.855$) was significantly higher than in the subsoil ($k = 0.255$, $1/n = 0.850$) indicating the greater potential for movement in the subsoil region. Adsorption of diflufenican at a single solution concentration was described by the linear distribution coefficient (K_d). Adsorption in the topsoil ($K_d = 345.6$) was similarly much higher than in the subsoil ($K_d = 37.8$) reflecting the lower organic content in

the subsoil and the greater binding potential of diflufenican. Desorption coefficients are not included in the PERSIST model and for the CALF model, the recommended adsorption increment value ($0.1 \times K_d$) was used.

Table 3 Isoproturon and diflufenican constants used in the computer models

Temperature (°C)	Moisture (%)	Isoproturon			Diflufenican		
		A* (days)	B*	Ea ⁺ (j/mol)	A* (days)	B*	Ea ⁺ (j/mol)
5	8.07	1654.7	-0.946	26624	1047.1	-0.363	40774
5	12.14	1654.7	-0.946	17221	1047.1	-0.363	41510
15	8.07	427.3	-0.617	26624	614.7	-0.39	40774
15	12.14	427.3	-0.617	17221	614.7	-0.39	41510

* Moisture constants + Activation energy

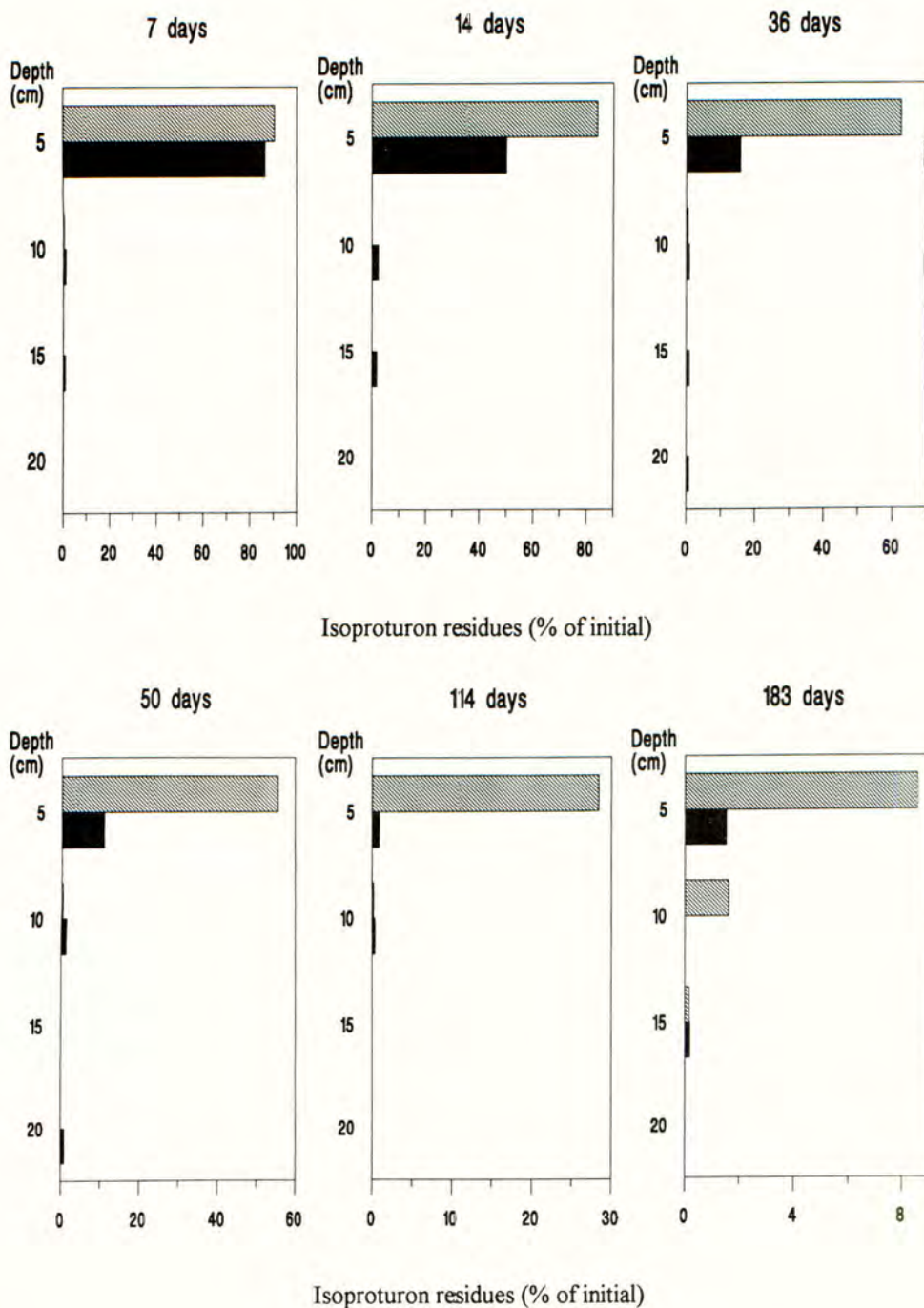
Field and column studies

The CALF predictions and observed residue data from both the column and field studies are shown in Figure 1 for isoproturon. The observed and PERSIST predicted residues for diflufenican are detailed in Table 4 and Figure 2. Diflufenican remained in the top 5 cm of the soil as would be anticipated from the degree of binding indicated by the adsorption studies, with degradation following first-order kinetics ($t_{1/2} = 217$ days, $r^2 = 0.818$). Like many other compounds (Hurle and Walker, 1980), the rate of degradation of diflufenican decreased considerably at lower residual concentrations. Considering the first six sampling times only, the regression coefficient (r^2) increased to 0.925 and the half-life reduced to 131 days. Isoproturon degraded quickly in both the field and column experiments, with less than 20% remaining after 36 days. This contrasted with the laboratory degradation studies where 48.4 to 81.0 % of applied remained after 33 days incubation at 15°C and 5°C, respectively. Movement of small amounts of residues was found down to the depth sampled in both the field (20 cm) and column studies (40 cm) but no isoproturon was detected in the column leachate. Under autumn application conditions when isoproturon is normally applied, transfer of greater concentrations through the soil profile might be expected. A spring application did not optimise differences in the climatic conditions between the South of England and West of Scotland. An autumn application would have been a more useful approach.

Prediction of persistence and mobility

The predictions of the PERSIST model closely followed the observed data for diflufenican residues (Table 4 and Figure 2), suggesting that the model and input data are satisfactory in predicting residues of this compound in this particular soil. The CALF model, using the laboratory derived degradation constants consistently overpredicted the isoproturon residues by a factor of 0.04 to 18.9, with the degree of overprediction increasing at lower concentrations (Figure 1). The CALF model predicts the movement of isoproturon more accurately than it predicts persistence, which it also overestimated in other studies (Blair et al., 1990; Mudd et al., 1983), although to a much lesser extent than found in these experiments.

Figure 1 The degradation and movement of isotroturon following spring application (▨ predicted; ■ observed)



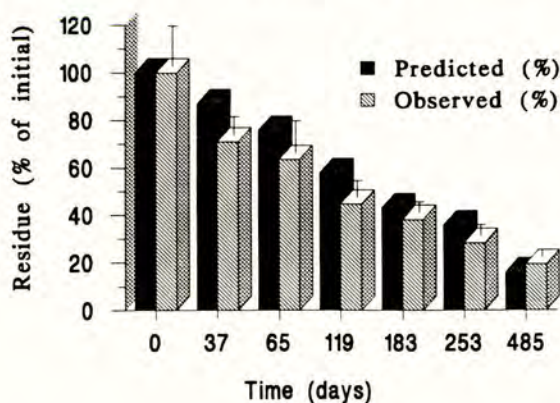
The use of shorter half-life values similar to those found by other workers would improve the CALF model predictions, suggesting that in this instance the laboratory degradation studies did not accurately reflect dissipation rates in the field. The predictions of other models are currently being explored using the isoproturon and diflufenican data.

Table 4 Predicted and observed diflufenican residues (% of initial)

Time (days)	Observed Residues (%)	Predicted Residues (%)
37	70.8 (8.2)	87.1
65	63.3 (14.3)	75.8
119	44.7 (7.3)	57.9
183	38.2 (4.7)	43.3
253	28.2 (5.0)	36.1
485	19.4 (3.0)	16.1

Figures in brackets indicate standard deviation of triplicate samples

Figure 2 Predicted and observed diflufenican residues



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STATISTICAL SIMULATION OF WATER AND PESTICIDE
MOVEMENT IN THE UNSATURATED ZONE.

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Please see page 141

MATHEMATICAL MODELLING OF PESTICIDE TRANSPORT FROM FARMLAND WITH STORM WATER

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ABSTRACT

A computer technique for modelling of liquid and solid run-off in agricultural catchments with complex land relief is considered. Transport of chemical compounds by rainstorm flow is described together with the development of geometrical model of a catchment. The model approximates the investigated territory relief and is applicable as a basis for problem solutions. The relief model is constructed by the use of the RELIEF program. The FLOW PATHWAY program determines the ways of storm water flow movement with the help of relief model elements (slopes and talweg network) along a curvilinear contour prescribed by the user, e.g. the water-edge bank line. LATERAL INFLOW program calculates the flow hydrograph with the help of FLOW, SEDIMENT and AGROCHEMICAL modules. It also estimates pollutograph of suspended sediments and agrochemicals. Problems of the program package interfacing with a geometric model of relief are also outlined. The interface enables the input of data for modelling, to perform and analyse results of calculations and to present graphs, tables and charts.

INTRODUCTION

At the present time, the problem of contamination and silting of water bodies by surface runoff from agricultural areas has assumed great importance. Agriculture is suffering major losses as a result of the washout of fertile topsoil with the fertilizers and toxic chemicals introduced into it.

Efficient planning of erosion control measures during the establishment of water conservation complexes at small river basins should be based on estimates of soil erosion and transport of nutrient elements and pesticides with the surface runoff. This should allow for the nonuniformity of distribution of the nonpoint sources of pollution over the agricultural watershed. One of the effective methods for estimation of the transport of substances from a watershed by surface runoff is mathematical modelling, the use of which makes it possible to consider a large number of natural and anthropogenic factors.

Effective measurements of pollutant loss from agricultural areas requires complex, physically-based models that simulate the significant processes affecting sediment and chemical loss from agricultural catchments. These models must also consider the effects of the spatial distribution of catchment parameters and are often termed as distributed parameter models. Such physically-based, distributed parameter models require four major submodels:

- a geometric model representing catchment topography and drainage patterns (mathematical image of the catchment area),
- a hydraulic model to simulate water movement through drainage network of the catchment,
- an erosion and sediment transport model; and
- a chemicals (nitrogen, phosphorus, and pesticides) transport and fate model.

APPROACH TO THE MODELLING OF WATERSHEDS

Construction of a geometrical model of a complex-relief area is an important part of the problem dealing with agrochemicals wash-out by nonpoint runoff. There are a lot of scenarios for the relief approximation, and the simplest ones consist in presentation of land slope(s) by plane, cascade of planes, or Wooding water catchments. But creation and development of geoinformation systems allowed to attain in the geometrical model more realistic representation of an area topography. The concepts outlined by Chery (1976), Beasley (1977), and Kuchment et al., (1983) correspond to such demands. In the first two works the catchment area is represented as a system of triangular and rectangular shape planes and channels network that represent catchment topography and ephemeral and perennial flow drainage network. But algorithmization of such approaches and software provision for them are, as we believe, a rather complicated problem. Beasley and his colleagues offered a more refined method. In it watersheds are represented as a system of square elements of overland flow plains ranging from 1 to 4 hectares in size. Concentrated flow through the catchment flow drainage network is modelled with rectangular cross-section channel elements of specified slope, width and hydraulic roughness. The model requires that all surface runoff exits out of the watershed from a single outlet cell and the channel network must be continuous.

The offered approach (Kolpak et al., 1982), (Bondarenko et al., 1988) is close to that of Beasley (1977). In this case, the territory is separated into regular square elements. But each element is represented by two triangular planes. This allows closer approximation of the relief model to reality, in particular to the talweg network. The software allows to obtain a flow hydrograph, pollutographs of sediments and agrochemicals within a geometrical model of relief at any contour. And in addition, the same software is applicable for data input, computations, and results output presentation as graphs, tables or charts.

STRUCTURAL SCHEME OF SOFTWARE

A part of the software used for the problem is shown in figure 1. Block 1 is the steering program; blocks 2, 3, and 4 implement the computational algorithms for building of a geometric relief model, find the runoff routes of storm waters along the planes of the relief model, and finally, compute the relationships of water flow moving along different runoff paths. These blocks have the most complex software. They are standardized, therefore the user need not change them. Blocks 5, 6 and 7, as follows from their names,

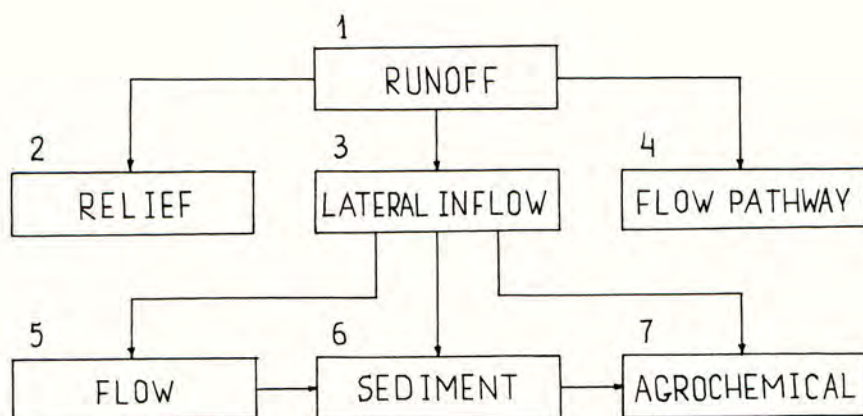


Figure 1. Module structure of software.

implement the computational algorithms for calculation of the runoff hydrograph, concentration of suspended matter in the flow, and transport of agrochemicals (it can be nitrogen, phosphorus or pesticide) from the slope. As the mechanism of formation of storm water runoff and transport of substances from the slope is further studied, these blocks can be improved and introduced into the software without changing blocks 2, 3, and 4.

RELIEF

Let us consider any territory G , enclosed by a rectangular contour S (on the plane of map). We fix the surface of the specified territory in a rectangular coordinate system $OXYZ$, superimpose the horizontal plane XOY onto the map reference plane, and direct the Z axis vertically upward through the left upper top of contour S . We draw vertical planes in this coordinate system parallel to the XOY and YOZ planes, respectively, with step dX along the X axis, step dY along the Y axis. We thus obtain a grid region G' consisting of nodes formed by the intersecting straight lines in the XOY plane. From the data of a topographical map, using the method of least squares, we calculate the heights of the relief at the nodes of grid region G' , the totality of which determines the geometric relief model (Kolpak et al., 1982). Naturally, the smaller dX and dY are, the more accurately the geometric model will correspond to the actual relief.

FLOW PATHWAY

Let us define terms necessary for FLOW PATHWAY module description. A geometrical model of a real catchment area fragment (top view) is presented in figure 2. It consists of 16 cells, each of two triangular planes. Numbers at the top and left part of the figure designate numbers of coordinate lines, and points of their crossing correspond

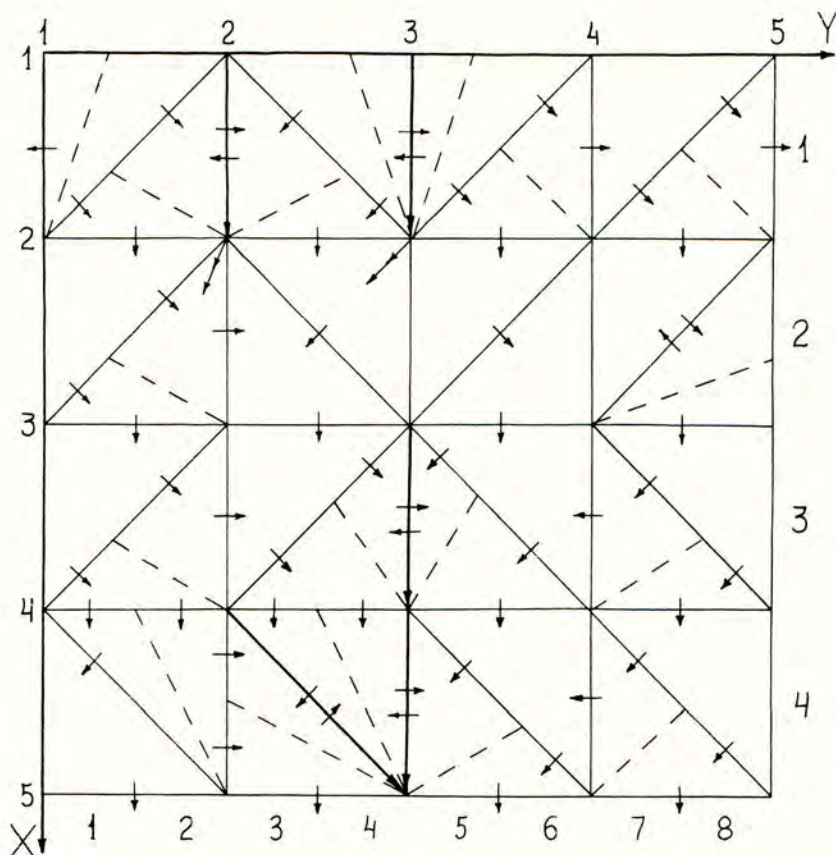


Figure 2. Direction of motion of water flow down the planes and talwegs of the geometric relief model.

to numbers of grid region G' nodes. For example, crossing, coordinate lines i and j produces node (i,j) . Numbers at the bottom and right part of the figure designate numbers of triangular planes of the relief model. For example, if coordinates originating from points designated by these figures (let it be figure 2 along the X axis and figure 7 along the Y axis) go parallel to the X and Y axes then the point of their crossing will be associated with the traingular plane $IJ=I*100+J$. When $I=2$ and $J=7$ it will be plane (207). And, finally, the line connecting two nodes in grid region G' $(i,j) - (i+1,j)$ or $(i,j) - (i,j+1)$ will be called sector. Sequence of such notations will be called L contour. The pointer indicates direction of water outflow from the plane. The dash line indicates the watershed divide, and double pointers indicate water flow from talweg to the plane.

The FLOW PATHWAY module determines the path of a water flow for a contour L specified in advance. In general, this contour is a broken line consisting of sectors

connecting the two adjacent nodes of grid region G' . For each of the sectors of the contour, the FLOW PATHWAY module plots the runoff-forming chains of triangular planes and thereby defines the individual watersheds, the runoff from which reaches contour L in a distributed manner, i.e., uniformly along the length of a sector. The nodes of the contour are also analyzed. If the runoff from a talweg enters the node of a contour, a runoff-forming chain is formed (which may include a graph of the talwegs), and in this case, a concentrated discharge to contour L is considered. In the computer representation, this will be an ordered recording of the numbers of the triangles. This recording will be called the runoff-forming cascade of planes (RCP).

So, RCP to sector (5,1)-(5,2) will include planes: (101) - (102) - (201) - (202) - (301) - (302) - (402) - (401). The RCP having a runoff into the node formed by two adjacent sectors is similarly constructed. The design of the RCP considers all possible cases of direction of motion of the flow at the geometrical model:

- runoff from one triangle to another: (101) - (102);
- runoff from one triangle to the two other adjacent to it: (102) - (103) and (201);
- the triangle with inflow from the two other adjacent to it: (202) and (204) - (203);
- the two adjacent triangles form a talweg: (102) and (103), and the system of such pairs of triangles forms the graph of talwegs, for example, sectors (3,3)-(4,3) and (4,3)-(5,3) and (4,2)-(5,3);
- two (three) talwegs have a runoff into one node of contour L: node (5,3);
- two (three) talwegs originate from the same node;
- the runoff from talweg (graph of a talweg) reaches a triangle: talweg (1,2)-(2,2) into plane (202).

LATERAL INFLOW

The system of runoff-forming cascade of planes is the initial information in the calculation of runoff hydrographs and concentration of substances in the runoff with the use of the LATERAL INFLOW module. The RUNOFF PATH and LATERAL INFLOW modules realized in the ES 1060 computer system in PL/1 language were set up by use of the principle of structural programming. The module construction makes it possible, without changing the hierarchical structure of the programs, to replace one module by another. For example, the runoff of water from a slope can be described by the Nesh equation, the kinematic water equation, and hydrodynamic equations. On the basis of each of these equations, one can construct a FLOW submodel that can easily be connected to the LATERAL INFLOW module.

FLOW CHARACTERIZATION

The one-dimensional continuity equation forms the basis of mathematical model of storm water flow down a flat slope. Its integration by the slope length, with allowance for the Manning equation, will give a typical non-linear first-order differential equation pertaining to the water cross-flow area on the slope (Moskovkin, et al., 1983). Its numerical solution by the known Runge-Kutta method allow information on the slope

flow layer depth to be obtained and specify the slope length and width, bottom layer roughness coefficient, as well as filtration intensity as a function of the soil humidity, water discharge at the slope inflow and that of the lateral inflow. This algorithm is implemented through FLOW PATHWAY.

SEDIMENT DETACHMENT AND MOVEMENT

Soil erosion, as it relates to nonpoint source pollution, can be viewed as two separate processes, - detachment of particles from the soil mass and transport of these particles into the water body. These processes are described by a particle transport differential equation of hyperbolic type, with allowance for lateral inflow. The particle detachment process can be described with the help of a concentration value corresponding to a transport capacity of the flow, while a sedimentation slope length averaged equation will produce an ordinary differential equation of the first order for suspended particles concentration in the storm water flow from the slope (Moskovkin, et al., 1983). The developed algorithm is implemented through SEDIMENT procedure.

PESTICIDE

Generally pesticides enter surface waters in solution or are adsorbed on soil particles. So the pesticide transport determination algorithm was developed together with FLOW and SEDIMENT algorithm. For this purpose a popular Freundlich isotherm was applied. A dynamic equilibrium concentration of pesticide in the solution was obtained and this enabled the determination of the adsorbed pesticide concentration (Moskovkin, et al., 1983). The algorithm is implemented through AGROCHEMICAL procedure.

INTERFACE

The solution of such complex problems require the input of large quantities of data. To facilitate operations with the program package, a user-friendly interface was developed. It is based on the idea to substitute mnemonic code for numeric input data. Let us take, for example, a water catchment area consisting of 1000 cells. It is necessary to set an individual input data "passport" for each cell. The data should correspond to a number of FLOW, SEDIMENT and AGROCHEMICAL models' parameters (over 20). All in all, the user has to input to PC memory up to 20000 numbers. Distribution of each parameter in the water catchment plane presents an involved mosaic-like picture. The interface enables the user to display on the screen this mosaic representing the parameter distribution. For this purpose with the help of "Insert" key a data bank is displayed on the screen as a table with N values of the parameter, - an individual colour corresponds to each value, - together with the catchment contour. The process is repeated for each parameter of the models. In this way a file is formed, containing "passport" data for each cell of the catchment. Other software are also implemented in the interactive mode.

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INFLUENCE OF AGRICULTURAL MANAGEMENT AND PESTICIDE SORPTION ON LOSSES TO SURFACE WATERS

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ABSTRACT

Phase III of the Brimstone Farm experiment, initiated in autumn 1993, is a collaborative government and industry research programme with the objective of developing management practices for reducing drainage losses of pesticides from cracking clay soils. In the first year of this four-year study, effects of drainage restrictors and half-rate applications of pesticides were studied on 12 replicated plot lysimeters using isoproturon and pendimethalin. Both practices resulted in reductions in peak concentrations and total losses. In these studies, isoproturon losses ranged from 1.7% of applied (half-rate) to 3.3% of applied (control). Equivalent losses for pendimethalin were 0.2 to 0.3% of applied. On unreplicated pilot plots, four compounds with a wide range of sorption properties were applied to determine the effects of tillage practices, soil incorporation of pesticides, and the use of a soil sealant. Losses (as a percentage of applied) in the four plots ranged from 2.8 to 5.2% for triasulfuron, 2.1 to 3.3% for isoproturon, 0.02 to 0.05% for prochloraz, and 0.009 to 0.04% for pendimethalin. The studies on reduced drainage, fine tillage and use of a soil sealant were promising enough to warrant inclusion in the 1994-1995 experimental programme.

INTRODUCTION

The loss of pesticides from soils depends on many factors, including the property of the chemical itself and soil structural development. The development of semi-continuous cracks and

macropores in clay soils can lead to rapid water movement to depth and the potential for rapid pesticide losses (Harris *et al.*, 1994). As a consequence, the movement of pesticides through clay soils, and the development of appropriate measures to reduce the loss is not well understood. This paper reports on measurements of the movement of a range of pesticides to drainage systems and presents results from the first year of a four-year study designed to follow up previous research at Brimstone Farm. The specific objective of the work was to reduce losses of pesticides following autumn applications to a cracking clay soil.

MATERIALS AND METHODS

Experimental design

The study was undertaken at the ADAS/RES collaborative plot facility at Brimstone Farm, Oxfordshire, (Cannell *et al.*, 1984, Harris *et al.*, 1994), which is established on a heavy structured clay (60% <2 μm) of the Denchworth Series. The site, at an altitude of about 130m OD, receives an average annual rainfall of 686 mm and is representative of many cereal-growing areas of Central England. The layout consisted of twelve core plots, providing three replicated treatments, plus four unreplicated pilot plots.

Effective drainage in this slowly permeable soil is provided by pipe-drains at 0.9 m depth with permeable backfill to within 0.35 m of the ground surface. A secondary drainage system is drawn at right-angles to the pipe drain at 0.55 m depth and 2 m spacing on each of the sixteen hydrologically isolated plots. On twelve plots this consisted of a conventional mole-drainage system, drawn in 1992 or 1993, but two plots have gravel-filled moles and two plots have close-spaced pipes, all installed in 1988 (Harris *et al.*, 1994). Although effective drainage was provided on all plots, a restrictor was also installed in the drainage pipe leading from each of the core plots. The restrictor consisted of a rotatable U-bend which could be raised to any height thus providing a means to prevent drainage leaving the plot until a watertable was established in the soil profile to the height of the U-bend.

Treatments

Replicated treatments 1-3 were established on the core plots together with unreplicated treatments a-d on the pilot plots. The treatments selected were:

- Treatment (1) Full-rate pesticide application, restricted drainage
- Treatment (2) Full-rate pesticide application, normal drainage (control)
- Treatment (3) Half-rate pesticide application, normal drainage

- Treatment (a) Cultivate in straw/prepare seedbed/drill/spray
- Treatment (b) Cultivate in straw/prepare seedbed/drill/spray/include soil sealant
- Treatment (c) Cultivate in straw/prepare seedbed/spray/incorporate/drill
- Treatment (d) Plough in straw/prepare fine seedbed/drill/spray

These treatments were chosen according to the following rationale. Reduced application rates should result in decreases in pesticide losses which are at least proportional to the reduced rate. The drainage restrictor has the potential for reducing pesticide losses due to a combination of increased storage in the soil profile as well as potentially encouraging the closure of cracks

and sealing the macropores. The fine tilth was tested to see if a finer surface structure also inhibited macropore flow. Likewise, the soil sealant had the potential for helping to reduce flow by 'plugging' soil cracks and/or reducing the infiltration of water into the soil. Finally it was considered that incorporation of the chemical into the soil may reduce the contact of pesticides with rapidly infiltrating water.

Agronomy

The site was tined, power harrowed and rolled in late September/early October and drilled to winter wheat on 21 October 1993. Additional cultivations were also undertaken to provide the appropriate treatment seedbed conditions. The herbicides isoproturon and pendimethalin were applied to the core plots (2 November) and applications of isoproturon, pendimethalin, triasulfuron and prochloraz were made to the pilot plots (4 November), see Table 1.

TABLE 1. Pesticide applications and measured sorption (K_d) values, with the exception of K_d for triasulfuron which is estimated, (Bromilow, Personal Communication).

	Pesticide	Trade name	Active ingredient	Sorption
Core plots	isoproturon	Arelon	Full-rate 2438 g/ha	2.9
			Half-rate 1219 g/ha	
	pendimethalin	Stomp 400	Full-rate 2000 g/ha	88
			Half-rate 1000 g/ha	
Pilot Plots	isoproturon	Tolkan Liquid	2500 g/ha	2.9
	pendimethalin	Stomp 400	2000 g/ha	88
	triasulfuron	Logran 20WG	7.5 g/ha	<1
	prochloraz	Sportak Sierra HF	405 g/ha	75

Hydrological monitoring and water sampling

Continuous measurements of drainflow and flow from the near surface-layer (measured in a single plough furrow) were made from all plots in V-notch weirs (Cannell *et al.*, 1984). The watertable was monitored in the centre of each plot using capacitive probes; on those plots where the drainage restrictor was employed the effect was also measured within the drainage system itself. All data were collected on a datalogger and automatically transferred by remote telemetry to the base-station.

Epic programmable water samplers delivered flow-related single samples through teflon tubing direct to darkened glass bottles (Harris *et al.*, 1991) from four drainflow events of winter 1993/94. All samples were taken from the plot drain before further degradation and dilution of pesticide concentrations in river systems could occur. For the core plots samples were analysed individually to provide concentrations against time as well as total loss. For the pilot plots, sub-samples were taken, proportional to flow, and then bulked to provide a single sample for analysis for each event. Samples were removed from site within 48 hours and stored at 4°C until extracted and analysed.

RESULTS

Weather patterns, drainage and water sampling

Under the wet conditions experienced at Brimstone Farm in autumn 1993 the onset of drainflow in mid-November was unusually early and occurred shortly after the pesticide applications. A rainfall event of 10.6 mm on 13/14 November resulted in drainflow on all plots and created the first sampled event. Thereafter drainflow events occurred in response to 45, 78 and 64 mm rainfalls in November, December and January respectively. Two further drainage events were sampled at approximately two week intervals starting on 8 and 17 December 1993 respectively and the final event was sampled on 1 January 1994. Total winter drainage (November-March) was on average 92 % of rainfall.

The drainage restrictors delayed drainage by four hours on average in Event 1 and reduced the depth to the watertable in the following periods of rainfall. As a consequence surface layer flow was noticeably increased on the four core plots where the restrictor was employed (Table 2).

TABLE 2. Runoff as drainage (D) and near surface layer flow (SL) from the core plots and drainage from pilot plots and winter rainfall. All units in mm.

1993 - 1994	Core plots Treatment 1		Core plots Treatment 2		Core plots Treatment 3		Pilot plots Treatments	Rainfall
	D	SL	D	SL	D	SL	D	
November	5.08	0.04	6.17	0.06	3.79	0.51	2.11	45.0
December	72.57	3.14	96.63	1.57	82.61	4.14	35.04	78.4
January	78.28	3.39	95.25	1.72	85.86	7.50	36.98	63.6
February	44.53	1.62	58.18	0.94	60.28	3.92	38.54	47.8
March	5.74	0.64	13.98	1.39	8.87	1.09	7.64	37.6

Pesticide movement

In the first drainage event sampled on the core plots, short-term peak concentrations of isoproturon were 115 µg/l where the herbicide was applied at half-rate, 190 µg/l where the drainage restrictors were in use, and 465 µg/l on the control plots. Later events showed smaller differences. Losses over the four events on the core plots for the same treatments ranged from 3.8 g to 15.3 g, equivalent to 1.7 to 3.3% of applied. However, by interpolating mean daily data over the full sampling period total losses were calculated as ranging from 8.5 g to 20 g (Figure 1). Losses of pendimethalin from the core plots were 0.02% to 0.03% of applied.

Data for losses in the bulk samples from the pilot plots are given in Table 3. Losses were equivalent to 2.1-3.2% of applied for isoproturon, 0.009-0.04% for pendimethalin, 2.9-5.2% for triasulfuron and 0.02-0.05% for prochloraz. Because of the lack of replication these results for the pilot plots must be confirmed with follow up experiments since variability

between the pilot plots, each with a different treatment, is similar to that observed between the core plots, receiving the same treatment. The results obtained with the soil sealant and the fine seed-bed were considered promising enough to warrant additional testing in the 1994-95 experimental program. Soil incorporation of pesticides had little apparent effect on drainage losses.



Figure 1 Interpolated mean cumulative isoproturon loss (core plots) over four drainage events

TABLE 3 Mean concentrations and total losses of each of the four pesticides, and drainflows (pilot plots) expressed as a percentage of the control (Treatment a)

Treatment	Mean concentrations			Total loss		
	Soil sealant	Incorporate pesticide	Fine seedbed	Soil sealant	Incorporate pesticide	Fine seedbed
	b	c	d	b	c	d
Triasulfuron	95	100	76	68	120	108
Isoproturon	100	80	60	74	93	76
Prochloraz	79	90	92	57	123	113
Pendimethalin	63	137	74	44	197	91
Drainage				71	140	132

DISCUSSION

Although the results are preliminary, based on one season only, and some of the treatment effects need confirmation, it is evident that manipulation of soil conditions and drainage treatments may prove to be successful in reducing the movement of pesticides to surface waters via sub-surface drainage. The studies on the core plots suggested that both the drainage restrictor and half-rate pesticide applications had positive effects on reducing peak concentrations and total losses of isoproturon and pendimethalin. The effect of the drainage restrictors was perhaps surprising given the wet conditions experienced and hence the short period over which they affected soil watertables. However, in companion work (Catt, Personal Communication, 1994) a reduction of nitrate loss of 10% resulted from the application of the restricted drainage treatment.

Useful reductions of at least 50% in peak concentration and total loss were achieved by half-rate applications for both isoproturon and pendimethalin. Data from the pilot plots demonstrated that losses, as a percent of applied, of the less mobile pendimethalin and prochloraz were much less than for isoproturon and triasulfuron, although triasulfuron was applied at much lower rates than for the other pesticides. The pilot experiments indicate that soil tillage and the use of a soil sealant warrant a more detailed examination.

Although only a small proportion of the amounts applied (up to 3.3% for the four events on the control plot), total losses were higher than seen previously at the site under drier conditions (Harris *et al.*, 1994) and reported by other workers (Wauchope 1978).

ACKNOWLEDGEMENTS

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A STEWARDSHIP PROGRAMME ON DIURON AIMED AT PROTECTING UK WATER QUALITY

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ABSTRACT

Diuron is now the most widely used residual herbicide in the non agricultural (amenity) market. Best practice guidelines for the use of diuron on porous and non porous surfaces were drafted to meet the EU drinking water standard. Training was undertaken to implement the best practice guidelines. Research showed that diuron sprayed over open drains or in the gullies/channel around non-porous surfaces posed the greatest risk to water quality. Preliminary results indicate that despite the rising levels of use, the number of water samples containing more than 1µg/litre of diuron is falling. Areas of future work are outlined.

INTRODUCTION

Diuron is now the main "total" residual herbicide used to maintain amenity areas. By "total" it is meant that the material is used to keep areas vegetation free. Being a urea based active it controls weed growth of a broad range of species by inhibiting chlorophyll production. Both its physical and chemical properties are well known. (Hance and Holly, 1990). Despite being strongly adsorbed onto soil particles it has been detected in water.

Non compliances (samples which have more than 0.1µg/litre) have been reported for this herbicide (DWI, 1993) from a number of water service company areas. To date, the quantity of herbicides found in water sources have been limited and do not pose a health or ecological risk, however, the European Union (EU) require, as part of the Drinking Water Directive, that no single pesticide exceed 0.1µg/litre in drinking water.

A number of possible routes to water exist:-

- a) Direct introduction via drains and gullies/channels.
- b) Use of high application rates and non targeted spraying on non-porous surfaces causing run-off from the target.
- c) Spraying during periods when the risk of wash-off from intense rainfall is high.
- d) Point source via incorrect disposal of washings or packaging.

DIURON STEWARDSHIP PROGRAMME

The programme was started in March 1992. It had the objective of minimising the amount the amount of herbicide reaching water sources. It set out to achieve this by:-

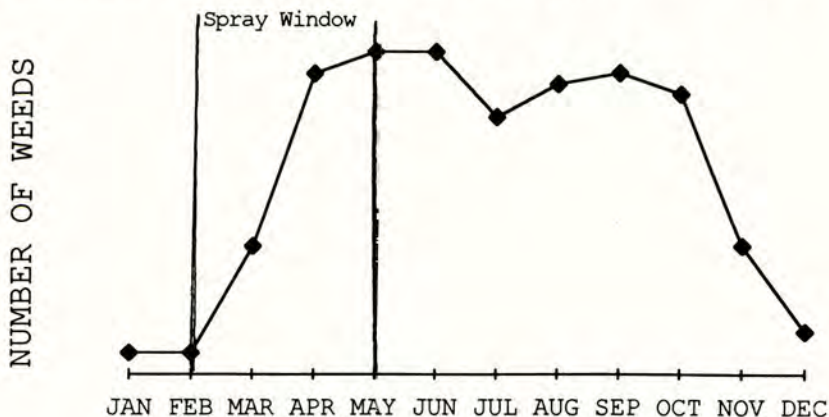
1. Defining the best practice for the active

On porous surfaces the maximum recommended application rates were reduced from 27 kg diuron to 7.2 kg diuron/ha. Tank mixes with foliar acting actives such as glyphosate and paraquat were included on the product labels. This enables diuron to act as the pre-emergence, seedling germination control component or in a mixture allowing additional rate reductions.

New label recommendations were approved for all products containing this active when used on non-porous surfaces. These label recommendations are:-

- a) No application permitted over drains or in gullies/channels.
- b) Only the lowest recommended rates for the task in hand should be used.
- c) Application to those areas where weeds can grow is the preferred approach. Unless absolutely necessary broadcast spraying must be avoided. Where it is used low water volumes are recommended which helps reduce any initial run-off.
- d) A spraying window of February to April, reflecting the period of the year when diuron works most effectively has been defined. (Figure 1).

FIGURE 1: The seasonal pattern of weed seedling emergence, and the diuron spray window for non porous surfaces. (Davies 1992)



2. Changing Management Strategies

Following the production of the best practice guidelines for this herbicide a large and diverse education and training programme was undertaken (Davies et al. 1993). Local authorities and other bodies managing weed control programmes on non-porous surfaces have adopted the new practices.

3. Preliminary Findings

a) Transport Mechanisms

During 1993 a study to identify the main transport mechanisms was carried out with the co-operation of Severn Trent Water Service and Thames Water Service Companies. Two river catchments where diuron had been detected were identified. By using questionnaires, interviews and asking to see copies of the spray records (which have to be recorded under the Food and Environment Protection Act) the following objectives were set:-

- 1) To monitor all diuron usage within each specific water catchment
- 2) Establish the primary routes to water for this herbicide.
- 3) Investigate the potential to develop future recommendations/management plans for diuron.

Where possible, interviews were carried out with the managers responsible for the vegetation control on the following non-agricultural land:-

- 1) Local authority use on pavements and in parks around the base of buildings.
- 2) Public utilities (e.g. electricity or gas companies).
- 3) Contractors responsible for national transport links i.e. Department of Transport.

Interviews were carried out in two phases, in the spring of 1993 to understand the organisations planned spraying programme and to collect historical data. The second contact was made in the autumn of 1993 to record what had actually happened.

Usage data was collected on:- Volumes, date, rate, type of surface treated and application equipment. Information on disposal procedures was also recorded:- i.e empty containers, unused product, tank mixings and washings.

Both Water Service Companies, in addition to providing historical data also carried out water sampling at key sites on a three week cycle.

Midlands Catchment

The only usage identified was on open soil surfaces on Public Utility areas. No local authority use on non-porous (hard) surfaces was recorded.

Where as diuron was detected in 1991 within this catchment, it was not detected in either 1992 or 1993. When used correctly on open soil surfaces diuron did not pose a significant risk to water quality within this catchment.

South East Catchment

Initially the survey boundary was within the motorway encircling London (M25). Diuron was only being used on open soil sites such as gravel areas. The uses were later in the year than the peak of occurrence of the active in the water samples. When a sampling point was established where the main river entered the survey area, similar peaks and levels of occurrence were recorded as were found at where the river left the area.

With this in mind the survey area was redefined. Efforts were directed outside the M25 on a more rural zone. Again, diuron was being applied to porous areas. In addition, one use of the herbicide was identified up stream from the water sampling point where over the previous three months high rates of diuron had been applied over all the authority's pavement surface. Application was made in line with the label recommendations at the time i.e. over open drains, in the gully/kerb lines and at a high rate. Although it is impossible to be certain that this was the probable cause of the residues in water. All of the new recommendations have now been adopted by this organisation and the levels of diuron in this water source have declined.

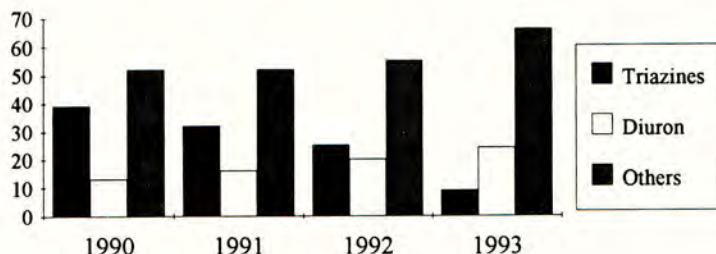
Direct introduction at high rates into drains and gullies was identified as the main route to water. Applications to porous surfaces or incorrect disposal are not significant.

b) Use Levels

The DOE (1990) study on herbicides used in the non crop areas of England and Wales included both total and selective herbicides. In all, some 500 tonnes of a.i. were estimated to have been applied. Triazines were estimated to be 39% of all of the pesticides used. (Figure 2).

Following the revocation of their non-agricultural uses in 1991 and the subsequent selling out period the last triazine stocks were applied in 1993. Customers changed to either diuron or glyphosate to maintain their sites in a safe and hygienic state. The proportion of diuron used increased from 13 to 24%.

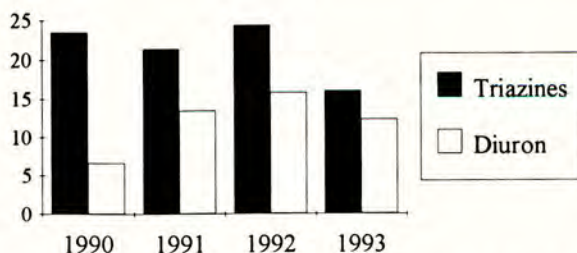
FIGURE 2: Proportion (%) of a.i. used in the non-agricultural market (DOE 1990)



Non Compliance trends

Each year since 1990, the Drinking Water Inspectorate have issued a breakdown by water company of the water quality results. The data for diuron and the triazines for each area have been collated and the frequency expressed as a percentage. (Figure 3).

FIGURE 3: The number of samples containing 0.1µg/l or above, triazine or diuron by the total number of samples tested expressed as a percentage over the four year period (DWI 1990, 1991, 1992, 1994).



Triazine levels fell in 1993 from an established plateau as use levels declined. Diuron non-compliances increased from 6.6% in 1990 to 15.8% by 1992. Despite a continued increase in use, 1993 shows a decline of non-compliances to 12%. It is probable that the stewardship campaign is the major influence in this positive trend.

4. The Future

Now that diuron has replaced the triazines as the major non-agriculture residual herbicide it is used more widely than before. To date this increased use combined with the clarification on its correct application has led to at least a containment of its risk to water quality. All members of the amenity agrochemical industry and their customers have combined to implement the stewardship programme. Although it is still early days it would seem that this effort is being rewarded.

The support of the water service and supply companies who hold the view that "the answer to water contamination by non-agricultural herbicides does not lie simply in the banning of the active ingredients (White & Pinkstone, 1993), has been central to the stewardship programme. Except for point source and accidental spillage the highest risk to water quality is posed by the use of herbicides on non-porous surfaces. Understanding the mechanisms and principles behind pesticide movement from non-porous surfaces to water is key to any future progress. Work in this area would enable the design of better application strategies (rates, formulations, actives, timings and methods).

Products containing diuron may soon be approved for use in the domestic (amateur DIY) market. The stewardship programme will have to be extended into this new market area, or there is a real risk of all of the excellent co-operative work of this initiative could be undermined.

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CLAY-BASED CONTROLLED RELEASE FORMULATION AS A TOOL FOR MINIMIZING PESTICIDE LEACHING

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ABSTRACT

For a field experiment controlled release formulations for the two herbicides trifluralin and terbuthylazine were produced using ^{14}C -labelled compounds. The formulations (beads of clay and alginate) were applied to lysimeters (diameter 60 cm, depth 70 cm) containing undisturbed soil cores of a loamy sand. In order to compare the behaviour of the controlled release formulations with the EC-formulated active ingredients, the latter were applied to separate lysimeters. After application of recommended amounts (trifluralin 1 kg/ha and terbuthylazine 0.75 kg/ha) in all cases corn was sown. Over a period of 18 months the leaching water was collected. The amount of leached radioactivity was measured. At the end of the experiment the distribution of the compounds in the soil/plant system was determined. Trifluralin leaching was less from the controlled release formulation than from the EC-formulation. In the case of terbuthylazine no clear difference could be observed.

INTRODUCTION

Frequently pesticides have to be applied in dosages larger than necessary for the control of the target organisms. The concentration of active ingredients in soil is reduced after application by volatilization, by fixation to soil particles, by degradation and by leaching. Controlled (slow) release formulations have been developed in order to reduce these adverse effects (e.g. Bahadir, 1990).

The use of natural substances as carrier material for controlled release (CR) formulations has different advantages (Johnson and Pepperman, 1995). They do not contaminate the soil with strange compounds and often have a low price. Gerstl, Mingelgrin and Nasser (1993) developed CR-formulations based on clay and alginate, which show reasonable release rates for several pesticides. The components are formulated as small beads (≈ 1 mm in diameter) with variable contents of the active ingredient.

Lysimeter experiments were used to compare the leaching behaviour of two herbicides (terbuthylazine, trifluralin), both formulated as emulsifiable concentrate and as clay-alginate beads. In order to follow the fate and the degradation of the active ingredients they were applied as ^{14}C -labelled compounds. Over a period of 18 months the leaching water was collected and analysed. The distribution of radioactivity in the soil and in the plants was determined at the end of the experiment.

MATERIAL AND METHODS

Used pesticides

The beads for the controlled release formulations were prepared according to the method of Gerstl and Mingelgrin (1993). In this method bentonite (Fisher) is used as the clay component and alginate (Fluka, Switzerland) as natural polymer. Clay, alginate, and the active ingredient are suspended in water. The polymerisation of the alginate is carried out by dropping the suspension into a CaCl₂-solution. Beads with a diameter of approximately 1 mm are formed and then dried at room temperature.

Trifluralin and terbutylazine were supplied by Ehrenstorfer with a degree of a purity of 99% and 99.9%, respectively. The EC-formulations used for the comparison were Gardoprim 500 flüssig® (Ciba-Geigy) and Elancolan® (DowElanco).

¹⁴C-Terbutylazine (ring uniform labelled) was supplied by NEN (DuPont) with a specific activity of 3.62 MBq/mg and a radiochemical purity of 98.5%. ¹⁴C-Trifluralin (ring uniform labelled) was supplied by Sigma with a specific activity of 1.63 MBq/mg and a radiochemical purity of 98.0%.

In order to get the EC-formulations radioactive labelled small amounts of the ¹⁴C-active ingredients were added to the suspensions (< 2%). The composition of the formulations applied to the lysimeters is shown in the following table.

TABLE 1. Amounts of pesticides applied to the lysimeters

	Elancolan	CR-Tri-fluralin	Gardoprim 500 flüssig	CR-Ter-butylazine
Radioactivity (MBq)	3.56	2.91	3.48	4.56
Amount of a. i. (mg)	27.10	28.60	20.80	21.90
Application area (m ²)	0.28	0.28	0.28	0.28
Application rate (kg/ha)	0.96	1.01	0.74	0.78

Course of the lysimeter experiments

Four lysimeters with a diameter of 60 cm and a depth of 70 cm were filled with undisturbed soil cores of a loamy sand (80.2% sand, 2.3% clay, 1.4% organic carbon) on March 1993. For the application of the pesticides at the end of May 1993 the top 2 cm layers of the soil was taken.

In the case of the CR-formulations 440 beads were applied onto the soil in a regular pattern and covered with the top soil layer. The average distance between two beads was 2.5 cm. The EC-formulations were emulsified in an amount of water corresponding to 400 l/ha and then mixed into the top soil layer (2 cm) in lab with the mixer. The contaminated soil was then put back to the lysimeters.

Corn was sown one week later, in a depth of 5 cm and with distances of 15 cm from seed to seed. The lysimeters were irrigated when weather conditions made it necessary. Leaching water was collected and analysed continuously. On 18th of October 1993 corn and weeds

were cut. Their fresh weight was recorded and the amount of radioactivity determined.

In the following year corn was sown on 11th of May 1994. The experiment was terminated to 10th of October 1994 by cutting the corn-plants and weeds and by sampling the soil in five layers.

Analysis

Corn and weeds were harvested separately, dried, homogenized, and aliquots combusted in the oxidizer. Afterwards radioactivity was measured by Liquid Scintillation Counting (LSC).

Roots from the first layer, 0-5 cm, were removed from the soil by sieving and then treated as described above.

Leaching water was also measured by LSC.

Soil was sampled with a hand auger. The first (0-5 cm) and the second (5-10 cm) layer, were extracted for 12 hours with methanol (shaker, room temperature). Extracted radioactivity was measured. The extracted soil was dried and aliquots combusted in the oxidizer, in order to determine the amount of non-extracted radioactivity. Samples of the third (10-20 cm), the fourth (20-40 cm) and the fifth layer (40-70 cm) were dried, and combusted and the total amount of radioactivity counted by LSC.

RESULTS

The amount of rainfall and irrigated water applied to the lysimeters and the leached radioactivity from the different lysimeters are shown in Figures 1 and 2.

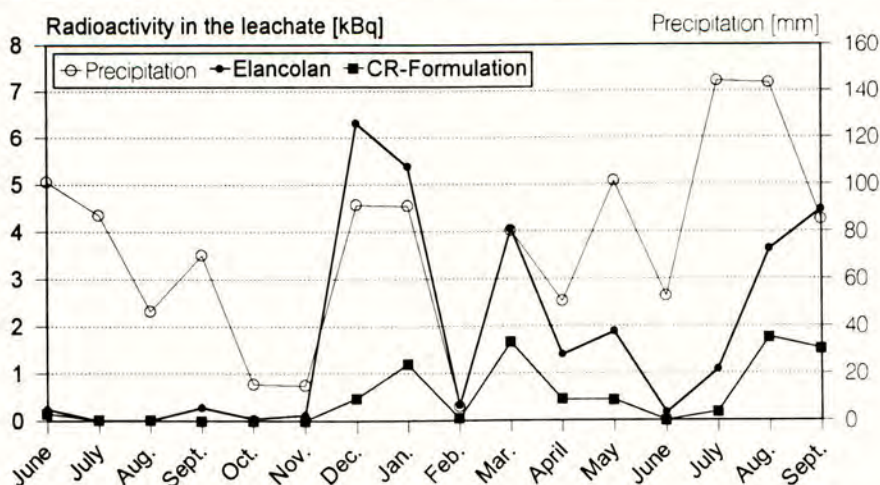


FIGURE 1. Monthly precipitation and leached radioactivity with time for **trifluralin**.

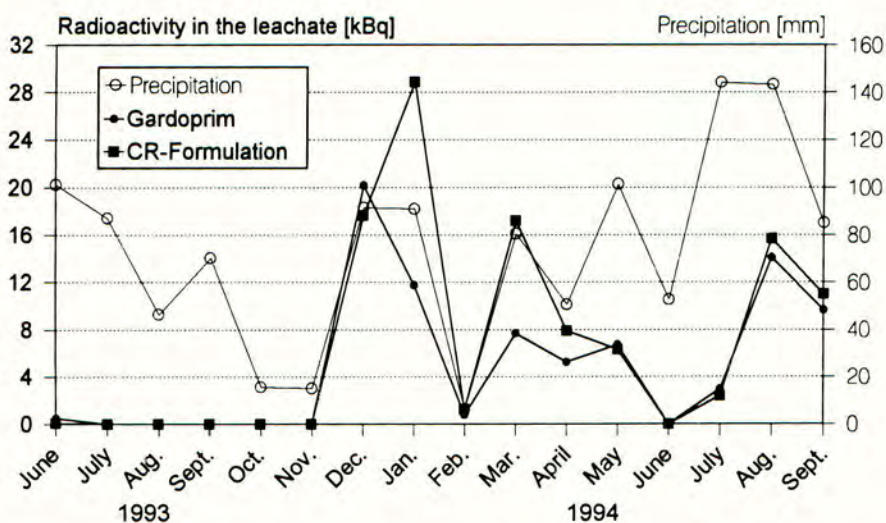


FIGURE 2. Monthly precipitation and leached radioactivity with time for **terbuthylazine**.

The complete balance of the fate of radioactivity for the four lysimeters is shown in table 2.

TABLE 2. Distribution and balance of radioactivity in the lysimeters after 18 months.

	Trifluralin				Terbuthylazine			
	EC-Formul.		CR-Formul.		EC-Formul.		CR-Formul.	
	kBq	%	kBq	%	kBq	%	kBq	%
Applied radioactivity	3560	100.0	2905.0	100.0	3477.0	100.0	4563.0	100.0
Leaching water	29.4	0.8	7.9	0.3	79.5	2.3	108.3	2.4
Plants								
Corn	4.5	0.1	6.7	0.2	6.3	0.2	12.5	0.3
Weeds	10.7	0.3	4.3	0.2	13.6	0.4	40.9	0.9
Roots	1.0	0.0	1.3	0.1	1.6	0.1	1.2	0.0
Sum plants	16.2	0.5	12.4	0.4	21.5	0.6	54.5	1.2
Soil								
0-5 cm:								
extracted	581.9	16.4	577.3	19.9	406.2	11.7	359.2	7.9
non-extracted	581.4	16.3	330.0	11.4	1865.8	53.7	1470.6	32.2
5-10 cm:								
extracted	179.0	5.0	66.2	2.6	126.6	3.6	286.6	6.3
non-extracted	184.7	5.2	58.7	2.0	29.7	0.9	961.8	21.1
10-20 cm (sum)	115.8	3.3	34.8	1.2	271.6	7.8	366.7	8.0
20-40 cm (sum)	45.5	1.3	11.7	0.4	77.9	2.2	120.8	2.7
40-70 cm (sum)	23.3	0.7	20.7	0.7	73.3	2.1	32.1	0.7
Sum soil	1711.6	48.1	1099.4	38.1	2851.2	82.0	3597.8	78.9
Balance		49.4		38.8		84.9		82.5

DISCUSSION

In all lysimeters the break through of the active ingredients or of radioactive substances derived from them started half a year after the application with increasing rainfall in late autumn. This and the whole course of the curves in figures 1 and 2 meet the expectations. In the case of trifluralin the CR-formulation always shows smaller amounts of leached radioactivity.

Over the 18 months the leaching of trifluralin is reduced to less than the half of the EC-formulation by using the CR-formulation. Due to the relatively high K_d -value of trifluralin the leaching was not substantial. During the experiment the concentration of trifluralin in the leachate was always below 0.1 $\mu\text{g/l}$.

The balance sheet shows, that there was no great difference in the uptake of trifluralin by plants, both corn and weeds. This is surprising because the concentration in the top soil (0 - 10 cm) of the lysimeter with the CR-formulation was higher than in the lysimeter with the EC-formulation. The amount of radioactivity in the lower layers was much higher in the case of Elancolan. If this leads to a long-term leaching behaviour has to be clarified by the identification of the radioactive substance which are existing there. From the results worked out by Golab (1979) it can be presumed that trifluralin is metabolized to a greater extent after 18 months.

Also the high portion of non-extractable residues found in the lysimeter experiment is similar to the results of other authors (Wheeler, 1979 and Golab, 1979). It is interesting, that more non-extractable residues are formed from the EC-formulation. An interpretation of this phenomenon is not possible at the moment. Further investigations have to clear up how the non-extractable residues are formed and which chemical structure they have.

The over-all balances of only ca. 50% and ca. 40% show that more than the half of the applied radioactivity left the open system during the 18 months of the experiment. The high volatility of trifluralin is known and causes part of the losses. The percentage of mineralization to CO_2 cannot be estimated. In a 12 week experiment Wheeler (1979) found only about 2% of the applied trifluralin was evolved as CO_2 .

No difference in the leaching behaviour of the two formulations of terbutylazine can be observed from the results shown in figure 2 and table 2. In both lysimeters concentrations between 0.5 and 1.0 $\mu\text{g/l}$ occurred in the leachate.

The distribution of radioactivity in the different soil layers and the formation of non-extractable residues is very similar in both lysimeters, that one applied with the EC-formulation and that with the CR-formulation. The over-all losses of radioactivity over the experimental period are smaller in the case of terbutylazine than with trifluralin. In no case they are reduced because of the slow release of the active ingredients from the CR-formulations.

Results can be summarised:

- no differences with regard to the leaching behaviour could be observed in the case of terbutylazine,
- the over-all losses of trifluralin were not reduced by formulating it in beads,

- the leaching behaviour of the CR-formulation of trifluralin is a little better than that of the tested EC-formulation, and
- the formation of non-extracted residues is reduced for trifluralin by using the CR-formulation.

With regard to the leaching behaviour in our experiment small advantages could be observed in the case of the trifluralin CR-formulation. The use of the CR-formulation of terbuthylazine did not furnish any advantages in comparison to the EC-formulation.

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POLYMERIC SYSTEMS FOR REDUCTION OF LEACHING OF HERBICIDES

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ABSTRACT

It was reported earlier (Narayanan et al., 1993a, 1993b, 1993c, 1993d, 1994) that certain polymers reduced the leaching of various families of pesticides (atrazine, dicamba, and metolachlor). The form-function of the effective backbones in the polymer were hypothesized. The polymer should be able to bind the active ingredient (A.I.), and should contain anchoring groups by which the bound A.I.-polymer could be held by the soil colloids either via electrostatic interaction, hydrophobic binding, or H-bonding. Certain active ingredients such as isoproturon and certain sulfonamides pose serious leaching problems that would restrict their application. Further, retarding the movement of certain highly elutable a.i.s such as dicamba, [even though not an immediate environmental problem (Wendt et al., 1994)], may expand the mode of application as a sustained release product.

Results of soil column studies on the influence of polymers on leaching of dicamba and flumetsulam are presented. The minimum effective ratio of the polymer/A.I. using commercially available formulations, and its effect on the nature of the soil are discussed. Further work is in progress including other active ingredients similar to isoproturon.

INTRODUCTION

This work is in continuation of our work reported earlier (Narayanan et al., 1993b, 1993d), wherein certain copolymers of vinylpyrrolidone and dimethyl aminoethyl methacrylate (Restrict 101) were found to reduce leaching of several active ingredients from a very porous soil with high sand (96.5%), and low soil organic matter [OM] (0.4%). This work has focused the effect of soil composition, polymer/A.I. ratios, and the polymer formulation. Restrict 101 is available as 20% polymer in aqueous solution. A solid version obtained via freeze-drying starch/polymer system was also evaluated. While the work is still in progress, we report our results and a working model is suggested.

EXPERIMENTAL METHODS

Materials

Commercially available Restrict 101 as 20% polymer in aqueous solution was used. For the solid version, Restrict 101 solid (Restrict 101 S), a product containing 75% polymer was used. This product was prepared typically from a slurry containing 75g corn starch and 1125g Restrict 101, which was freeze-dried in a laboratory unit. Commercial formulations for the active ingredients were used (Banvel (48% wt/V) for dicamba, and Broadstrike (75% wt/wt) for flumetsulam).

Preparation of columns, treatment applications, and bioassay

Columns 10 cm in diameter and 120 cm long were constructed from PVC (polyvinyl chloride) and prepared according to the published procedure (Narayanan et al., 1993d). After preparation, columns were packed with Wooster silt-loam soil [sand = 25%; silt = 60%; clay = 15%; (OM) = 4.1%; and pH = 7.2], secured in an upright position, saturated with water from the bottom up, and allowed to drain overnight. Columns were treated with commercial formulations of herbicide at 10 times the field rate (to increase detectability) of dicamba at 2207 ppm A.I., and flumetsulam at 136 ppm A.I. Two ml of A.I./polymer solution was applied evenly to a central area (3 cm diameter) of the surface of each column by dispensing from a pipette. Rates and concentrations of A.I.s and polymers are listed in Table 1.

Table 1. Quantities of formulated herbicides and adjuvants per liter water for each treatment¹

Polymer :A.I. ratio (by wt)	Dicamba			Flumetsulam		
	Banvel (ml/l)	Restrict 101 ¹ (g/l)	Restrict 101 S ⁵ (g/l)	Broad- strike (g/l)	Restrict 101 (g/l)	Restrict 101 S (g/l)
1:1	4.60	11.01	2.94	0.18	0.69	0.18
0.5:1	4.60	5.50	1.47	0.18	0.34	0.09
0.125:1	4.60	1.38	0.37	0.18	0.09	0.02
0:1 ²	4.60	0.00	0.00	0.18	0.00	0.00
1:0 ³	0.0	10.10	2.94	0.0	0.69	0.18

¹assuming 2 mL solution volume applied to each column. ²A.I. blank. ³polymer blank. ⁴20% aqueous solution. ⁵solid containing 75% polymer, 25% inerts.

Water was applied to the columns one day after treatment, in quantities to simulate rainfall amounts of ~ 3.8 cm (300 ml/column in 10 ml increments). Columns were split in half 36 hours after the simulated rain, and planted with alfalfa (dicamba) or canola (flumetsulam) in rows (perpendicular to the column), with 2 cm spacing. Plant growth was assessed visually from the column top at periodic intervals. The distance measured from top of the soil to the first row of plant growth in cm is reported in Tables 2 and 3.

RESULTS AND DISCUSSION

Table 1 summarizes the results from dicamba. The commercial Restrict 101 reduced movement of dicamba from the soil. The minimum polymer/A.I. ratio for reduction of movement in Wooster silt-loam soil was 0.125. The effective R_f value was found to be ~ 0.69 (the inconsistency of the data with 1:0.5 A.I./polymer ratio is under investigation). This compares fairly well with results reported earlier [0.59, (Narayanan et al., 1993d)] with polymer/A.I. at 1.0, based on ¹⁴C assay from Florida soil with high sand and low OM content. The freeze-dried Restrict S was not effective in reducing the movement of dicamba, the R_f value being 0.95. The negative effect of starch may arise from the competing binding sites for the A.I. and the reduced anchoring effect of the composite complex. Starch is probably a poor binder to the soil.

Table 2. Relative movement of dicamba during column elution

Treatment		Dicamba - alfalfa, distance (cm) from top of the soil to the first row of plant growth		
Polymer	A.I./polymer wt. ratio	column, left	Column, right	Average distance, cm
Restrict 101, Liquid	1:1	16	15	15.5
Restrict 101, Liquid	1:0.5	24	26	25
Restrict 101, Liquid	1:0.125	16	17	16.5
Restrict 101, Liquid	1:0	28	26	27.5
Restrict 101, Liquid	0:1	0	0	0
R_f at effective polymer/A.I. $\geq 0.125 = 19/27.5 = 0.69$				
Restrict 101 S	1:1	28	30	29
Restrict 101 S	1:0.5	25	27	26
Restrict 101 S	1:0.125	28	26	27
Restrict 101 S	1:0	30	31	30.5
Restrict 101 S	0:1	0	0	0
R_f at effective polymer/A.I. $\geq 1 = 29/30.5 = 0.95$				

Table 3 summarizes the results with flumetsulam. There was no significant effect in the relative movement of flumetsulam with or without treatment. Use of Restrict 101 S actually showed a wash off effect, i.e., an increase in the rate of movement of the A.I. These results can be rationalized in the following manner: The A.I. probably binds too strongly with the polymer matrix, and the binding to the soil particles is poor. Presence of starch offers additional binding sites to the A.I. without offering binding sites to the soil, and acts as an elutant. A knowledge of relative adsorption of the A.I. to starch/polymer/soil particles, and relative interaction of the above matrices in the presence of water will be very helpful in the choice of the polymer.

Work is underway in the evaluation of relative binding energies via computer assisted molecular model simulations for various minimum energy conformations

Table 3. Relative movement of flumetsulam during column elution

Treatment		Flumetsulam - canola, distance (cm) from top of the soil to the first row of plant growth		
Polymer	A.I./polymer wt. ratio	column, left	Column, right	Average distance, cm
Restrict 101, Liquid	1:1	27	27	27
Restrict 101, Liquid	1:0.5	26	25	25.5
Restrict 101, Liquid	1:0.125	24	25	24.5
Restrict 101, Liquid	1:0	26	29	27.5
Restrict 101, Liquid	0:1	0	0	0
R_f at all levels of polymer tested ~ 1				
Restrict 101 S	1:1	29	31	30
Restrict 101 S	1:0.5	25	27	26
Restrict 101 S	1:0.125	24	26	25
Restrict 101 S	1:0	23	24	23.5
Restrict 101 S	0:1	0	0	0
R_f at effective polymer/A.I. $\geq 1 = 30/23.5 = 1.27$				

SUMMARY

Restrict 101 reduced movement of dicamba from the Wooster silt-loam soil. The minimum polymer/A.I. was 0.125. The effective R_f value was ~ 0.69. There was no significant effect with flumetsulam movement with Restrict 101. Starch modified Restrict 101 was less effective with dicamba, and showed wash off effect with flumetsulam. Further work is in progress.

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A FIELD EXPERIMENT TO COMPARE THE MOVEMENT OF DIURON FROM WETTABLE POWDER AND CONTROLLED RELEASE FORMULATIONS IN A BRAZILIAN SOIL

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ABSTRACT

Movement of the widely used soil-applied herbicide diuron was measured in soil columns and in field plots in a silty loam soil in Brazil. The behaviour of a wetttable powder (WP) formulation and controlled release (CR) granules based on a lignin matrix and lignin-alginate beads were compared. The CR formulations were found to significantly reduce leaching in the soil column experiment. However, over the short period of the field trial the movement of diuron in the soil from the WP formulation was found to be small and only very low amounts of diuron were released from the CR formulation. The release of diuron from the CR granules used had previously been evaluated under laboratory controlled conditions by testing the release into water. The usefulness of laboratory experiments for prediction of the behaviour of CR formulations in the field is also assessed.

INTRODUCTION

The leaching of pesticides into ground water is a major environmental concern. The number of pesticides found in ground and surface water has been found to be growing steadily (Van der Linden, 1994). Improved analytical techniques enable the detection of contaminants at much lower levels than previously possible. Problems occur particularly when crops are grown in permeable sandy soils, or in areas with heavy rainfall.

When applied by conventional methods pesticides are invariable subject to losses such as leaching, run-off, evaporation and degradation. CR formulations aim to provide optimum levels of pesticides at the target site over the desired time period. They also aim to reduce losses of pesticides and potentially minimise chances of leaching of pesticides into ground water. There are many examples in the literature of CR formulations reducing the mobility of pesticides in soil, for example by starch encapsulation of pesticides (Fleming et al., 1992).

It has been predicted that the importance of degradable and natural polymers in CR systems will increase in the future (Wilkins, 1994). Lignin is naturally occurring biodegradable polymer which is the waste or by-product of many forestry and agricultural industries worldwide. The formation of a lignin-pesticide matrix has been shown to provide the controlled release of many pesticides which have been evaluated under laboratory and field conditions (Wilkins, 1990). Alginates have also been used to encapsulate herbicides

using its gel-forming properties. Although the release from this hydrophilic polymer is usually too fast for moderately soluble herbicides, the addition of a hydrophobic phase in which the herbicide partitions, effectively controls the liberation of the active ingredient (Pepperman & Kuan., 1993). In the alginate formulations studied lignin forms an hydrophobic domain in the matrix that reduces the release of diuron.

The evaluation of soil-applied CR formulations under field conditions is very complex due to the wide range of soil properties and climatic conditions which potentially affect the release, distribution and availability of the pesticide. Hence the formulations are usually initially evaluated under laboratory controlled conditions, often by testing the release of the pesticides into water and soil under leaching or non-leaching conditions (Ali & Wilkins, 1992). Soil column experiments are frequently performed to test the leaching potential of pesticides in soils and evaluate CR formulations (Fleming et al., 1992).

MATERIALS AND METHODS

CR formulations

Lignin matrix formulation were made according to the method of Wilkins & Cotterill (1993). The lignin and diuron were mixed together in a ratio of 1:1 and then heated under melt conditions (175-185 °C) for approximately 10 minutes. On cooling the glassy matrix was crushed in a hammer mill and the granules sieved to obtain sizes between 0.71-1.0 mm. Two lignins were used, a soda bagasse lignin obtained from steam-exploded sugar cane bagasse (da Silva et al., 1989), and a mixed hardwood organosolv lignin (Lora et al., 1991).

Lignin-alginate beads were prepared according to the following procedure. Diuron was dispersed in distilled water using an ultrasonic bath, and lignin and sodium alginate added resulting in concentrations of 2.5, 3.12 and 6.25 % respectively. When the sodium alginate had been dissolved the resulting viscous dope was added dropwise through a syringe needle into a stirred barium chloride solution (5% w/w) to obtain spherical beads. These were left in the bath for 15 minutes for complete gelation of the alginate. After separation using a funnel the beads were washed, allowed to release water due to syneresis for 48 hours and were then oven-dried at 50°C.

Release studies in water

The lignin matrix granules (bagasse and mixed hardwood lignins) were evaluated using a static immersion test (Wilkins & Cotterill, 1993). Granules (40 mg) were immersed in 300 ml of double distilled water (30 °C). Samples were taken for analysis by HPLC every day for the first week, after 10 days and then every week thereafter. After each sampling the water was replaced with fresh. The aqueous samples were analyzed for diuron using a reverse phase column (ODS, 150×4.6 mm, 5 µm packing) using a mobile phase of methanol (75 %) and water (25 %) at 1 ml/min. Detection was using a UV holochrome at 254 nm.

The lignin-alginate beads containing 40-50 mg of diuron were placed in 100 ml distilled water. The bottles were kept agitated in a rotary shaker over the duration of the experiment. At each sampling time the water was completely withdrawn and fresh water was added. The samples were analyzed for diuron using HPLC.

Soil Columns

The soil used in the columns was taken from the same area as the field plots, and was a silty loam Oxisol, with an organic carbon content of 2.6 %. The soil was passed through a 2 mm mesh sieve, and dried in an oven (40 °C) for 6 hours. The soil was then packed into a column made from 4 segments of PVC tubing (ID 3 cm, length 20 mm) taped together. The soil was supported by a thin wire mesh on the bottom section. Diuron (equivalent to 16.5 mg) was applied to the columns as the technical grade herbicide, bagasse lignin matrix granules (50 % diuron) and lignin-alginate granules. A circle of filter paper was placed on top of the column and then water was applied at a rate of approximately 1 ml/min over 3 hours. After application of water the columns were allowed to drain for one hour before splitting the soil into the four sections. The soil was then dried overnight and a sub-sample (10 g) was then extracted with methanol (10 ml) in a centrifuge tube by shaking for 24 hours. The tubes were then centrifuged at 2000 rpm for 15 minutes. The supernatant was analyzed for diuron using HPLC (conditions as for the aqueous samples but with a mobile phase of methanol:water 7:1).

Field Plots

Three circular plots of 4 m² on cleared soil under the same long term management were set up, and a rain gauge was installed. The first plot received a conventional spray application of diuron at approximately 16 kg/ha, similar to those used for general plant clearance. The second plot received a CR formulation (mixed hardwood lignin matrix granules 0.71-1.0 mm) at an identical application rate. The final plot was used as a blank for calibration.

Rainfall was simulated by addition of water by hand. The maximum amount that could be applied was limited by the infiltration rate of the soil, and 17 litres per plot was applied twice a day. This was equivalent to a simulated rainfall of 8.5 mm of rainfall per day. The rain gauge was read daily to measure any natural rainfall.

Samples from the field site were taken every 2 weeks with a soil corer (diameter 2.5 cm). Five random samples covering 0.012 % of the plot area were taken at depths of 0-10, 10-20, 20-30 and 30-40 cm for each plot. The surface 1 cm was removed to eliminate the CR granules from the analysis. The soil samples were then analyzed in a similar manner to the soil column analysis. However, as the concentrations in the field were much lower, preliminary analysis of the sampling procedure led to the use of the "method of addition". To allow low concentrations of diuron to be detected the samples were spiked with known amounts of diuron in acetone to ensure that the concentrations were in the calibration range for the HPLC analysis. The lowest detection limit of the methodology was found to be 1.65 ppm at a confidence level of 95 %.

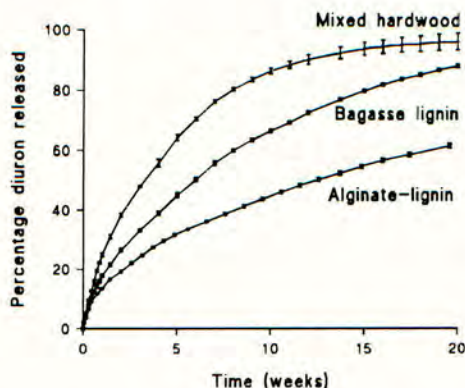
The analysis method for determination of soil concentrations took into consideration any differences in extraction efficiency due to changes of the soil organic matter with depth. Changes in extraction efficiency due to changes in organic matter distribution and quality with time due to the watering regime were also taken into account. The average extraction efficiency was found to be 93 %.

RESULTS

Release studies in water

The release of diuron from the CR formulations (bagasse and mixed hardwood lignin matrices and the alginate beads) is shown in figure 1.

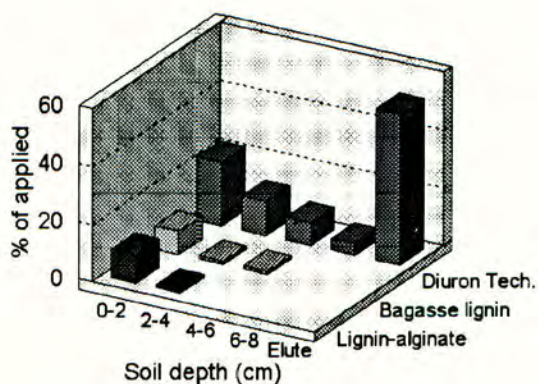
FIGURE 1. Cumulative release of diuron from CR granules into water (error bars represent the standard deviation of 3 replicates)



Soil columns

The movement of diuron from the CR formulations and technical grade diuron in the soil columns after the addition of water (simulating 519 mm rainfall) is shown in figure 2. It can be seen that the CR granules substantially reduce the mobility of diuron in the soil.

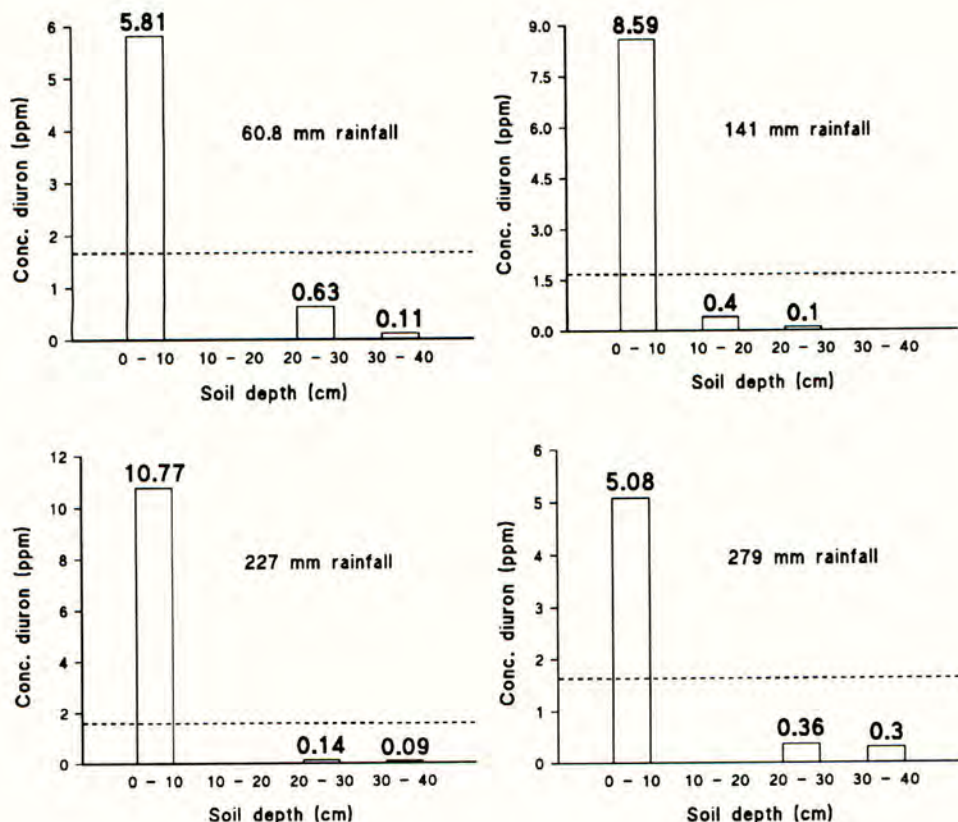
FIGURE 2. Distribution of diuron from technical grade and CR formulations in soil columns



Field plots

Over the time period of the field studies the movement of diuron in the soil was found to be minimal from the WP formulation. For the CR lignin granules no diuron was detected in the soil, hence any diuron released from the granules was retained in the top 1 cm of soil which was not included in the analysis. For the WP formulation the concentrations of diuron recorded in the soil with the simulated rainfall are shown in the figure 3. Note that values below 1.65 ppm were below the detection limit and should be read as zero.

FIGURE 3. Concentrations of diuron recorded in the soil plots



DISCUSSION AND CONCLUSIONS

Although diuron is not highly mobile in soil it was used as a model compound for the experiment as it fulfils more than one criteria defined by Creeger (1986) characterising it as a possible danger in groundwaters. Diuron has a water solubility of 42 mg/l and a soil half-life of 90-180 days (Worthing & Hance, 1991).

The soil column experiments suggest that more than 50% of the technical grade diuron would leach to depths greater than 8 cm in the field if it were to receive a similar watering regime. In practice the soil column analysis does not reflect the field conditions closely due to the following factors:

(i) Time scale - the soil columns received a total of 519 mm of simulated rainfall in a period of only 3 hours. The field plots however received a total of 280 mm water over a period of 56 days. In the soil columns there would have been negligible degradation of diuron, but in the field plots degradation would occur.

(ii) Microbial action - the soil used in the soil columns was dried in an oven before being used. This means that the inherent microbial community in the soil may have been destroyed,

again reducing any chances of degradation of diuron in the soil columns.

(iii) Evaporation - the evaporation of moisture by the sun under field conditions produces an upward movement of water in the surface layers of the soil. Consequently diuron may have been moved upwards as well as downwards in the soil. Hence soil column analysis with no evaporative cycle would exaggerate the results of leaching in soil.

(iv) Movement of water along the soil / column border is greater than movement through the soil. This again would lead to exaggerated results of leaching in column experiments. To minimise this factor a column with a wide as possible diameter should be used.

In conclusion, HPLC analysis can be used to analyze diuron residues in soil following the methodology described, to detection limits of 1.65 ppm with 95 % confidence. Soil column experiments are ideal for determining the leaching potential of a pesticide, but care must be taken with the results in that they do not reflect field conditions for the various reasons outlined above. Calibration to field conditions are difficult due to the inherent heterogenous of conditions in the field. The field results showed that diuron has little leaching potential due to its high affinity for organic matter. Hence with respect to the possibility of groundwater contamination the need to formulate diuron in CR formulations is minimal, however other considerations such as surface runoff to waterways may be minimised by using CR formulations. Further research needs to be concentrated on more mobile pesticides such as atrazine, 2,4-D, lindane, endrin, and 2,4,5-T which have all been detected in groundwaters.

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