

Simulation of water movement and isoproturon behaviour in a heavy clay soil using the MACRO model

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Abstract

In this paper, the dual-porosity MACRO model has been used to investigate methods of reducing leaching of isoproturon from a structured heavy clay soil. The MACRO model was applied to a pesticide leaching data-set generated from a plot scale experiment on a heavy clay soil at the Oxford University Farm, Wytham, England. The field drain was found to be the most important outflow from the plot in terms of pesticide removal. Therefore, this modelling exercise concentrated on simulating field drain flow. With calibration of field-saturated and micropore saturated hydraulic conductivity, the drain flow hydrographs were simulated during extended periods of above average rainfall, with both the hydrograph shape and peak flows agreeing well. Over the whole field season, the observed drain flow water budget was well simulated. However, the first and second drain flow events after pesticide application were not simulated satisfactorily. This is believed to be due to a poor simulation of evapotranspiration during a period of low rainfall around the pesticide application day. Apart from an initial rapid drop in the observed isoproturon soil residue, the model simulated isoproturon residues during the 100 days after pesticide application reasonably well. Finally, the calibrated model was used to show that changes in agricultural practice (deep ploughing, creating fine consolidated seed beds and organic matter applications) could potentially reduce pesticide leaching to surface waters by up to 60%.

Introduction

By-pass flow through macropores in drained heavy clay soils may result in the rapid movement of water and pesticide to adjoining ditches and streams. This may cause reduced pesticide efficacy and environmental contamination. It is, therefore, important to understand fully the macropore flow processes that lead to high concentrations of pesticides reaching field drains particularly if these losses are to be reduced.

Isoproturon (3-(4-isopropylphenyl)-1,1-dimethyl urea) is a soil-applied urea herbicide commonly used to control annual grasses and annual broad leaved weeds in winter and spring cereals in the UK. Recently, isoproturon (IPU) has been found in lowland streams and rivers at concentrations exceeding the 0.1 $\mu\text{g l}^{-1}$ maximum acceptable concentration in drinking water set by the European Union (NRA, 1995, White and Pinkstone, 1995). The occurrence of isoproturon in drinking water (Drinking Water Inspectorate, 1995) prompted a UK review of the product by the Pesticide Safety Directorate (PSD, 1995).

A moderately persistent herbicide such as isoproturon applied to winter cereals on a drained heavy clay soil has

been shown to represent a potentially serious contamination threat to water courses (Johnson *et al.*, 1994, Harris *et al.*, 1993). Isoproturon is applied to about half of Britain's cereal acreage (ENDS, 1995), while clayey soils occupy about 45% of the cereal growing area in England and Wales (Cannell *et al.*, 1978). The potential pollution threat is therefore clear.

The mechanistic dual-porosity model MACRO (Jarvis, 1994) was used to simulate soil water movement and isoproturon behaviour at an instrumented field site on a heavy clay soil at Wytham, in southern England. The model was first calibrated against the Wytham dataset, and was then used to investigate how changes in agricultural practice might lead to reductions in pesticide leaching. The Isoproturon UK Task Force gives specific guidelines on reducing isoproturon leaching from structured clay soils (IPU UK Task Force, 1995). The model was used to assess the potential effectiveness of some of these recommendations. Previous work at Wytham has suggested that incorporated organic matter can also reduce isoproturon leaching (Johnson *et al.*, 1997). Therefore, the effectiveness of this approach was also assessed using the model.

The MACRO model

The MACRO model (Version 3.1) is a non-steady state model of water flow and solute transport in macroporous field soils. The model considers a complete water balance including unsaturated and saturated water flow, canopy interception and root water uptake. It can be used to simulate non-reactive tracers or pesticides and includes descriptions of processes such as convective-dispersive transport, canopy interception and wash-off, sorption, biodegradation and plant uptake. It can be used to simulate water flow in both one and two flow domains. When two flow domains are considered, the macropores and micropores operate as individual, though interacting, flow regions, with each flow region being characterised by a degree of saturation, a conductivity and a flux. This model is therefore well suited to simulating pesticide behaviour in a heavy clay soil, such as at Wytham, where leaching is known to be strongly influenced by macropore flow (Kneale, 1986 and Haria *et al.*, 1994). Only a brief description of the model is presented here, since a full description has been given by Jarvis (1994).

SOIL WATER FLOW

Water movement in the micropores is calculated with the Richards' equation including a sink term to account for root water uptake. The soil hydraulic properties are described by the functions of Brooks and Corey (1964) and Mualem (1976):

$$S_{mi} = \left(\frac{\theta_{mi} - \theta_r}{\theta_b - \theta_r} \right) \quad (1)$$

$$\Psi_{mi} = \Psi_b S_{mi}^{-1/\lambda} \quad (2)$$

$$K_{mi} = K_b S_{mi}^{n+2/\lambda} \quad (3)$$

where the subscript *mi* refers to micropores, ψ , K , S and θ are the soil water pressure head, hydraulic conductivity, degree of saturation and soil water content respectively, θ_r is the residual water content, λ is the pore size distribution index and n is the micropore tortuosity factor. ψ_b denotes the pressure head defining the boundary between macropores and micropores, θ_b is the equivalent water content (i.e. with the micropores fully saturated) and K_b is the 'boundary' (or saturated micropore) hydraulic conductivity. Water flow in macropores is calculated with Darcy's law assuming a unit hydraulic gradient and a simple power law function to represent the unsaturated hydraulic conductivity:

$$K_{ma} = (K_s - K_b) \left(\frac{\theta_{ma}}{\theta_s - \theta_b} \right)^{n^*} \quad (4)$$

where the subscript *ma* refers to macropores, K_s is the saturated hydraulic conductivity, θ_s is the saturated water

content and n^* reflects the pore size distribution and tortuosity of the macropores. If the macropores become saturated at any depth in the soil, lateral flow to drainage systems is calculated as a sink term to the vertical one-dimensional water flow, by applying seepage potential theory to layered soils (Leeds-Harrison *et al.*, 1986).

The surface boundary condition in MACRO partitions net rainfall into an amount taken up by micropores and an excess amount of water flowing into macropores. This partitioning is determined by a simple description of the infiltration capacity of the micropores.

PESTICIDE TRANSPORT AND TRANSFORMATIONS

Transport in micropores is predicted using the convection-dispersion equation for a sorbing solute subject to plant uptake and degradation. In the macropores, mass flow is assumed to dominate, so that dispersion and diffusion are neglected. The solute concentration in water routed into the macropores at the surface is calculated assuming complete mixing of resident water in a shallow 'mixing depth' with incoming rain. Sorption sites are partitioned into one fraction that equilibrates with the macropore fluid and the remaining fraction that equilibrates with the micropore liquid (van Genuchten and Wagenet, 1989). An instantaneous equilibrium between solution and sorbed phases and a linear sorption isotherm are also assumed.

Degradation is predicted in the model assuming first-order kinetics. Four separate reference degradation rate coefficients may be specified in the model since the pesticide may be stored in two phases and in two domains (van Genuchten and Wagenet, 1989). Field degradation rate coefficients μ are predicted from the laboratory-measured reference values μ_{ref} using simple functions F_w and F_t to account for soil moisture and temperature effects (Boesten and van der Linden, 1991):

$$\mu = \mu_{ref} F_w F_t \quad (5)$$

where the soil moisture response function is given by:

$$F_w = \left(\frac{\theta}{\theta_b} \right)^B \quad (6)$$

where B is an empirical exponent, and the soil temperature function is given by a numerical approximation of the Arrhenius equation (Boesten and van der Linden, 1991), modified for low soil temperatures:

$$\begin{aligned} F_t &= e^{\alpha(T-T_{ref})}; & T > 5^\circ\text{C} \\ F_t &= \left(\frac{T}{5} \right) e^{\alpha(5-T_{ref})}; & 0 \leq T \leq 5^\circ\text{C} \\ F_t &= 0; & T \leq 0^\circ\text{C} \end{aligned} \quad (7)$$

where T is the actual soil temperature, α is an exponent depending on the molar activation energy, and T_{ref} is the temperature at which μ_{ref} is measured. Soil temperatures

are calculated from air temperatures using the heat conduction equation. Thermal conductivity and heat capacity are calculated from the known physical properties of the soil. The top boundary condition for heat flow is approximated by the air temperature, while the temperature at the bottom boundary is predicted from an analytical solution of the heat conduction equation assuming that the temperature at the soil surface approximates a sine wave on an annual basis.

Crop uptake of pesticide is modelled as a function of the water uptake rate, the concentration in solution and an 'exclusion factor' (Boesten and van der Linden, 1991) which can take values from zero to unity.

MASS EXCHANGE BETWEEN DOMAINS

Exchange of water and solute between the two pore systems is calculated using approximate first-order expressions. Mass exchange by solute diffusion is driven by the concentration difference and water exchange by the degree of saturation in both micro- and macropores. In both cases, the mass transfer is controlled by an effective diffusion pathlength which reflects the aggregate size distribution and flowpath geometry (Jarvis, 1994).

Materials and methods

FIELD SITE INSTRUMENTATION, SAMPLING PROCEDURES AND SAMPLE ANALYSIS

Only a brief description of the field site and instrumentation is presented here, since a detailed description is given by Johnson *et al.* (1996). The experimental field site used for this study was located at the Oxford University Farm, Field 10C, Wytham, Oxfordshire (51°46.4'N, 1°18.7'W, elevation 76 m). The soil in this field is a Stagno-eutric gleysol (FAO) belonging to the Denchworth series (calcareous variant). The Ap horizon to 260 mm depth has a clay content of 57% and an organic carbon content of 3.1%, while the corresponding figures for the Bg horizon at 260 to 540 mm depth are 63% and 0.9%. The field slopes at 2–5° in a South Easterly direction towards a drainage ditch. The field is drained by a series of mole drains running across the slope (0.5 m depth and 3 m spacing) and field drains running down the slope (0.75 m depth and 50 m spacing). The field drains are permanent features constructed from slotted plastic drainage tubes laid under a 0.35 m thick, 0.1 m wide layer of aggregate. The mole drains must be re-installed approximately every five years by dragging a beam mole plough through the soil. The mole drains empty into the field drains via the aggregate layer.

The experimental plot (25 m × 50 m) was situated between two field drains. The plot was isolated hydrologically from the rest of the field such that field drain flow, overland flow and lateral sub-surface flow could be moni-

tored continuously using large tipping buckets and V-notch weirs linked to loggers. Additionally, auto-samplers (Dalog, Alton, UK) were placed on each of the above outflows and were set to remove 1 litre samples at regular intervals during storm events. The aim of this instrumentation was to monitor continuously the amount of drainage and concentration of pesticide leaving the plot throughout the field season. Rainfall at the site was monitored using tipping bucket gauges connected to loggers (Campbell Scientific Inc., USA). Soil water potential and soil water content were monitored continuously using Pressure Transducer Tensiometers (PTTs) and capacitance probes respectively. Soil water content was also monitored weekly with a neutron probe (Didcot Instruments, UK). The soil water, soil and rainwater were also sampled regularly and analysed for pesticide concentration.

During the 1993–94 season, the field was in winter wheat cultivation. The field was deep ploughed, cultivated with a power harrow and drilled by October 1993. The mole drains were installed in October 1992. It is suspected that the hydraulic performance of the mole drains had decreased significantly in the year following their installation (Johnson, *et al.*, 1996), although the mole drains were not excavated to confirm this suspicion. Isoproturon was applied to the plot on 12 March 1994. The application rate was calculated by determining the isoproturon content of filter paper discs placed within the plot during pesticide application. The application rate was calculated to be 0.9 kg ha⁻¹, with a standard deviation of 0.23 kg ha⁻¹. This application rate was considerably less than the current UK maximum permissible application rate of 2.5 kg ha⁻¹.

A brief description of the sampling and analysis protocols used in this project is given below (for a full description, see Johnson *et al.*, 1996). To assess isoproturon persistence, 1 kg of soil was collected from the upper 2 cm of the soil surface at approximately weekly intervals. These samples were analysed for isoproturon by taking four 50 g samples and extracting with 100 ml methanol prior to determination by HPLC. ¹⁴C-labelled isoproturon was used to test the efficiency of this extraction technique and the results indicated that recovery varied between 87 and 100%. Both aqueous and methanol samples were analysed for isoproturon using HPLC. A C18 column SupelcosilTM LC-ABZ (Supelco UK, a branch of Aldrich-Sigma Ltd) was used (4.6 mm × 0.25 m) with acetonitrile + water (35 + 65 by volume) as eluent. Detection was made at 240 nm, and peak purity was checked by comparing the absorbance at 220 nm.

DRIVING DATA

The driving data consisted of hourly rainfall, daily maximum and minimum temperature and daily potential evaporation collected from a meteorological station situated 600 m from the field site. Potential evaporation was calculated using the Penman equation (Penman, 1963). The

hourly rainfall data from the meteorological station was cross checked against the data from the field site rain gauges and showed good agreement.

MODEL PARAMETERISATION

The soil profile consisted of 15 layers, varying from 20 mm thickness at the top of the profile to 100 mm thickness at the base (Table 1). The values of saturated hydraulic conductivity and bulk density were varied down the profile. All other parameters had either one value for the whole profile or one value for the topsoil (0–260 mm) and another for the subsoil (260–960 mm), corresponding to the A and B horizons in the field. The model input parameter values were estimated from a combination of field measurements, laboratory data, literature values, and model calibration. Bulk density was derived from field data, residual water content was set to zero, while the default values in the model were used for both wilting point water content and for micropore tortuosity ($n = 0.5$). Values of critical and sensitive soil hydraulic parameters defining the macropore domain (i.e. the saturated and boundary hydraulic conductivities, K_s and K_b , saturated and boundary water contents, θ_s and θ_b , boundary pressure head ψ_b and the macropore tortuosity factor n^*) were estimated by model calibration against the measured drain hydrographs (Tables 1 and 2). Initial estimates were obtained using either field data or default values in the model. These estimates were subsequently adjusted and refined during model calibration. The results of this calibration procedure indicate that the Wytham soil is characterized by macroporosities (i.e. $\theta_s - \theta_b$) of c. 2% and 0.5% in the topsoil and subsoil respectively, while the small

Table 1. The soil hydraulic properties used in the model.

Depth interval (mm)	Saturated hydraulic conductivity K_s (mm h ⁻¹)	Bulk density γ (kg l ⁻¹)
0–20	100	1.15
20–40	100	1.15
40–60	100	1.15
60–80	100	1.24
80–100	100	1.24
100–150	50	1.24
150–200	40	1.24
200–260	30	1.24
260–360	20	1.54
360–460	20	1.54
460–560	20	1.54
560–660	10	1.54
660–760	10	1.54
760–860	10	1.54
860–960	10	1.54

Table 2. The soil physical and hydraulic properties used in the model.

	Depth interval (mm)	
	0–260	260–960
Boundary hydraulic conductivity K_b (mm h ⁻¹)	0.01	0.01
Boundary soil water tension Ψ_b (mm)	200	200
Saturated water content θ_s (m ³ m ⁻³)	0.52	0.42
Boundary water content θ_b (m ³ m ⁻³)	0.50	0.415
Wilting point water content θ_w (m ³ m ⁻³)	25	25
Residual water content θ_r (m ³ m ⁻³)	0	0
Tortuosity factor (micropores) n	0.5	0.5
Tortuosity factor (macropores) n^*	3	2
Effective diffusion path length (mm)	40	40

values of n^* (= 3 and 2 in topsoil and subsoil respectively, Table 2) suggest that the macropore domain has a narrow pore-size distribution dominated by a few large, vertically-continuous, pores. The large values of K_s (especially in the topsoil) and the small values of K_b , confirm the importance of these macropores for saturated water flow in such a heavy clay soil.

The crop parameters are listed in Table 3. The leaf area indices were estimated from literature values (Jarvis, 1994) and field observations. Default values were used for the leaf area development form exponents, x_1 and x_2 , and the root adaptability factor. The correction factor for wet canopy evaporation was set initially to the default value and was subsequently altered slightly during model calibration. Similarly, the maximum canopy interception capacity was set initially to the default value and was subsequently adjusted during calibration. The root depth and root distribution factors were estimated from field observations and default values were used for both the critical soil air content for water uptake and the critical pressure head for water uptake.

The first-order degradation rate coefficient μ was set to 0.038 d⁻¹ (0–260 mm) and 0.019 d⁻¹ (260–960 mm), at a reference temperature of 15°C, based on pesticide residue data obtained at the site in both the 1992/3 and 1993/4 field seasons (Johnson *et al.*, 1994, Johnson *et al.*, 1996). The same degradation rate coefficients were used for the liquid and solid phases in both the micropores and macro-

Table 3. The crop parameter values used in the model.

Parameter	Value
Dates of emergence, maximum leaf area and harvest	30 September, 19 July, 2 August
Leaf area indices, minimum, maximum and harvest	0, 6.0, 5.0
Leaf area development 'form' exponent x_1	2.0
Leaf area development 'form' exponent x_2	0.7
Root adaptability factor	0.1
Correction factor for wet canopy evaporation	1.25
Canopy interception capacity (mm), maximum	4
Root depth (mm), minimum and maximum	0.01, 0.7
Root distribution factor	75
Critical pressure head for water uptake (m)	-10
Critical soil air content for water uptake ($\text{m}^3 \text{m}^{-3}$)	0.05

pores. Parameters describing the effects of moisture and temperature on degradation (B and α , see Eqns 6 and 7) were set to default values in the model (= 0.7 and 0.08 respectively). The sorption coefficient K_d was set to 2.3 l kg^{-1} at zero to 260 mm depth and 0.7 l kg^{-1} at 260 to 960 mm depth based on the results of the equilibrium batch sorption experiments described by Johnson *et al.* (1997).

Solute transport parameters were set to default values in the model (dispersivity = 10 mm, diffusion coefficient = $4.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, impedance factor = 0.5, mixing depth = 10 mm and the fraction of sorption sites in the macropore domain = 0.1). The solute concentration factor was set to 1 (i.e. passive crop uptake), while the fraction of the pesticide irrigation intercepted by the crop was also set to 0.1. Pesticide application day and rate were set according to observed field data and there was assumed to be no pesticide in the rainwater.

INITIAL CONDITIONS

Initial soil water contents were calculated by the model assuming a drainage equilibrium with a water table at the base of the profile. The soil profile was assumed free from solute at the start of the simulation and an initial soil temperature of 10°C was assumed for all depths in the profile.

REDUCING PESTICIDE LEACHING

Once MACRO had been calibrated, the model was used to investigate how changes in agricultural practice could reduce pesticide leaching.

Fine Seed Beds and Deep Ploughing

The Isoproturon UK Task Force was set-up by three major isoproturon manufacturers to give guidance to farmers, advisers, distributors and manufacturers on avoiding isoproturon contamination. It detailed some specific guide-

lines on reducing isoproturon leaching from cracking clay soils (IPU UK Task Force, 1995). These guidelines included i) creating fine consolidated seedbeds to slow the downward movement of water, improve isoproturon sorption, and maximise the efficacy of isoproturon, and ii) ploughing as deeply as possible prior to drilling to remove cracks in the soil. It must be remembered however that while these measures may seem relatively easy to carry out, in practice this may not be the case. For example, there may only be a three week interval each year in which the farmer can prepare the land for drilling after harvesting the previous years crop. If the soil is excessively wet during this period, it will be difficult to deep plough and create fine seed beds. Indeed, some cereal farmers on heavy clays do not plough every year because of this difficulty (Mr D. Sharp, Farm Manager, Oxford University Farm, pers. comm.).

Fine seed beds on a heavy clay soil may be created by first rotovating the ploughed soil with a power harrow to a depth of 50–80 mm, followed by rolling. When deep ploughing the heavy clay soil at Wytham, a plough depth from 200–260 mm may be expected. Fine seed beds and deep ploughing were simulated by changing the parameters in the model that reflect the soil structure. The effective diffusion pathlength was reduced from 40 mm to 30 mm. The macroporosity above plough depth was increased by increasing the saturated water content (Table 4) and the macropore tortuosity factor was increased between the soil surface and 200 mm depth (Table 4).

Incorporated Organic Matter

Previous work at Wytham has suggested that incorporated organic matter can reduce isoproturon leaching from heavy clay soils (Johnson *et al.*, 1997). While spreading organic matter seems a relatively simple procedure, the logistics may well be difficult in practice if there is only a three week interval each year in which the farmer can get on the field to spread manure between harvesting the preceding

Table 4. Changing the saturated water content and tortuosity factor values used in the model to simulate fine seed beds and deep ploughing.

Depth interval (mm)	Saturated water content θ_s (vol %)		Tortuosity factor (macropores)	
	Old values	New values	Old values	New values
0-20	52	53	3	4
20-40	52	53	3	4
40-60	52	53	3	4
60-80	52	53	3	4
80-100	52	53	3	4
100-150	52	53	3	4
150-200	52	53	3	4
200-260	52	53	3	3
260-360	42	42	2	2
360-460	42	42	2	2
460-560	42	42	2	2
560-660	42	42	2	2
660-760	42	42	2	2
760-860	42	42	2	2
860-960	42	42	2	2

crop and ploughing, cultivating and drilling the following crop. Also, larger arable farms may not have access to significant quantities of animal manure. Legislative changes have resulted in sewage sludge now being applied increasingly to arable land. Repeated applications may increase the organic carbon content of the soil in the long-term, and therefore increase the proportion of pesticide that is sorbed by the soil.

Undisturbed soil columns taken from Wytham have shown that ploughed-in animal manure and straw was found between 100-200 mm depth (Johnson *et al.*, 1997). Johnson *et al.* (1997) also showed that pure manure had an isoproturon K_d of between 20.5-770 ($l\ kg^{-1}$), that the manure layer had a K_d of between 2.2-4.5 ($l\ kg^{-1}$), that straw had a K_d of between 14.5-83.5 ($l\ kg^{-1}$), that the straw layer had a K_d of between 3.3-4.5 ($l\ kg^{-1}$), and that soil sampled from above the manure layer had an isoproturon K_d of between 2.2-2.5 ($l\ kg^{-1}$). Thus, to simulate the influence of incorporated organic matter, the sorption coefficient for isoproturon (K_d) was increased at 100-150 mm and 150-200 mm depth in the following steps: 2.3, 3, 5, 10, 25 and 50 ($l\ kg^{-1}$). A maximum K_d of 50 $l\ kg^{-1}$ was used because it would require impractical amounts of organic matter to increase K_d above this value.

Results and Discussion

WATER BALANCE AND DRAIN FLOW

The water balance for the field season is shown in Table 5. Throughout the season, the monthly modelled drain

flow totals agree well with the observed drain flow totals. No runoff was predicted by the model, in agreement with the measurements which showed that runoff is only a minor process in terms of water transport from the plot (Table 5). This is to be expected, provided the drainage system functions properly, since the soil is macroporous (large K_{sat} , Table 1) and calcareous, with a stable aggregate structure. Figure 1 shows the cumulative drainage via the field drain over the whole field season. Drainage was simulated well in the wet part of the field season from mid-December until early February. However, from mid-February onwards the simulation is poor, with drain flow being overestimated in both February and May (Table 5), perhaps because of inaccuracies in simulating evapotranspiration. Estimating the evaporative demand within environmental fate models is known to be difficult (Armstrong *et al.* 1995). Figure 2 shows the observed and modelled drain flow for several typical storm events in January. The shapes of these drain flow hydrographs are well simulated, as is the total amount of drainage.

SIMULATION OF ISOPROTURON BEHAVIOUR

After pesticide application on 12 March 1994, two main storm events transported pesticide from the plot. These events were on 30 March 1994 and on 8 April 1994 respectively. Unfortunately, these event hydrographs were not well simulated by the model. No drain flow was predicted by the model on 30 March 1994. Only 0.23 mm of drainage was collected from the plot on this day, although

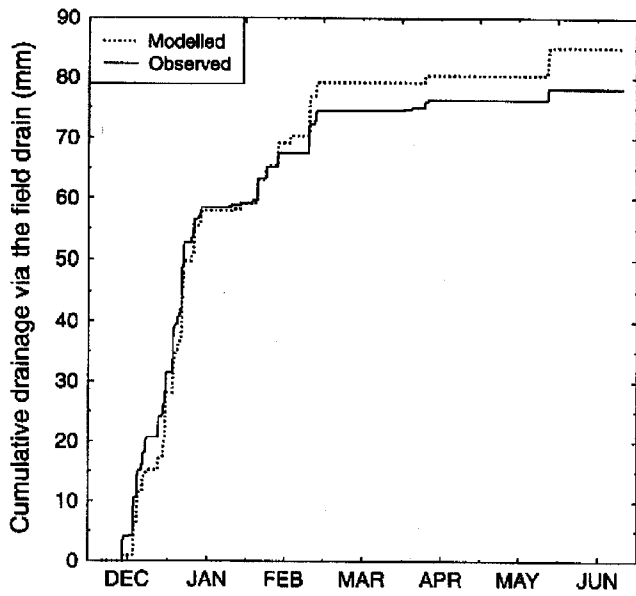


Fig. 1. Cumulative drainage via the field drain from 14 December 1993 to 23 June 1994.

over 30 days had elapsed since drain flow was last observed. Such a small drain discharge following a long dry period represents a severe test of the water balance component of the model. Even only slight overestimation of evapotranspiration by the model during the preceding 30 day period could account for the failure to predict drainage for this event. Drainage was predicted for the second event on 8 April 1994 (Figure 3), although the simulated drain flow hydrograph for this event was a poor match to the observed data. The peak of the simulated hydrograph occurred over an hour after the observed peak, while the shape of the modelled hydrograph was far too broad. The isoproturon concentrations predicted for the second event were of the right order of magnitude (Fig. 3), with the maximum concentration and chemograph shape showing acceptable agreement with the measurements. However, the simulated maximum concentration occurred over two hours later than in the measurements, largely due to the underestimation in the time to peak discharge in the hydrograph. In Fig. 3, the observed drain flow rate appears

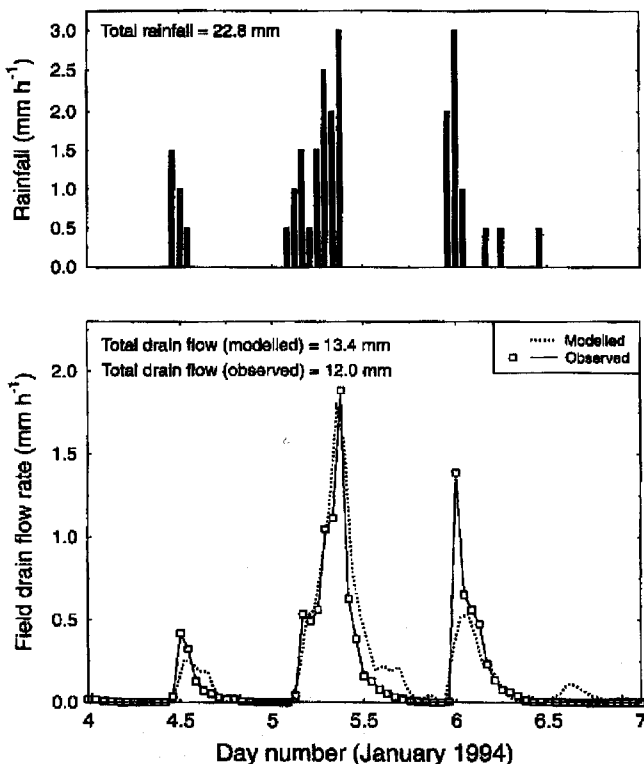


Fig. 2. Observed and modelled field drain flow from 4 January 1994 to 7 January 1994.

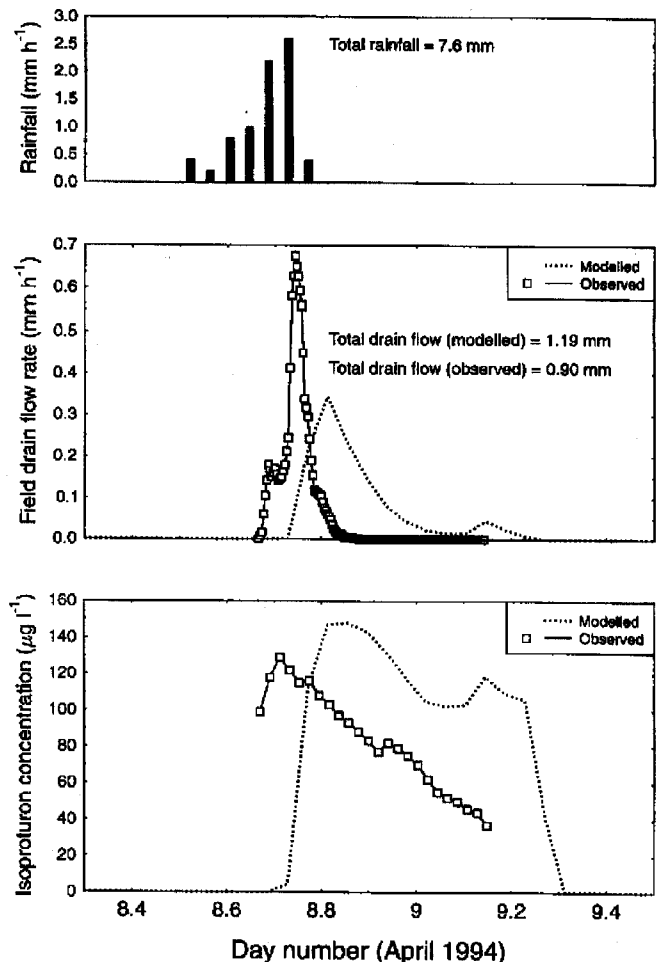


Fig. 3. Modelled and observed field drain flow and isoproturon concentrations in response to the second storm event after isoproturon application.

Table 5. Water balance for the field season.

	Rainfall mm	Runoff mm observed	Runoff mm modelled	Drain flow mm observed	Drain flow mm modelled
14–31 December	66	0.49	0	31.5	28.1
January	86	0.58	0	27.7	31.0
February	64	0.48	0	15.4	20.2
March	42	0.00	0	0.1	0
April	48	0.11	0	1.7	1.2
May	83	0.02	0	2.0	4.6
1–23 June	13	0	0	0	0
TOTAL	402	1.68	0	78.4	85.1

to be zero from day 8.83 to day 9.14. However, a very low flow rate was recorded during this period, so that the auto-samplers continued to take samples.

Figure 4 shows a comparison between observed and modelled isoproturon residues in the top 20 mm of the profile. Immediately after pesticide application on 12 March, the observed isoproturon soil residue was significantly larger than that predicted. This lack of agreement may reflect variability and/or uncertainty in one or more

of the following : the actual amount of pesticide applied, the bulk density in the surface 20 mm, and the depth of soil actually sampled. With respect to the latter, bulk soil samples were taken, so that it not easy to define accurately the actual depth sampled as the surface is not completely plane.

Five days after application, the observed residues had decreased from more than 5 mg kg⁻¹ to less than 2 mg kg⁻¹ (Figure 4), indicating a half-life of less than 5 days. Laboratory degradation studies show that the half-life of isoproturon measured in a wide range of soils is between 10–20 days at 20°C (PSD, 1995), while a typical field half-life under autumn conditions, with temperatures around 10°C, is 30 days (according to the PETE database, Nicholls, 1994). It is not surprising that the model fails to reproduce this unusually rapid initial decrease in the observed isoproturon soil residues, since a topsoil degradation half life of approximately 18 days at a reference temperature of 15°C was assumed. Volatilisation soon after pesticide application is unlikely to account for much of this rapid decrease in concentration, because, isoproturon is not an especially volatile compound (vapour pressure at 20°C is 3.33 × 10⁻⁶ Pa). It is unlikely that large quantities of isoproturon were leached from the soil surface during the first five days after application as only 4.8 mm of rain fell during this period. Another possible explanation could be the formation of non-extractable isoproturon soon after application. Again this is unlikely because, Johnson *et al.* (1996) found that the recovery efficiency of the extraction procedure used in these experiments was between 87 and 100%. Pore-scale interaction between sorption and degradation is another possible explanation for the initial rapid phase of degradation while soil residues were high. If it is assumed that only pesticide in solution is degraded, and sorption follows a Freundlich isotherm, then the effective bulk soil degradation rate coefficient will be dependent on the solution-phase concentration, and will be larger at larger initial concentrations.

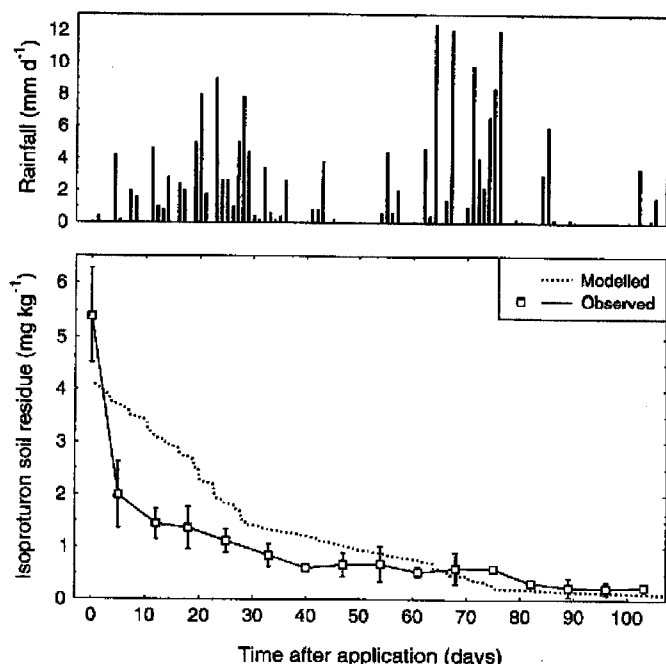


Fig. 4. The observed and modelled isoproturon residue present in the top 20 mm of the soil profile. The error bars on the observed data represent two times the standard deviation. The standard deviation was calculated using three separate soil samples removed from different areas of the plot on the same day. The isoproturon was applied to the soil on 12 March 1994 at a rate of 0.9 kg ha⁻¹.

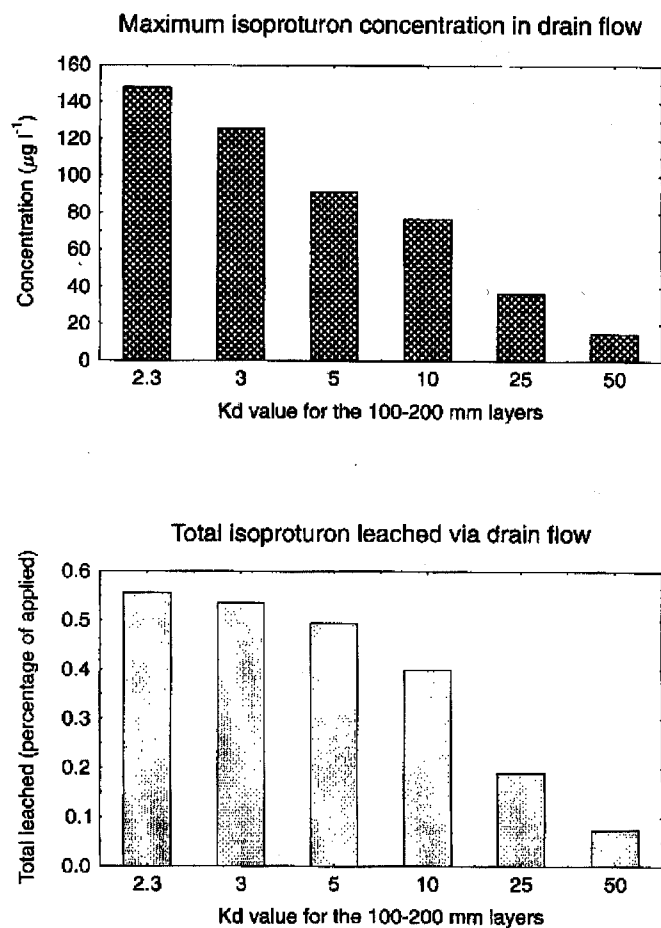


Fig. 5. The effect of increasing the isoproturon sorption coefficient K_d in the 100–200 mm layers on both the maximum isoproturon concentration and the total amount of isoproturon leached via the drain flow.

From 10 to 100 days after pesticide application, the model generally overestimated the decrease in the residue amount in the surface 20 mm of soil. It is difficult to determine the reasons for this without data for soil layers deeper than 20 mm, but it could be due either to an inappropriate parameterization of the water and temperature response functions for degradation, or to an overestimate of downward leaching in the model.

REDUCING PESTICIDE LEACHING

Fine Seed Beds and Deep Ploughing

Changes in the parameters in the model that reflect soil structure to simulate fine seed beds and deep ploughing decreased the predicted maximum concentration of isoproturon in drain flow from $148 \mu\text{g l}^{-1}$ to $70 \mu\text{g l}^{-1}$. The model also predicted a corresponding decrease in the total amount of isoproturon leached via drain flow from 0.56% to 0.22% of the amount applied. Thus, the model suggests that if these farming practices were routinely adopted pesticide leaching via field drains could be reduced.

Incorporated Organic Matter

Figure 5 shows the model predictions of the effects of incorporated organic matter, expressed as an increase in K_d in the 100–200 mm layer, on both the maximum isoproturon concentration in the drain flow and the total amount of isoproturon leached. Johnson *et al.* (1997) have shown that it is not unreasonable to expect the K_d to increase from 2.3 kg to around 5 l kg^{-1} if organic matter is incorporated in the 100–200 mm layer at Wytham. Figure 5 shows that such an increase in K_d results in a c. 40% reduction in the maximum isoproturon concentration, but only a slight decrease in the total amount of isoproturon leached. This modelling suggests that incorporated animal manure or sewage sludge may reduce acute toxic impacts resulting from the movement of pesticide from heavy clay soils to adjoining ditches and streams, but that chronic effects may not be alleviated at normal manure and sludge application rates.

Conclusions

Following calibration of hydraulic properties, drain flow hydrographs from a heavy clay soil under a winter cereal crop were well simulated by MACRO during extended periods of above average rainfall, with the shape and size of the hydrographs agreeing well. However, two significant drain flow events after pesticide application in early spring were less well simulated by the model, probably due to an overestimation of evapotranspiration during a period of low rainfall around the pesticide application day. The chemograph shape for these storm events was not well simulated by the model due to the errors in simulating drain flow. However, for the second event, both the maximum isoproturon concentration and the total load were closely matched. Although the model failed to predict a rapid initial decrease in the observed pesticide soil residues, the amount remaining in the surface 20 mm 100 days after application was reasonably well predicted.

The calibrated MACRO model was used to simulate the effect of creating fine seed beds and deep ploughing on pesticide leaching from this soil. The model predicted that the maximum concentration of isoproturon in the drain flow and the total amount of isoproturon leached via the drain flow would decrease by c.50 and 60 % respectively. The calibrated MACRO model then simulated the effect of organic matter on pesticide leaching; application of organic matter to the soil in practical amounts reduced the maximum concentration and the total amount leached by c.40 and 10 % respectively. This modelling exercise has shown that both i) incorporation of animal manure or sewage sludge and ii) creating fine seed beds and deep ploughing may offer effective methods of reducing the movement of pesticide from heavy clay soils to adjoining ditches and streams. Further field experiments and modelling work are needed to confirm the effectiveness of these strategies.

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References

- Armstrong, A., Addiscott, T. and Leeds-Harrison, P. 1995. Methods for Modelling Solute Movement in Structured Soils. In: Stephen T. Trudgill Ed., *In Solute Modelling in Catchment Systems*. 133-161. Wiley, Chichester, UK.
- Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. *J. Environ. Qual.*, 20: 425-435.
- Brooks, R.H. and Corey, A.T. 1964. Hydraulic properties of porous media. *Hydrology Paper no.3*, Colorado State University, Ft. Collins, CO, 27 pp.
- Cannell, R.Q., Davies, D.B., Mackney, D and Pidgeon, J.D. 1978. The suitability of soils for sequential direct drilling of combine-harvested crops in Britain: a provisional classification. *Outlook on Agriculture*, 9: 306-316.
- Drinking Water Inspectorate. 1995. *Drinking Water 1994*. HMSO, London., 226pp.
- ENDS. 1995. Herbicide restricted to protect water supplies. *ENDS Report*, 246: 33-33.
- Haria, A.H., Johnson, A.C., Bell, J.P., and Batchelor, C.H. 1994. Water movement and isoproturon behaviour in a drained heavy clay soil: 1. Preferential flow processes. *J. Hydrol.*, 163: 203-216.
- Harris, G.L., Hodgkinson, R.A., Brown, C., Rose, D.A., Mason, D.J. and Catt, J.A. 1993. The influence of rainfall patterns and soils on losses of isoproturon to surface water. *Proc. Crop Protection Conf. Northern Britain, Dundee, 22-25 March*, British Crop Protection Council, 247-252.
- IPU UK Task force. 1995. *A stewardship programme to protect water quality*. AgrEvo UK Crop Protection Limited, Ciba Agriculture, Rhône-Poulenc Agriculture Limited, 11pp.
- Jarvis, N.J. 1994. The MACRO Model (Version 3.1) - Technical Description and Sample Simulations. *Reports and Dissertations no. 19, Dept. Soil Sci., SLU, Uppsala, Sweden.*, 51pp.
- Johnson, A.C., Haria, A.H., Bhardwaj, C.L., Völkner, C., Batchelor, C.H., and Walker, A. 1994. Water movement and isoproturon behaviour in a drained heavy clay soil: 2. Persistence and transport. *J. Hydrol.*, 163: 217-231.
- Johnson, A.C., Haria, A.H., Bhardwaj, C.L., Williams, R.J. and Walker, A. 1996. Preferential Flow Pathways and Their Capacity to Transport Isoproturon in a Structured Clay Soil. *Pesticide Sci.*, 48: 225-237.
- Johnson, A.C., Worrall, F., White, C., Walker, A., Besien, T.J., and Williams, R.J. 1997. The potential of incorporated organic matter to reduce pesticide leaching. *Toxicol. Environ. Chem.*, 58: 47-61.
- Kneale, W.R. 1986. The Hydrology of a Sloping Clay Soil at Wytham, Near Oxford, England. *J. Hydrol.*, 85: 1-14.
- Leeds-Harrison, P.B., Shipway, C.J.P., Jarvis, N.J. and Youngs, E.G. 1986. The influence of soil macroporosity on water retention, transmission and drainage in a clay soil. *Soil Use Manag.*, 2: 47-50.
- Muallem, Y. 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Wat. Resour. Res.*, 12: 513-522.
- Nicholls, P.H. 1994. Physicochemical evaluation: the environment, an expert system for pesticide preregistration assessment. In: *Proc. 1994 BCPC Conference - Pests and Diseases*, Brighton, 1337-1342.
- NRA. 1995. *Pesticides in the Aquatic Environment*. Report for the National Rivers Authority by the National Centre for Toxic and Persistent Substances. HMSO, London. Water Quality Series No. 26: 92pp.
- Penman, H.L. 1963. *Vegetation and hydrology*. Tech Comm 53, Commonwealth Bureau of Soils. Harpenden.
- PSD. 1995. *Evaluation of Fully Approved or Provisionally Approved Products. Evaluation on: Isoproturon*. MAFF, PSD, York, UK., 195pp.
- Van Genuchten, M.T. and Wagenet, R.J. 1989. Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.*, 53: 1303-1310.
- White, S.L. and Pinkstone, D.C. 1995. The occurrence of pesticides in drinking water. *British Crop Protection Council Monograph No. 62: Pesticide Movement to Water*, 263-268.