The Science of The Total Environment, Volume 318, Issues 1-3, 5 January 2004, Pages 73-88

Using a linked soil model emulator and unsaturated zone leaching model to account for preferential flow when assessing the spatially distributed risk of pesticide leaching to groundwater in England and Wales

I.P. Holman[1], I.G. Dubus[2], J.M. Hollis and C.D. Brown

Cranfield University at Silsoe, Silsoe, Bedford MK45 4DT, United Kingdom

[1] Corresponding author: I.P. Holman

Tel: +44 (0)1525 863000

Fax: +44 (0)1525 863344

Email: i.holman@cranfield.ac.uk

[2] Present address for I.G. Dubus :

BRGM, 3, avenue Claude Guillemin, BP 6009, 45060 Orléans Cedex 2, France

Correspondence address: Cranfield University at Silsoe, Silsoe, Bedford MK45 4DT, United Kingdom

Abstract

Although macropore flow is recognized as an important process for the transport of pesticides through a wide range of soils, none of the existing spatially distributed methods for assessing the risk of pesticide leaching to groundwater account for this phenomenon. The present paper presents a spatially distributed modelling system for predicting pesticide losses to groundwater through micro- and macropore flow paths. The system combines a meta version of the mechanistic, dual porosity, preferential flow pesticide leaching model MACRO (the

MACRO emulator), which describes pesticide transport and attenuation in the soil zone, to an attenuation factor leaching model for the unsaturated zone. The development of the emulator was based on the results of over 4000 MACRO model simulations. Model runs describe pesticide leaching for the range of soil types, climate regimes, pesticide properties and application patterns in England and Wales. Linking the MACRO emulator to existing spatial databases of soil, climate and compound-specific loads allowed the prediction of the concentration of pesticide leaching from the base of the soil profile (at 1 m depth) for a wide range of pesticides. Attenuation and retardation of the pesticide during transit through the unsaturated zone to the watertable was simulated using the substrate attenuation factor model AQUAT.

The MACRO emulator simulated pesticide loss in 10 of 12 lysimeter soil-pesticide combinations for which pesticide leaching was shown to occur and also successfully predicted no loss from 3 soil-pesticide combinations. Although the qualitative aspect of leaching was satisfactorily predicted, actual pesticide concentrations in leachate were relatively poorly predicted. At the national scale, the linked MACRO emulator / AQUAT system was found to predict the relative order of, and realistic regional patterns of, pesticide leaching for atrazine, isoproturon, chlorotoluron and lindane. The methodology provides a first-step assessment of the potential for pesticide leaching to groundwater in England and Wales. Further research is required to improve the modelling concept proposed. The system can be used to refine regional groundwater monitoring system designs and sampling strategies and improve the cost-effectiveness of the measures needed to achieve “good status” of groundwater quality as required by the Water Framework Directive.

[Words = 349]

Keywords

Pesticide, leaching, groundwater, model, macropore, spatial

1. Introduction

The scale of the threat to groundwater quality from diffuse source pollutants has led many countries to develop methodologies to assess the vulnerability of groundwater resources to chemical contamination at various scales (e.g. Diaz-Diaz et al. 1999; Holman et al. 2000). Groundwater vulnerability maps, which delineate the land surface according to the potential for pollutants to reach groundwater resources, have been generated using a variety of ranking or scoring methods to produce qualitative (e.g. Palmer et al. 1995) or semi qualitative (e.g. Secunda et al. 1998) output. These maps usually assess the overall potential for chemical contamination of aquifers and are not specific to individual compounds or classes of compounds (e.g. Aller et al. 1987). Although these maps are useful for supporting policies with regard to the general protection of water resources, they are not suitable for driving detailed monitoring programmes for pollutants.

The contamination of groundwater by crop protection products leads to expensive treatment where the water is used for drinking water purposes. The threat of contamination has encouraged the development of techniques to assess the groundwater vulnerability to pesticide contamination, including semi-empirical methods based upon relationships of a limited number of physical properties with pesticide concentrations (e.g. Shukla et al. 1996; Troiano et al. 1999) and more quantitative techniques relating to pesticide movement and attenuation. The latter include analytical solutions of the convection-dispersion equations, such as the Attenuation and Retardation Factors (Loague et al. 1996; Souter & Musy, 1999) and the Leaching Index (Diaz-Diaz et al. 1999), and numerical solutions of the convection-dispersion equations (mainly based on PRZM or PRZM2- e.g. Stewart & Loague, 1999; or LEACHM- e.g. Souter & Musy, 1999). Although macropore flow is recognized as an important transport process for pesticide leaching through a wide range of soils (Brown et al.

2000; Flury, 1996), none of the methodologies for evaluating the potential transfer of pesticides to depth at a large scale incorporates a description of this process.

The present paper reports on a methodology for assessing the potential for pesticides to leach to groundwater in England and Wales which incorporates a description of preferential flow. The assessment is based on the combination of (i) spatially distributed data, (ii) an emulator of the macropore flow model MACRO and (iii) a leaching model for the unsaturated zone.

2. Methodology

2.1 Strategy

The aim of the work reported in the present paper was to develop a diffuse source groundwater pollution module for the Prediction Of Pesticide Pollution In the Environment (POPPIE) system. POPPIE was initially developed to predict pesticide concentrations in surface waters and is used by the Environment Agency of England and Wales for driving and refining pesticide monitoring programmes (Brown et al. 2002). The purpose of the groundwater module is to predict the concentrations of agricultural pesticides reaching the watertable of any groundwater unit in England and Wales likely to be abstracted by small, locally used, wells. Groundwater is present in almost all geological deposits in these two countries and many locally important groundwater supplies are abstracted from deposits classified as non-aquifers (Palmer et al. 1995).

Development of the groundwater module for POPPIE was restricted by limitations imposed by the necessity to integrate the module into an existing software system. The proposed methodology had to: i) be applicable for all arable areas of England and Wales; ii) utilise existing national spatial databases of climate, soils and their properties, land use, pesticide

usage and depth to groundwater held within POPPIE at a 2 km x 2 km resolution; and, iii) be able to predict concentrations for most pesticides applied to arable crops in England and Wales. Given the importance of preferential flow processes in the transport of pesticides to depth in a wide range of soils (Brown et al. 2000; Flury et al. 1995), it was decided to base the soil leaching component of the POPPIE groundwater module on the dual-porosity model MACRO (Jarvis, 2002). MACRO was used to simulate pesticide leaching within the reactive soil zone (ca. the top metre of soil) where most pesticide sorption and degradation occur. Below this, transfer of pesticides within the unsaturated zone was simulated using an Attenuation Factor model (Hollis, 1991). Although this latter approach does not account for preferential flow, it was still considered appropriate as there is little information on how a pesticide might behave in the unsaturated zone of a dual porosity and dual permeability aquifer (Besien et al., 2000) that could support the use of a preferential flow model. Given the potential importance of preferential flow in chalk aquifers in England and Wales, model predictions should be considered to provide a potential for leaching as opposed to quantitative estimates. Running MACRO within the system in real-time was not considered an option since the model has a long run-time. Furthermore, running the model itself would have entailed parameterisation for all 412 soil types in the national soil database of England and Wales, an effort considered to be unnecessary because many of the soils have similar physical and chemical properties. In order to avoid unnecessary detailed parameterization and run-time constraints whilst capitalising on the 'state-of-the art' nature of the model, a meta-version of MACRO (or 'MACRO emulator') was developed.

2.2 Simulation of pesticide leaching in the reactive zone

The MACRO model

MACRO is a physically-based, macropore flow model, with the total soil porosity divided into two flow domains (macropores and micropores), each characterised by a flow rate and solute concentration (Jarvis, 1994; Jarvis, 2002). Soil water flow and solute transport in the micropores are modelled using Richards' equation and the convection-dispersion equation, respectively, whilst fluxes in the macropores are based on a simpler gravity approach with mass-flow (Beulke et al., 2001). Exchange between macropores and micropores is calculated according to approximate, physically-based expressions using an effective aggregate half-width. Pesticide degradation is modelled using first-order kinetics whilst sorption is assumed to be at instantaneous equilibrium and to be described by a Freundlich isotherm. The model has been endorsed by the FOCUS working group on leaching (FOCUS, 2000) and is used in Europe within the pesticide registration context to assess the leaching potential for compounds to surface waters via drainage and to groundwater. MACRO has been evaluated in a significant number of studies (e.g. Jarvis et al. 1994; Vanclooster et al. 2000) and was recommended for use within pesticide registration in a comparative study investigating the potential for five preferential flow models to simulate field (Beulke et al. 2001) and lysimeter (Beulke et al. 1998) data. Version 4.1 of the model was used in the present study.

Selection of representative MACRO input data

Soil data

Parameterisation and run-time constraints prevented the running of the model for all soil types. In order to select a limited but valid range of soil types representative of agricultural conditions across England and Wales, groupings based on each of the Soil Leaching Potential classes (e.g. H1, H2 etc.) depicted on the Environment Agency's national series of groundwater vulnerability maps (Palmer et al. 1995) were selected. Further subdivision (e.g. H1a, H1b etc.) of specific classes was made (Table 1) to ensure that each leaching class or sub-class contained soils with only a limited range of physical characteristics consistent with

a single set of MACRO input parameters. MACRO was parameterised for each of the 10 resulting soil leaching classes using soil information data (organic carbon content, bulk density, particle size distribution, typical soil structure, water retention data) available in the national soil database (Hallett et al. 1995) and expert judgement. Parameters were chosen as follows: the pore size distribution index in the micropores (ZLAMB) was calculated by fitting the Brooks and Corey equation (Brooks and Corey, 1964) to the water release curve; expert judgement was used to establish the water tension at the boundary between micropores and macropores (CTEN) as this cannot readily be independently estimated; the water content equivalent to this tension (XMPOR) was then derived from the water release curve, whilst the conductivity at the boundary (KSM) was estimated from the above values using the equation given by Laliberte et al. (1968) and Jarvis et al. (1997); the pore size distribution index in the macropores (ZN) was calculated from CTEN using equations built into MACRO_DB (Jarvis et al., 1997); the saturated hydraulic conductivity was derived using the pedotransfer functions for soils in England and Wales by Hollis and Woods (1989). Aggregate half-widths were selected from basic descriptions of soil structure using the rules proposed by Jarvis et al. (1997).

Climate

Excess Winter Rain (XWR, the long term average amount of precipitation falling between the start of the Field Capacity season and the end of March less evapo-transpiration) varies from <150 to 700 mm in the main arable areas of the UK (Jones & Thomasson, 1985). This range was subdivided into 6 climate classes, each representing between 1.3×10^6 and 4.1×10^6 ha of land (Figure 1). Long term weather datasets were obtained from a UK Meteorological Office weather station in each of the climate classes and single years were selected for each of the six climate classes to give XWR values around the mid point of the range specified (Figure 1) and a roughly even distribution of rainfall across the year. The annual weather data were repeated four times to give a four year leaching period. The length of simulation was selected

on the basis of computational limitations, but was considered sufficient to allow the movement of compounds through the soil profile for most of the combinations of pesticide parameters used (see below).

Pesticide properties and application data

Sensitivity analyses for the MACRO model (Dubus & Brown, 2002) demonstrated that the two input parameters which most influence model predictions for pesticide loss through leaching are generally the sorption distribution coefficient normalised to organic carbon (Koc) and the pesticide half-life (DT50), i.e. the time required for a given quantity of compound to degrade by 50%. Koc values typically range from 1 to >10,000 ml/g while DT50 values vary between 1 and >3000 days (Nicholls, 1994). Larger Koc values indicate stronger sorption and larger DT50 values indicate greater persistence. From experience, less mobile compounds with a Koc > ca. 500 ml/g are only likely to leach to depth if they are also very persistent in soil. However, it is unlikely that compounds with a DT50 > ca. 1 year would be registered for use in agriculture due to their potential to accumulate in soil. Also, compounds with small Koc and large DT50 values are not used in modern agriculture because of their undesirable environmental mobility and persistence. Allowing for these restrictions, DT50 values were allow to vary between 2 and 350 days while Koc values ranged from 2 to 500 ml/g and unrealistic combinations of the two parameters were avoided. This resulted in a total of 49 combinations of Koc and DT50 which were used in the modelling (Table 2). The Freundlich exponent was set to unity, thereby assuming linear sorption. Degradation rates in the subsoil were corrected from those in the topsoil using the equation presented by Jarvis et al. (1997) which assumes that degradation of the compound sorbed is negligible and that the degradation rate in solution is proportional to the soil organic carbon.

Pesticides were considered to be applied to a winter wheat crop at a rate of 1000 g a.i. /ha on 15 October (scenarios involving autumn applied pesticides) or on 15 April (scenarios

involving spring applied pesticides) in the first year of simulation. No crop interception by the wheat crop was considered. Application dates are representative of management practices in the UK (Hough, 1990). The correction of application dates according to rainfall data around the time of application was considered to be outside the scope of the paper. Differences between the different weather scenarios might therefore originate to some extent from the timing of application with respect to rainfall events.

MACRO simulations

Soil leaching classes I2 and L are very organic rich or impermeable, respectively. As such, they have an inherently low pesticide leaching risk and were not considered in the analysis. Arable agriculture does not occur in England and Wales in areas with > 700 mm of Excess Winter Rain. Therefore the total number of combinations which were considered in the modelling was 4704, i.e. 49 DT50/Koc combinations, 48 soil/climate combinations (8 soils, 6 climates) and a pesticide application in either spring or autumn. MACRO input files were generated automatically using the SENSAN software (Doherty, 2000) and daily pesticide concentrations in water percolating at the bottom of the representative profiles were simulated by the model over a four-year period. Average annual concentrations were calculated for each of the 4 years simulated and the largest of these concentrations was taken.

MACRO emulator

The MACRO emulator comprises a series of look-up tables constructed from the results of the 4704 MACRO runs using different input data for soil, weather and pesticide characteristics. The tables were indexed by i) soil leaching potential class; ii) average annual hydrologically effective rainfall (AAHER); iii) season of application (either spring or autumn); iv) pesticide half-life; and, v) pesticide sorption distribution coefficient.

AAHER is derived from weekly values of HER calculated by the 'Meteorological Office Rainfall and Evaporation Calculation System' (MORECS- Thompson et al. 1981) using daily observational data from the Meteorological Office's network of weather stations. Over the long term XWR and AAHER should be similar, but the weekly values of HER within the POPPIE databases allow AAHER to be calculated over time periods different from that of the long term XWR.

Using the MACRO emulator

For any pesticide, the look-up tables within the MACRO emulator were used to identify the appropriate maximum annual average concentration that relates to the specific soil leaching classes and AAHER of the grid square from the relevant national datasets, and the half-life and Koc values of the pesticide. Where a desired pesticide parameter lay between the values in the look-up tables, linear interpolation routines were used to derive appropriate maximum annual average concentrations (Appendix 1). More than one soil type occurs in most of the 2 km x 2 km grid squares in the POPPIE dataset, and a weighted average concentration was thus calculated based upon the proportion of each soil in the grid square.

The maximum annual average concentrations derived were then linearly scaled to match the seasonal pesticide loading using the ratio of the seasonal pesticide loading to the 'standard' pesticide loading of 1000 g/ha considered in the MACRO runs. The seasonal pesticide loadings were calculated from monthly loadings (held within the POPPIE database), which had been derived by downscaling regional pesticide usage survey data using 2 km x 2 km cropping statistics. The average 'Autumn' pesticide loading was calculated by summing the monthly pesticide loadings for September to January and dividing by the number of years in the simulation period. Similarly the average 'Spring' pesticide loading is calculated using monthly pesticide loadings for February to August.

2.3 Simulation of pesticide leaching in the unsaturated zone

The Substrate Attenuation Model

Current regulatory practice for pesticides is to simulate pesticide leaching through soil at 1 m depth. The predicted concentration at this depth is used as a protective surrogate estimator of the pesticide concentration in groundwater. Groundwater is deeper than 1 m in most areas of England and Wales, and the concentration of pesticide in the recharge impacting on a groundwater surface is smaller than that leaving the base of the soil profile due to adsorption, dispersion and degradation during transit through the unsaturated zone.

The AQUAT model (Hollis, 1991) is used to predict maximum annual average concentration impacting upon the watertable as this model uses the same soil and climate datasets as those used in the prediction of pesticide concentrations at 1-m depth. The model applies an attenuation factor (AF) to the predicted maximum annual average soil leachate concentrations leaving the base of the soil profile derived from the MACRO emulator ($Conc_{soil}$, in µg/l) to derive the maximum annual average concentration impacting upon the watertable ($Conc_{substrate}$, in µg/l):

$$Conc_{substrate} = AF * Conc_{soil} \quad (1)$$

The attenuation factor calculates the amount of attenuation that will occur during the estimated transit time (in days) of the pesticide in the unsaturated substrate zone (T_d), assuming a first-order rate constant for degradation:

$$AF = \exp\left(-T_d * \left(\frac{0.693}{DT50_{subtrate}}\right)\right) = \exp\left(-T_d * \left(\frac{0.693}{\left(\frac{OC_{topsoil}}{OC_{substrate}}\right) * DT50_{soil}}\right)\right) \quad (2)$$

The pesticide half-life in the substrate ($DT50_{substrate}$) is derived by increasing the topsoil half-life ($DT50_{soil}$) according to the ratio of the topsoil and substrate organic carbon contents ($OC_{topsoil}$ and $OC_{substrate}$, respectively). This reflects the decrease in pesticide losses due to the decrease in degradation in the substrate resulting from limited microbial activity.

The time taken by the pesticide to leach out of the substrate (T_d) is estimated from:

$$T_d = \frac{z * Rf * 100}{Fw} \quad (3)$$

where *z* is the thickness of the unsaturated zone (m) based on values from an Environment Agency dataset within POPPIE, *Rf* is a retardation factor for pesticide flow (dimensionless) and *Fw* is the unsaturated substrate water flux (cm/day) or pore water velocity.

Fw is based on the proportion of AAHER (mm) which infiltrates to the saturated zone, allowing for runoff. The proportion is based upon the dimensionless Base Flow Index (BFI) which is predicted for specific soil types using the empirical analyses of the Hydrology Of Soil Types classification (Boorman et al. 1995). The pore water velocity depends on the water content in the unsaturated zone, which is assumed to be constant throughout the year, and represented by the water content at -5 kPa tension (assumed to represent field capacity). However, not all the water held in the substrate is available for displacement via piston flow as some water will be held at such strong tensions as to be effectively 'immobile'. Hence, only the 'mobile' volumetric water fraction, calculated as the volumetric water fraction

between -5 kPa and -200 kPa tension (θ_5-θ_{200}) is used when calculating *Fw*. Equation (3) then becomes:

$$Td = z * Rf * 100 * \left(\frac{\theta_5 - \theta_{200}}{\left(\frac{AAHER * BFI}{365 * 10} \right)} \right) \quad (4)$$

The 'retardation factor' *Rf* for pesticide flow (Eq. 5) is an index of the retardation of pesticide leaching through soils due to sorption (Loague et al. 1996). Its development derives from soil thin-layer chromatography and it is suitable for calculating movement in the unsaturated substrate zone because we assume that pesticide flow occurs predominantly as bulk matrix flow.

$$Rf = 1 + \frac{\left(\left[\rho_{substrate} * K_{oc} * OC_{substrate} * 0.01 \right] + \left[\left(\theta_{0\,substrate} - \theta_{5\,substrate} \right) * K_{aw} \right] \right)}{\theta_{5\,substrate} - \left(0.5 * \theta_{1500\,substrate} \right)} \quad (5)$$

where $\rho_{\text{substrate}}$ is the bulk density of the substrate (g/cm^3), $\theta_{0\,\text{substrate}}$ is the porosity (dimensionless), θ_{1500} is the volumetric water content at -1500 kPa tension and K_{aw} is the Henry's Law constant (dimensionless).

In this approach, the pesticide is partitioned between the solid, liquid and gas phases by adsorption, diffusion and volatilisation as it leaches through porous material. Within the unsaturated substrate, the retardation factor is based on pesticide-specific solid/water and water/gas partition coefficients calculated from Koc and Kaw values and the substrate water and air fractions. The substrate water fraction available for partitioning is assumed to be the water fraction at -5 kPa less half of the water content at -1500 kPa tension (assumed to represent wilting point), as some of the water is held at tensions that render it unavailable for

physico-chemical interactions. The substrate air fraction is calculated as the difference between total volumetric porosity and volumetric water content at -5kPa tension.

3. Model evaluation and discussion

3.1 MACRO emulator output

Examples of output from the MACRO emulator are shown in Figures 2 to 4 for a range of pesticide physico-chemical properties, soil types, climate and application timing. The relative vulnerability to leaching was found to be significantly influenced by all factors considered in the approach (i.e. soil class, climate class, pesticide properties and timing of application). The large sensitivity of the MACRO emulator to the two pesticide parameters (Figure 2) is similar to that described for the MACRO model (Dubus & Brown, 2002). The largest concentrations were predicted for the soils which are prone to by-pass flow (soil classes H1a and I1c) (Figure 3). Increasing AAHER generally caused greater leaching up to a maximum value (Figures 3 and 4) above which the greater volume of leaching water diluted pesticide loadings, thereby resulting in a decrease in the predicted average concentration.

3.2 Evaluation of the MACRO emulator using lysimeter data

Data for two sets of lysimeter studies investigating the leaching of isoproturon, linuron, dichlorprop and bentazone (Bergström et al. 1994; Brown et al. 2000) were compared to predictions from the MACRO emulator (Tables 3 and 4). The appropriate soil leaching class was estimated from the lysimeter soil data and the AAHER was estimated from the measured average amount of annual percolation. Pesticide concentrations were calculated by the MACRO emulator for the appropriate soil class, AAHER, published half life and Koc and application season (autumn for the UK data and spring for the Swedish data). Finally, the

predicted concentrations were corrected for the actual application rates used in the studies (Tables 3 and 4) and converted to overall leachate loads using the measured drainage volumes from each lysimeter.

The MACRO emulator was found to predict leaching qualitatively (i.e. successful predictions of leaching in 10 out of 12 lysimeters for which positive detections of pesticide were reported and the absence of pesticide leaching in the three lysimeters which showed no pesticide detection) although quantitative estimates were only within an order of magnitude of concentrations measured in the lysimeters for 2 of the lysimeters presented in Tables 3 and 4. This may be attributed to: i) the fact that MACRO runs that were undertaken did not incorporate a lysimeter bottom boundary condition and ii) the lack of soil-specific parameterisation of MACRO for the lysimeters. Preferential flow was found by Jarvis et al. (1994) to have a stronger influence on pesticide loss in the lysimeters with the Mellby and Nantuna sands (Table 4) than would be expected on the basis of the texture of these two soils. Also, these authors have emphasised that an underestimation of concentrations measured in the five Swedish lysimeters is likely if modelling is undertaken using generic sorption and degradation data derived from the literature. Furthermore, for the UK lysimeters, the Ludford lysimeters were not representative of the H1a soil class, whilst the MACRO model itself under-predicts losses from the Enborne lysimeters (Beulke et al. 1998).

3.3 Evaluation of the modelling system linking the MACRO emulator and AQUAT using national monitoring data

A limited evaluation of the POPPIE groundwater module was carried out for pesticides detected in groundwater in the UK, using national scale monitoring data collected by the Environment Agency (Department of the Environment, Transport and Regions, 1998). Compounds were selected to cover a range of detection frequencies (common to infrequent),

spatial application patterns (national to regional) and crops. The chosen compounds were isoproturon (only registered for use on cereals), atrazine (registered for use on maize and until 31 August 1993 for non- agricultural uses), lindane (formerly registered for application to cereals, grass, brassicas, fruit and for non- agricultural uses) and chlorotoluron (registered for use on cereals).

The linked MACRO emulator / AQUAT system was operated within the bespoke POPPIE GIS at a 2 km x 2 km resolution since soil, climate and pesticide application datasets within POPPIE are available at this resolution (Brown et al. 2002). Figure 5 presents predicted maximum annual average concentrations of atrazine and isoproturon which are likely to impact upon groundwater in England and Wales, using climate and seasonal pesticide loading data for the period 1993-96 inclusive. Predicted atrazine concentrations were greatest in the south-west of England as would be expected from its primary agricultural usage in continuous forage maize cultivation. Out of the four compounds considered, predictions for isoproturon were the most spatially widespread, in accordance with its extensive usage with a wide range of cereals and its common detection in groundwater (Department of the Environment, Transport and Regions, 1998).

Table 5 shows the predicted numbers (and percentages) of 2 km by 2 km grid squares in England and Wales falling into classes of maximum average annual pesticide concentration. Data on the annual percentage of samples from public water supply boreholes with pesticide concentration >0.1 μg/l are also provided. The comparison of these two types of data is limited to some extent. First, the measured data are point samples in time (rather than annual average concentrations). Secondly, the measured data give a proportion of samples, rather than a proportion of boreholes sampled (the number of samples will differ between boreholes). Thirdly, the relatively coarse grid size used in this study (2 km x 2 km) allows the larger concentrations from 'hot spots' to be diluted by lower concentrations from other soils in the grid square. Also, the model cannot predict pesticide contamination resulting from

point or linear source applications, such as from non-agricultural usage on railways, woodland and amenity areas and pesticide disposal, spillage or sprayer 'washings'. For example, almost all herbicides applied to the West German railways were detected in nearby groundwater samples (Schweinsberg et al. 1999). Finally, the model cannot incorporate site-specific factors, such as pesticide runoff from adjacent impermeable strata and abstraction- or flood-induced infiltration of surface waters containing pesticide concentrations into groundwater.

This paper has described the first attempt at integrating preferential flow into the evaluation of the potential for groundwater contamination from pesticides. Further research and refinement of the modelling concept presented are required to address the main outstanding limitations. These include that a preferential flow model was not used to simulate water and solute flow in the unsaturated zone, the crop in MACRO was not adjusted to crop growth stage, application dates were not adjusted to rainfall data and there was no integration of detailed information on the unsaturated zone of aquifers.

With these limitations in mind, it can be considered that the linked MACRO emulator / AQUAT system successfully predicted the relative order of pesticide leaching to groundwater for the compounds studied. Poor predictions for atrazine were attributed to the significant non-agricultural usage of the compound in the UK prior to 1993. Overall, the first-step evaluation exercise described in the present paper suggested that the system developed was indicative of the likely potential for transfer of pesticides to groundwater and that the system could be used for its intended purpose, i.e. the refinement and targeting of pesticide monitoring programmes.

4. Conclusions

Pesticides are one of the few groups of diffuse source pollutants for which statutory water quality standards exist. As such it is desirable for regulators to be able to target groundwater monitoring systems to those localities where exceedences may occur on the basis of quantified predictions. All existing spatial modelling systems for pesticide leaching which provide quantified predictions are based on analytical or numerical solutions of the convection-dispersion equation. However, given the importance of preferential (or by-pass) flow processes in the transport of pesticides to depth in a wide range of soils, new methodologies are required which can account for by-pass flow within a spatial context.

The development and first-step evaluation of an integrated modelling system for predicting likely concentrations of agricultural pesticides leaching to the watertable throughout England and Wales is described. The integrated system links the interpolated results from more than 4000 simulations with the mechanistic, dual porosity, soil leaching model MACRO (the MACRO emulator) with an attenuation factor model for the unsaturated zone.

In a evaluation exercise against data for pesticide leaching from two sets of lysimeter studies, the MACRO emulator simulated pesticide loss in 10 of 12 lysimeter soil-pesticide combinations for which pesticide leaching was shown to occur and also successfully predicted no loss from 3 soil-pesticide combinations. However, the MACRO emulator tends to under-estimate the measured data. Evaluation against a wider range of soils is recommended to assess whether further subdivisions of the existing 10 soil leaching potential classes are required to improve predictions.

The system comprising the MACRO emulator and AQUAT was tested against national monitoring data for the presence of pesticides in UK aquifers. The current system uses spatially-weighted averages to predict concentrations in grid squares with more than one soil type. This allows the larger concentrations from ‘hot spots’ to be diluted by lower concentrations from other soils in the grid square. Given the problems associated with

comparing measured data with predicted average annual concentrations, the model successfully predicted the relative magnitude and regional patterns of leaching to groundwater of all 4 compounds selected for national study. Nevertheless, it is recommended that improved resolution datasets of soil types and pesticide application rates are incorporated.

It is considered that within the constraints imposed by the resolution of the data and the scale of operation, both the MACRO emulator and the system linking the MACRO emulator and the AQUAT model satisfactorily predicted the likelihood of pesticide leaching in the two simple evaluation exercises reported. This provides a first-step evaluation of the system which is to be used for the targeting and refinement of regional groundwater monitoring systems for the presence of pesticides in groundwater. Use of the system is likely to lead to an improvement in the cost-effectiveness of measures needed to ensure the "good status" of groundwater quality as required by the Water Framework Directive.

Acknowledgements

The authors gratefully acknowledge the funding of this study by the Environment Agency of England and Wales (project reference E1-066). The views expressed in this paper are those of the authors and do not necessarily reflect the views of the sponsor. We also appreciate the helpful comments of two anonymous referees.

5. References

Aller L, Bennet T, Lehr JH, Petty RJ, Hackett G. DRASTIC: A standardised system for evaluating groundwater pollution potential using hydrogeological settings. EPA/600/2-87/035, US Environmental Protection Agency, Ada, Oklahoma 1987, 643 pp.

Bergström L, Jarvis N, Stenström J. Pesticide leaching data to validate simulation models for registration purposes. J Env Sci and Health 1994; A29 (6): 1073-1104.

Besien TJ, Williams RJ, Johnson AC. The transport and behaviour of isoproturon in unsaturated chalk cores. J Contamin Hydrol 2000;43:91-110.

Beulke S, Brown CD, Dubus IG. Evaluation of preferential flow models to predict the movement of pesticides to water sources under UK conditions. SSLRC research project JF3728 for MAFF PL0516, 1998, 101pp.

Beulke S, Brown CD, Jarvis NJ. MACRO: a preferential flow model to simulate pesticide leaching and movement to drains. In: JBHJ Linders (ed.), Modelling of environmental chemical exposure and risk, 117-132. Kluwer Academic Publishers, The Netherlands, 2001.

Beulke S, Brown CD, Dubus IG, Harris G. Evaluation of uncalibrated preferential flow models against data for isoproturon movement to drains through a heavy clay soil. Pest Manag Sci 2001; 57:537-547.

Beven K, Germann P. Macropores and water flow in soils. Water Res Res, 1982; 18:1311-1325.

Boorman DB, Hollis JM, Lilly A. Hydrology of Soil Types: A hydrologically-based classification of the soils or the United Kingdom. Institute of Hydrology Report No. 126, Wallingford, UK, 1995, 137 pp.

Brooks RH, Corey AT. Hydraulic properties of porous media. Hydrology paper 3. Colorado State University, Fort Collins, USA, 1964.

Brown CD, Bellamy PH, Dubus IG. Prediction of pesticide concentrations found in rivers in the UK. Pest Manag Sci 2002; 58 (4): 363-373.

Brown CD, Hollis JM, Bettinson RJ, Walker A. Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. Pest Manag Sci 2000; 56: 83-93

Department of the Environment, Transport and Regions . Digest of Environmental Statistics. Vol. No. 20. Stationary Office, London, 1998, 338 pp

Diaz-Diaz R, Loague K, Notario JS. An assessment of agrochemical leaching potentials for Tenerife. J. Contam Hydrol 1999; 36(1-2): 1-30.

Doherty J. PEST – model-independent parameter estimation. Watermark Computing, Corinda, Australia, 2000, 151 pp.

Dubus IG, Brown CD. Sensitivity and first-step uncertainty analyses for the preferential flow model MACRO. J Env Qual 2002; 31 (1): 227-240

Flury M. Experimental evidence of transport of pesticides through field soils - A review. J Env Qual 1996; 25 (1): 25-45.

Flury M, Leuenberger J, Studer B, Fluhler H. Transport of anions and herbicides in a loamy and a sandy field soil. Water Res. Res. 1995; 31: 823-835.

FOCUS. FOCUS groundwater scenarios in the EU plant protection product review process. Report of the FOCUS Groundwater Scenarios Workgroup, EC document Sanco/321/2000 rev. 2, 2000, 202 pp.

Hallet SH, Thanigasalam P, Hollis JM. SEISMIC: a desktop information system for assessing the fate and behaviour of pesticides in the environment. Computers and Electronics in Agriculture 1995; 13: 227-242.

Hollis JM. Mapping the Vulnerability of Aquifers and Surface Water to Pesticide Contamination at the National/Regional Scale. In: Walker A (editor). Pesticides in Soils and Water: Current Perspectives. BCPC Monograph 47, 1991: pp. 165-174.

Hollis JM., Woods SM. The measurement and estimation of saturated soil hydraulic conductivity. Unpublished research report, Cranfield University, Silsoe, UK, 1989, 25 pp

Holman IP, Palmer RC, Leonaviciute N. Using soil and Quaternary geological information to assess the intrinsic groundwater vulnerability of shallow aquifers: an example from Lithuania. Hydrogeology Journal 2000; 8: 636-645.

Hough MN. Agrometeorological aspects of crops in the United Kingdom and Ireland: a review for sugar beet, oilseed rape, peas, wheat, barley, oats, potatoes, apples and pears. EUR 13039 EN, Commission of the European Communities, Luxembourg, 1990, 303pp.

Jarvis NJ. The MACRO model (version 3.1). Technical description and sample simulations. Monograph reports & dissertations 19, Department of Soil Sciences, Swedish University of Agricultural Sciences, Uppsala, Sweden, 1994.

Jarvis NJ. The MACRO model (version 4.3) - Technical description. http://www.mv.slu.se/bgf/Macrohtm/document.htm 2002, 41 pp.

Jarvis NJ, Stahli M, Bergström L, Jonsson H. Simulation of dichlorprop and bentazon leaching in soils of contrasting texture using the MACRO model. J Env Sci and Health 1994; A29 (6): 1255-1277.

Jarvis NJ, Nicholls PH, Hollis JM, Mayr T, Evans SP. MACRO-DB: a decision support tool for assessing pesticide fate and mobility in soils. Environ Softw 1997; 12:251-265.

Jones RJA, Thomasson AJ. An agroclimatic databank for England and Wales. Soil Survey Technical Monograph No. 16. Soil Survey, Harpenden, 1985, 45 pp.

Laliberte GE, Brooks RH, Corey AT. Permeability calculated from desaturation data. J Irrig Drain Div ASCE 1968;94:57-69.

Loague K, Bernkopf RL, Green RE, Giambelluca TW. Uncertainty of groundwater vulnerability for agricultural regions in Hawaii: Review. J Env Qual 1996; 25(3): 475-490.

Nicholls PH. 'Physicochemical Evaluation: The Environment' an experts system for pesticide preregistration assessment. In: Proceedings 1994 Brighton Crop Protection Conference – Pest and Diseases, 1994, pp. 1337-1342.

Palmer RC, Holman IP, Lewis MA. Guide to groundwater vulnerability mapping in England and Wales. HMSO, London, 1995, 46 pp.

Schweinsberg F, Abke W, Rieth K, Rohmann U, Zullei-Seibert. Herbicide use of railway tracks for safety reasons in Germany? Toxicology Letters 1999; 107:201-205.

Secunda S, Collin ML, Melloul AJ. Groundwater vulnerability assessment using a composite model combining DRASTIC with extensive agricultural land use in Israel's Sharon region. J. Env Manag 1998; 54(1): 39-57.

Shukla S, Mostaghimi S, Bruggemann AC. A risk-based approach for selecting priority pesticides for groundwater monitoring programs. Trans. of the ASAE 1996; 39(4): 1379-1390.

Souter M, Musy A. Global sensitivity analyses of three pesticide leaching models using a Monte-Carlo approach. J Env Qual 1999; 28(4): 1290-1297

Stewart IT, Loague K. A type transfer function approach for regional-scale pesticide leaching assessments. J Env Qual 1999; 28(2): 378-387.

Thompson, N, Barrie JA, Ayles, M. The Meteorological Office Rainfall and Evaporation Calculation System: MORECS. Hydrological Memorandum, No. 45, Meteorological Office, Bracknell, 1981 69 pp.

Troiano J, Marade J, Spurlock F. Empirical modelling of spatial vulnerability applied to a norflurazon retrospective well study in California. J Env Qual 1999; 28(2): 397-403.

Vanclooster M, Boesten JJTI, Trevisan M, Brown CD, Capri E, Eklo OM, Gottesbüren B, Gouy V, van der Linden AMA. A European test of pesticide leaching models: methodology and major recommendations. Agric Water Manag, 2000; 44:1-19.

Table 1 Description of pesticide leaching potential classes considered in the modelling

Soil Leaching Potential (after Palmer et al. 1996)	MACRO subclass*	Main soil characteristics of MACRO sub-class	Important characteristics with regard to pesticide leaching
H1	a	Soils affected by shallow groundwater and susceptible to by-pass flow	Small drainable pore space and coarse, dense soil structure resulting in common 'by-pass' flow events
H1	b	Soils that are shallow and overly rock or shattered rock at 40cm or less.	Attenuation limited by shallow soil
H2	-	Sandy or sandy over soft sandstone soils with low organic carbon content	Low organic carbon content and large drainable pore space
H3	a	Sandy or sandy over soft sandstone soils with larger organic carbon content than H2 soils,	Similar large drainable pore space to H2 soils, but larger organic carbon content, both in the topsoil and subsoil layers.
H3	b	Soils that are relatively shallow, overlying rock, rock rubble or 'clean' gravel at, or within 60cm depth.	Attenuation limited by relatively shallow soil
I1	a	Deep, relatively coarse textured soils unaffected by marked seasonal	Relatively large drainable pore space

		waterlogging	
I1	b	Deep, medium textured soils unaffected by marked seasonal waterlogging.	Moderate drainable pore space
I1	c	Deep loamy and clayey soils with slowly permeable subsoil layers that cause periodic waterlogging.	Small drainable pore space in the lower subsoil layers
I2	-	Lowland organic soils drained for agricultural use or mineral soils with peaty topsoils	Inherently low pesticide leaching risk due to very high organic carbon content and associated strong sorption
L	-	Soils with dense subsoils and/or impermeable substrates which restrict downward water movement.	Inherently low leaching risk due to impermeable substrates

* Sub-division of the Soil Leaching Potential class to ensure a limited range of physical characteristics consistent with a single set of MACRO input parameters

Table 2 Combinations of Koc and half-life (DT50) used in the MACRO simulations

	Koc (ml/g)							
DT50 (days)	2	5	10	20	50	100	200	500
2	✓	✓	✓	✓	✓	✓	✓	✓
5	✓	✓	✓	✓	✓	✓	✓	✓
10	✓	✓	✓	✓	✓	✓	✓	✓
20	✓	✓	✓	✓	✓	✓	✓	✓
50	n.c.	n.c.	✓	✓	✓	✓	✓	✓
100	n.c.	n.c.	n.c.	n.c.	✓	✓	✓	✓
200	n.c.	n.c.	n.c.	n.c.	✓	✓	✓	✓
350	n.c.	n.c.	n.c.	n.c.	n.c.	✓	✓	✓

n.c. combination not considered in the modelling

Table 3 Comparison of measured total pesticide losses with predictions from the MACRO emulator for UK lysimeter studies (Brown et al. 2000).

Soil series	SLP class	Mean observed loss (mg/m^2)	Predicted total loss (mg/m^2)
		Isoproturon (2.50 kg a.i/ha)	
Enborne	H1a	3.91	0.63
Ludford	H1a	3.24	0.93
Cuckney	H2	0.28	0.22
Sonning	H3b	0.92	0.04
Isleham	I2	0	0
		Linuron (0.74 kg a.i /ha)	
Enborne	H1a	0.016	0.01
Ludford	H1a	0.154	0.02
Cuckney	H2	0	0
Sonning	H3b	0.024	0
Isleham	I2	0	0

SLP: Soil Leaching Potential (Table 1)

Table 4 Comparison of measured total pesticide losses with predictions from the MACRO emulator for Swedish lysimeter studies (Bergstrom et al. 1994)

Soil series	SLP class	Mean observed loss (mg/m^2)	Predicted total loss (mg/m^2)
		Dichlorprop (1.6 kg a.i /ha)	
Lanna clay	H1a	0.322	0.001
Melby sand	H2	0.048	0.002
Hassla loam	I1b	0.073	0
		Bentazone (1.2^1/0.6^2 kg a.i /ha)	
Nantuna clay	H1a	0.038	0.214
Nantuna sand	H2	0.175	0.023

SLP: Soil Leaching Potential [1]1990, [2]1991

Table 5 Comparison between pesticide concentrations predicted by the MACRO emulator/AQUAT system against measured pesticide detections in groundwater samples in England and Wales. The measured data were extracted from a report by the Department of the Environment, Transport and Regions (1998).

Compound	Percentage of grid squares[1] with predicted maximum average annual concentration (µg/l)			Annual percentage of measured samples over 0.1 µg/l (1992-96)
	<0.01	0.01 - 0.05	>0.05	
Isoproturon	80.4	18.0	1.6	4.4 - 12.2
Atrazine	96.2	3.7	0.1	0.9 - 13.5
Chlorotoluron	96.5	3.5	0.0	0.3 - 2.2
Lindane	99.8	0.2	0.0	0.0 - 1.7

[1] 38111 grid squares in England and Wales

Figure captions

Fig. 1. Division of England and Wales into climate classes based on Excess Winter Rainfall

Fig. 2. MACRO emulator predictions from the MACRO emulator of annual average concentrations of pesticide leaching to 1 m depth within a soil leaching class H1a for a spring application of 1000 g a.i. /ha of pesticides with varying DT50 and Koc and an Average Annual Hydrologically Effective Rainfall (AAHER) of 200 mm

Fig. 3. MACRO emulator predictions from the MACRO emulator of annual average concentrations of pesticide leaching to 1 m depth for an application of 1000 g a.i. /ha of a pesticide with DT50=50 days and Koc = 200 ml/g in (a) spring and (b) autumn with varying soil class and AAHER

Fig. 4. MACRO emulator predictions of annual average concentrations of pesticide leaching to 1 m depth within a soil leaching class H1b for a spring application of 1000 g a.i. /ha of pesticides with DT50=20 days and varying Koc and varying AAHER

Fig. 5. Predicted maximum annual average concentration (µg/l) of (a) atrazine and (b) isoproturon in recharge impacting upon groundwater in England and Wales

Fig. 1. Division of England and Wales into climate classes based on Excess Winter Rainfall

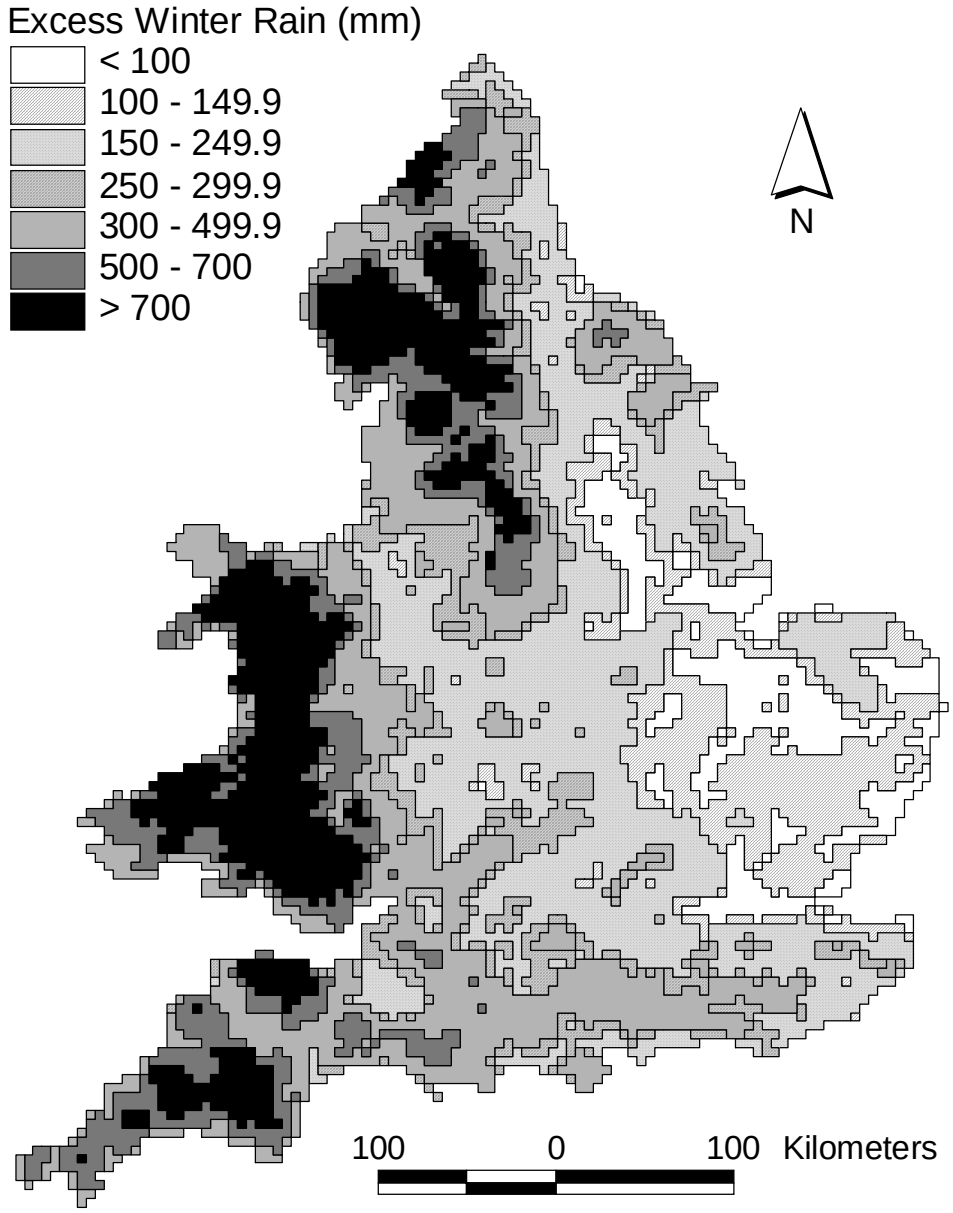


Fig. 2. MACRO emulator predictions from the MACRO emulator of annual average concentrations of pesticide leaching to 1 m depth within a soil leaching class H1a for a spring application of 1000 g a.i. /ha of pesticides with varying DT50 and Koc and an Average Annual Hydrologically Effective Rainfall (AAHER) of 200 mm

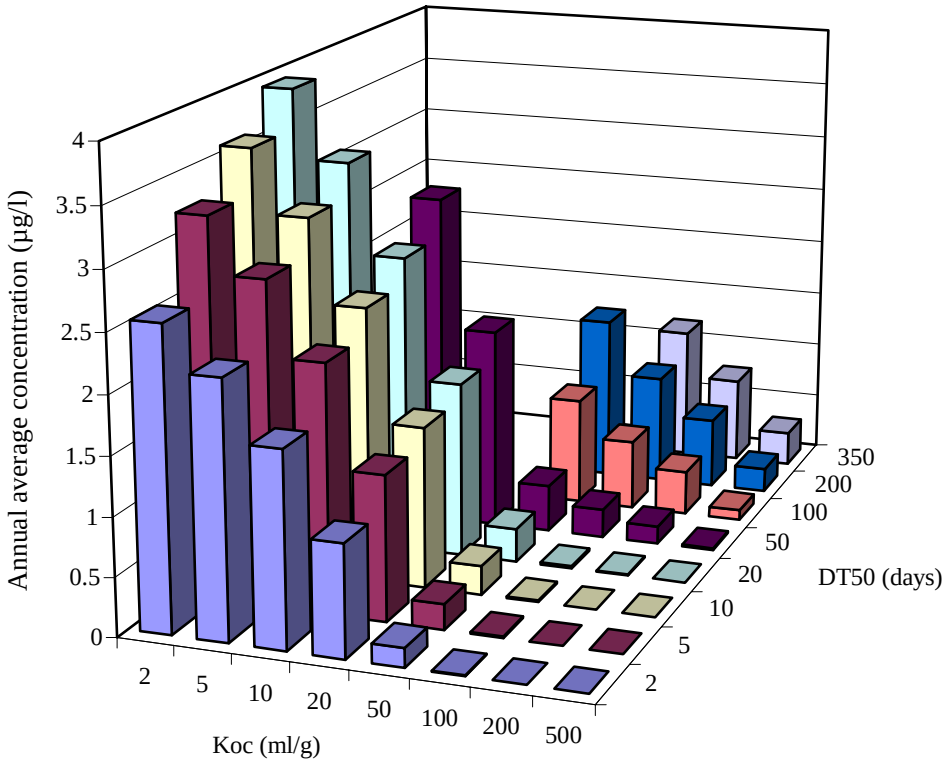
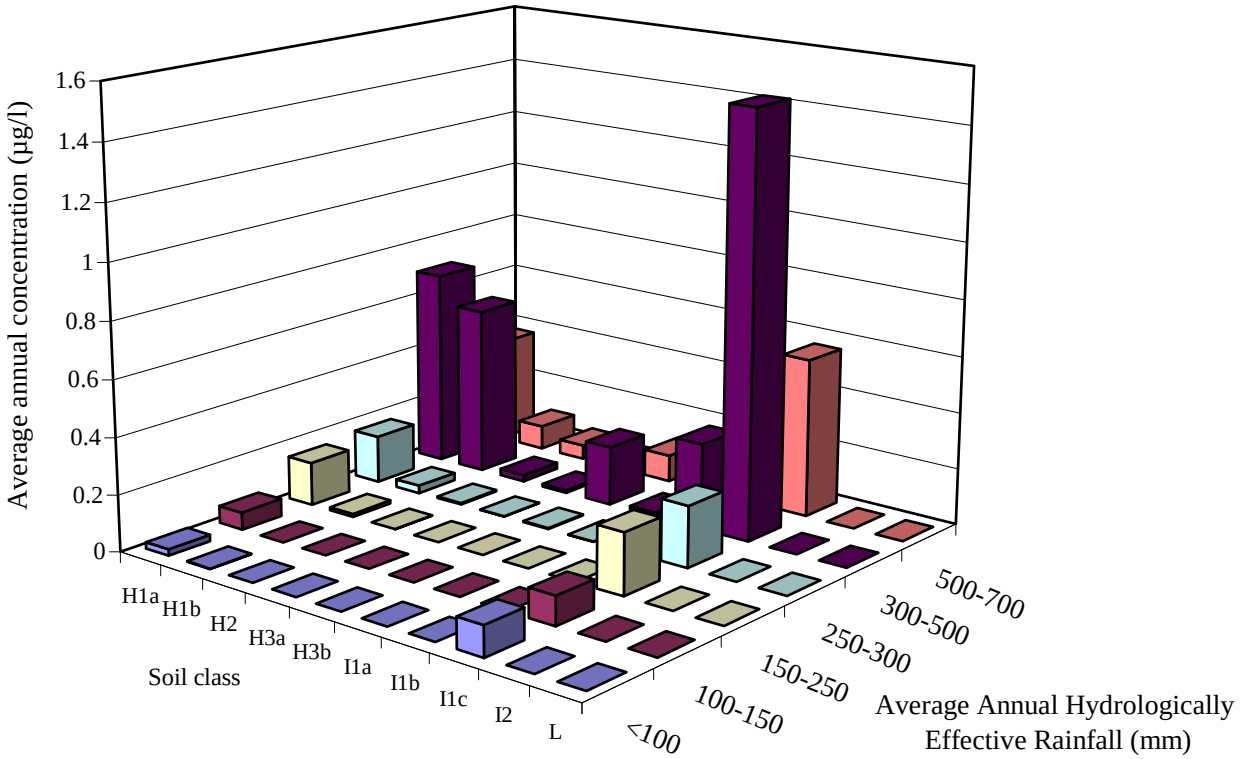


Fig. 3. MACRO emulator predictions from the MACRO emulator of annual average concentrations of pesticide leaching to 1 m depth for an application of 1000 g a.i. /ha of a pesticide with DT50=50 days and Koc= 200 ml/g in (a) spring and (b) autumn with varying soil class and AAHER

(a)



(b)

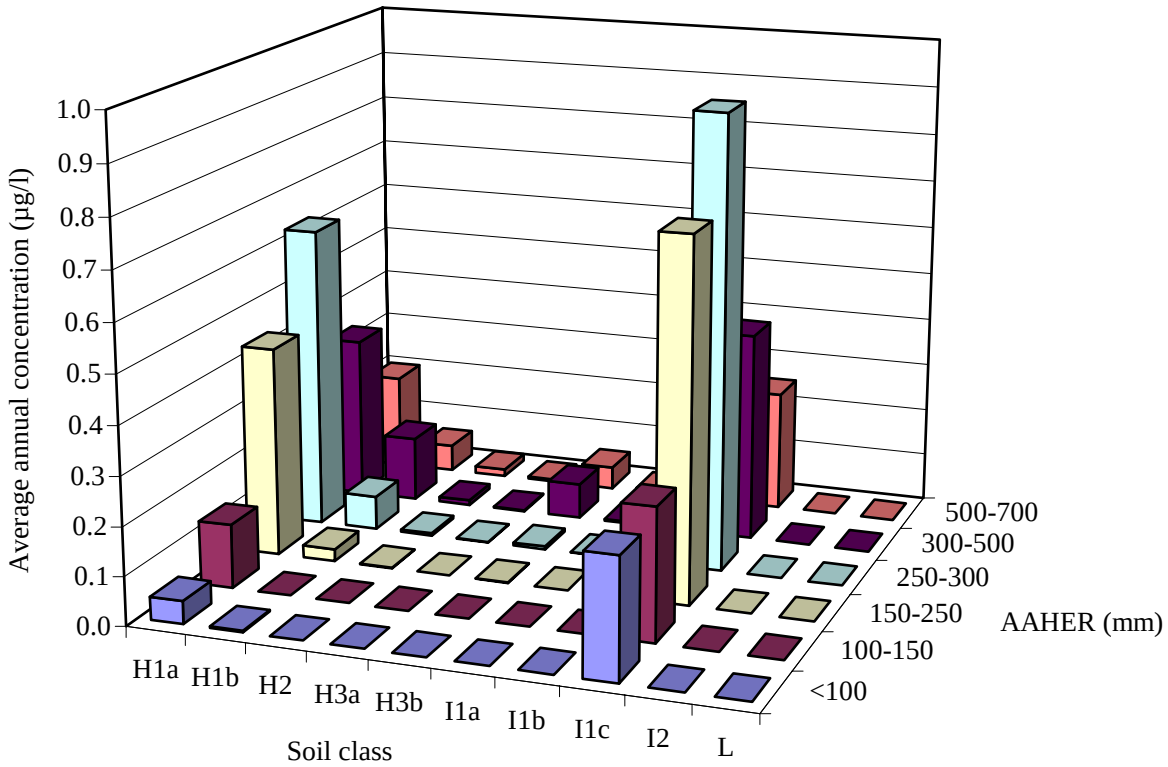

Average annual concentration (µg/l)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
H1a
H1b
H2
H3a
H3b
I1a
I1b
I1c
I2
L
Soil class
500-700
300-500
250-300
150-250
100-150
<100
AAHER (mm)

Fig. 4. MACRO emulator predictions of annual average concentrations of pesticide leaching to 1 m depth within a soil leaching class H1b for a spring application of 1000 g a.i. /ha of pesticides with DT50=20 days and varying Koc and varying AAHER

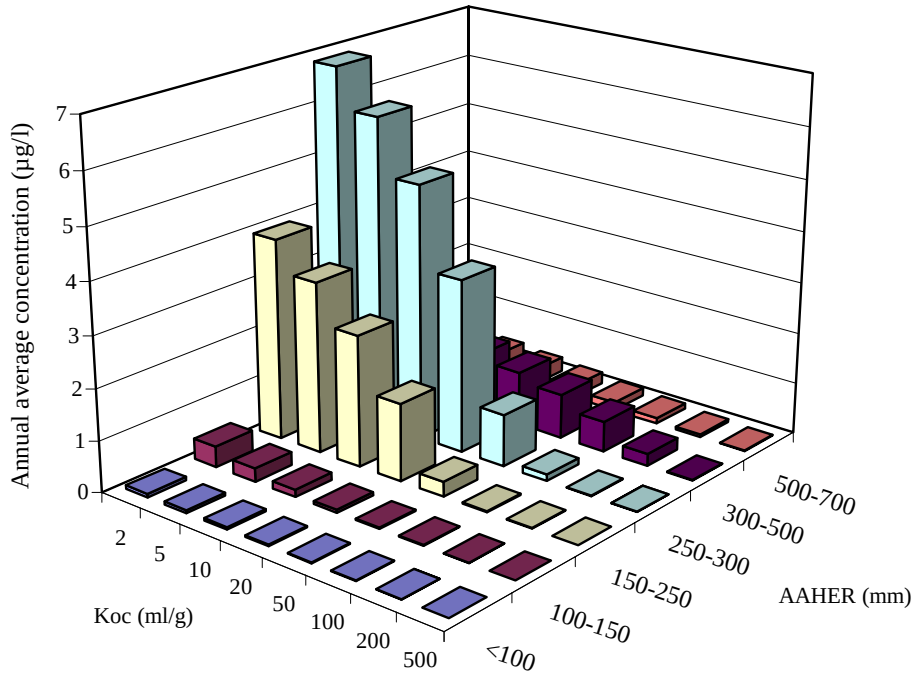
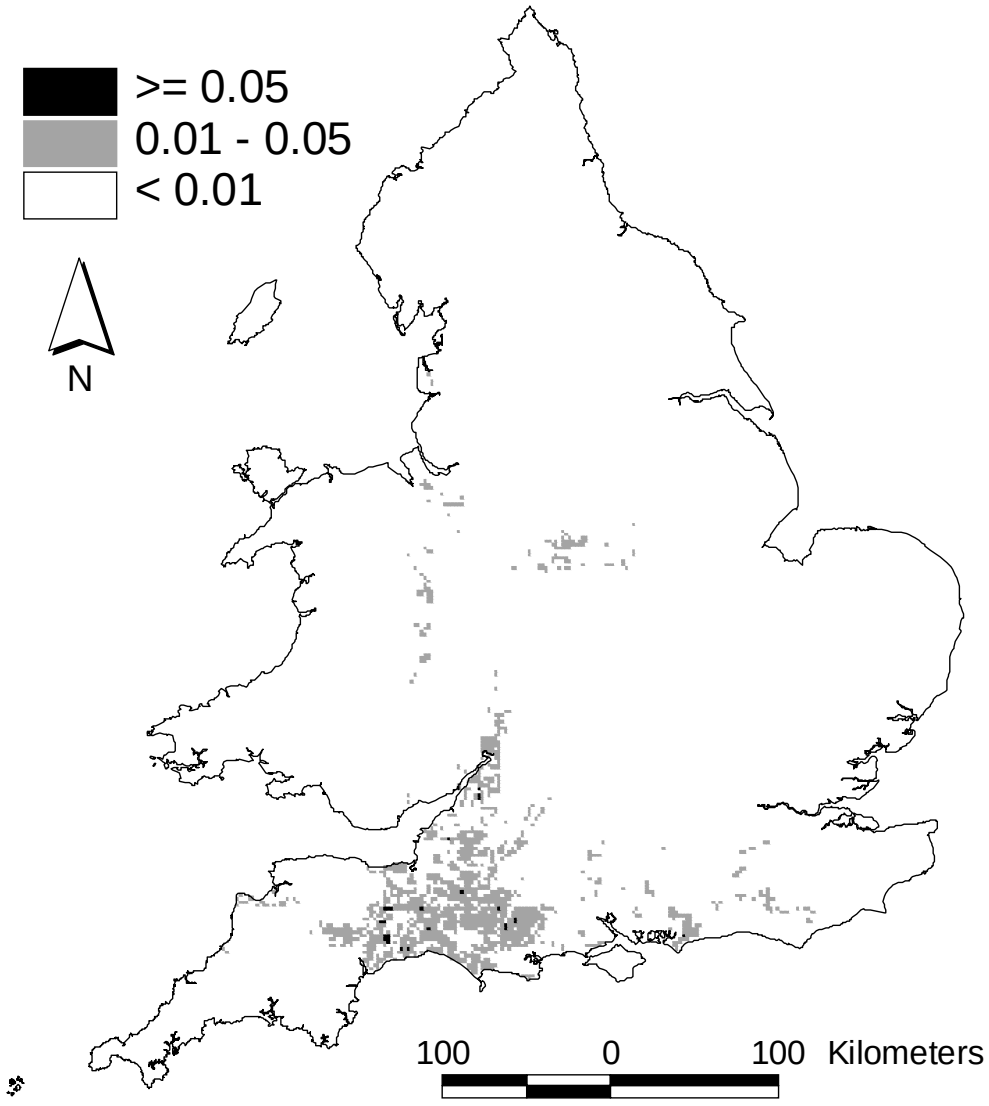
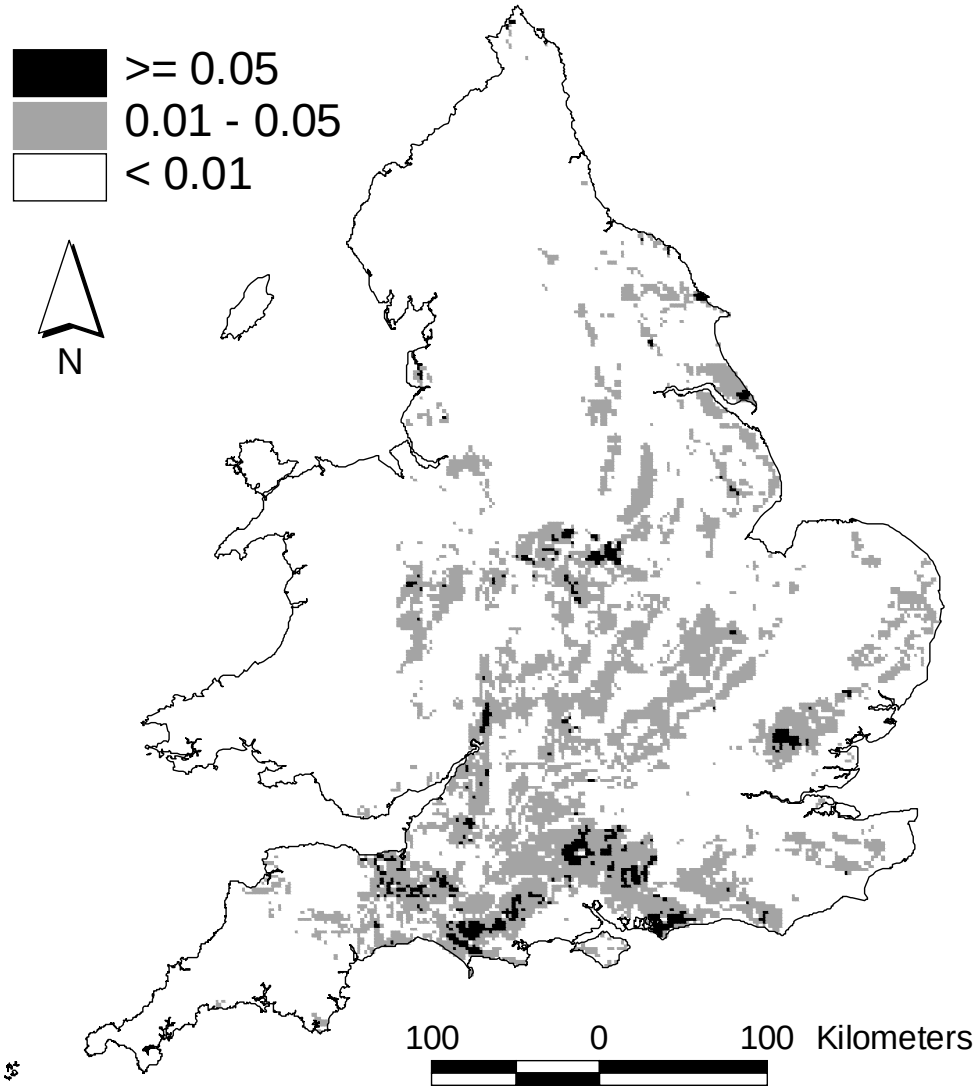


Fig. 5. Predicted maximum annual average concentration (µg/l) of (a) atrazine and (b) isoproturon in recharge impacting upon groundwater in England and Wales

(a)



(b)



Appendix 1: Description of the MACRO emulator

For each application scenario and soil and climate class, available data are maximum annual concentrations predicted by MACRO for a number of combinations of Koc and DT50. The combinations are presented in Table 2 while an example of resulting concentration data is provided in Fig. 2.

For a given pesticide, let *k* be the sorption distribution coefficient (Koc, ml/g) and *d* the time required to have 50% of the pesticide degraded (DT50, days)

Case 1: if $d<2$ or $d>350$ or $k<2$ or $k>500$ or ($k<10$ and $d>20$) or ($k<50$ and $d>50$) or ($k<100$ and $d>200$)

It is considered that pesticides having these properties are unlikely to be registered for use in the UK and the scenario is therefore outside the scope of the emulator.

Case 2: if ($d=2$ or $d=5$ or $d=10$ or $d=20$ or $d=50$ or $d=100$ or $d=200$ or $d=350$) and ($k=2$ or $k=5$ or $k=10$ or $k=20$ or $k=50$ or $k=100$ or $k=200$ or $k=500$) and the (k,d) combination does not meet the conditions of Case 1

The MACRO model has already been run for this particular combination of *k* and *d* and the predicted pesticide concentration in percolating water is directly returned from the appropriate look-up table.

Case 3: if neither conditions for Case 1 and Case 2 are met

The (k,d) combination lies between the MACRO runs available and the predicted concentration for this particular (k,d) combination is estimated as follows:

$$Ck,d = Ck,d1 + \frac{(d - d1)}{(d2 - d1)} \times (Ck,d2 - Ck,d1)$$

where:

k1 is the Koc value within the look-up tables closest to *k* with $k1 \leq k$

k2 is the Koc value within the look-up tables closest to *k* with $k \leq k2$

d1 is the *DT50* value within the look-up tables closest to *d* with $d1 \leq d$

d2 is the *DT50* value within the look-up tables to *d* with $d \leq d2$

$$Ck,d1 = Ck1,d1 + \frac{(k - k1)}{(k2 - k1)} \times (Ck2,d1 - Ck1,d1)$$

$$Ck,d2 = Ck1,d2 + \frac{(k - k1)}{(k2 - k1)} \times (Ck2,d2 - Ck1,d2)$$