Identification of key climatic factors regulating the transport of pesticides in leaching and to tile drains

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Abstract

BACKGROUND: Key climatic factors influencing the transport of pesticides to drains and to depth were identified. Climatic characteristics such as the timing of rainfall in relation to pesticide application may be more critical than average annual temperature and rainfall. The fate of three pesticides was simulated in nine contrasting soil types for two seasons, five application dates and six synthetic weather data series using the MACRO model, and predicted cumulative pesticide loads were analysed using statistical methods.

RESULTS: Classification trees and Pearson correlations indicated that simulated losses in excess of 75th percentile values (0.046 mg m^{-2} for leaching, 0.042 mg m^{-2} for drainage) generally occurred with large rainfall events following autumn application on clay soils, for both leaching and drainage scenarios. The amount and timing of winter rainfall were important factors, whatever the application period, and these interacted strongly with soil texture and pesticide mobility and persistence. Winter rainfall primarily influenced losses of less mobile and more persistent compounds, while short-term rainfall and temperature controlled leaching of the more mobile pesticides.

CONCLUSIONS: Numerous climatic characteristics influenced pesticide loss, including the amount of precipitation as well as the timing of rainfall and extreme events in relation to application date. Information regarding the relative influence of the climatic characteristics evaluated here can support the development of a climatic zonation for European-scale risk assessment for pesticide fate.

Keywords: pesticide; climate; weather; vadose zone; modelling; leaching; drainage

1 INTRODUCTION

Pesticide fate models are increasingly used in combination with geospatial information to assess the risk of pesticide contamination of surface water and groundwater.[1–3] The definition of environmental scenarios relevant to the transport of pesticides to water resources is typically based on a combination of information regarding climate, cropping, soils and, in some instances, the subsoil.[4,5] Historically, climatic zonations for such purposes have been arbitrarily based on average annual temperatures and cumulative annual rainfall,[5–7] or on minimum and maximum temperature, amount of rainfall and other factors.[8] However, other climate characteristics, such as the timing of rainfall in relation to pesticide application or rainfall over a specific period, may have a stronger role in the determination of pesticide loss and would be preferable for climatic zonation purposes. Although numerous sensitivity analyses of pesticide fate models have been undertaken,[9,10] the relative importance of climatic factors (i.e. season and timing of application, seasonal precipitation and recharge and temperature) in relation to environmental and management factors has yet to be determined for a wide range of conditions in a systematic way.

The authors used the MACRO model (version 4.3)[11] to predict losses of three hypothetical pesticides in response to synthetic weather data for selected soils in north-western Europe. The aim was to identify key climatic factors influencing pesticide loss in soils with contrasting susceptibility to leaching to depths up to 1 m. The modelling scenarios comprise leaching to groundwater and transport to tile drains for multiple seasons, soil types, pesticides, weather

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series and pesticide application dates, resulting in over 1500 MACRO simulations. The relation between MACRO predictions and climate characteristics was then assessed using both univariate and multivariate statistics.

2 METHODS

The MACRO model simulates the influence of preferential flow on water flow and solute transport in soil.[11] This phenomenon is widely recognised as contributing to the rapid and significant transport of agricultural contaminants to depth, including pesticides.[12] MACRO divides the total soil porosity into two flow domains (micropores and macropores), each characterised by a different flow rate and solute concentration.[13] The model has been extensively used in European registration to estimate the risk of pesticide transfer to surface water through drainage systems[5] and is capable of simulating transfers of water and solutes in soils of contrasting texture, from clay soils where preferential flow dominates fluxes to sandy soils where leaching is mainly due to matrix flow. The latter process is simulated by Richards' equation and the convection–dispersion equation.[11]

Models are commonly used in risk assessment to simulate pesticide loss under a wide range of environmental and management conditions, but all models have limitations. It is assumed that MACRO represents most of the key processes that influence pesticide fate and transport, and that these processes, including the influence of weather, are properly represented in the model. The authors feel that MACRO adequately represents the dominant processes, because the model has been extensively evaluated in the present study area[14–18] and elsewhere.[19–23] Based on these previous studies, MACRO is an appropriate model for simulating leaching and drainage in both light- and heavy-textured soils. For example, MACRO has been shown to simulate drainage flow and solute transport in loamy sand soil,[20] as well as in a structured clay soil,[19] with reasonable accuracy, based on comparison with measured data.

The present study involved forward simulations with MACRO, based on the earlier modelling undertaken for UK conditions.[17] MACRO was used to generate statistics for 54 modelling scenarios reflecting variations in soil type, season, applied pesticide and leaching either to 1 m depth or to tile drains at depths of 0.6–0.8 m. The transport scenarios are referred to as 'leaching' or 'drainage' scenarios respectively. Soil series investigated here were selected on the basis of previous work in England and Wales, involving broad classes of soils. Leaching scenarios consist of four soil series (listed here in order of increasing clay, from 9 to 40% in the top two layers): Cuckney (CU), Hall (HA), Ludford (LU) and Enborne (EN). Drainage scenarios consist of five series with 13–56% clay in the top two layers: Quorndon (QU), Clifton (CL), Brockhurst (BR), Hanslope (HS) and Denchworth (DE). The MACRO model was parameterised on the basis of measured properties, where possible, and by expert judgement as described in prior research conducted on these same soils.[17] The bottom boundary condition was set to free draining (leaching scenarios) or zero flux (drainage scenarios).

Modelling was conducted for three hypothetical pesticides with contrasting mobility and persistence in the environment, based on organic carbon partition coefficient (K_{oc}) and half-life (DT_{50}). Pesticide 1 is mobile and slightly persistent, having a K_{oc} of 20 L kg^{-1} and a DT_{50} of 8 days at a temperature of 20 °C. Pesticide 2 is moderately mobile and moderately persistent ($K_{oc} = 100\,\mathrm{L\,kg^{-1}}$ and $DT_{50} = 23$ days at 20 °C), and pesticide 3 is moderately mobile and very persistent ($K_{oc} = 220\,\mathrm{L\,kg^{-1}}$ and $DT_{50} = 88$ days at 20 °C). A single pesticide application at a rate of 0.02 kg ha^{-1} was simulated in the first year, and losses were predicted for 6–20 years. The length of simulation (6 years for pesticide 1, 10 years for pesticide 2, 20 years for pesticide 3) was adjusted on the basis of prior modelling trials to allow complete transfer of the three pesticides to depths up to 1 m. Six weather time series were synthetically generated using the RainSim software[24] to express the variability in weather for a station in Oxford, UK (Latitude 51°45′20″N - Longitude 1°15′22″W).

For leaching scenarios, the total number of MACRO simulations was: two application seasons × four soils × three pesticides × six weather series × five application dates = 720.

The number of MACRO simulations for drainage scenarios was: two application seasons × five soils × three pesticides × six weather series × five application dates = 900.

Thus, there are 24 unique season–soil–pesticide scenarios for the leaching case, and 30 such scenarios for the drainage case. Within-season application dates for spring scenarios were 1 April, 16 April, 30 April, 15 May and 31 May, while those for the autumn scenarios were 1 September, 15 September, 30 September, 15 October and 31 October. Significant rain (59 mm) occurred on the 1 September application date associated with the fifth weather series. This application date was excluded from the analysis because farmers following good agricultural practice would not apply pesticides under such conditions. The final datasets consisted of 708 leaching and 885 drainage simulations, and the main MACRO output of interest was cumulative pesticide loss after a maximum of 20 years. Cumulative pesticide loss was emphasized for several reasons. Chronic effects such as adverse reproductive outcomes and cancer typically result from multiple exposures to compounds. Agricultural drains are conduits to streams, for which exceedances typically are based on multiple measurements over time. Finally, cumulative loads are highly relevant for receiving waters such as estuaries, which can be

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affected by contaminants in streams that flow through agricultural areas.

A number of statistics were derived for each of the six weather series as follows:

Rx [$x = -91, -61, -30, -20, -14, -10, -7, -6, -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5, 6, 7, 10, 14, 20, 30, 61, 91, 122, 152, 183, 213, 244, 274, 305, 335, 365, 729, 1095, 1825, 3650, 5475, 7300$] is the *cumulative rainfall* (in mm) for the period from day x to the pesticide application date in the case of antecedent rain ($x < 0$) or from the application date to day x ($x > 0$);
Cy [$y = 2, 5, 10, 20, 50, 100$] is the number of *days* after application until y mm of cumulative rainfall occur;
Tx [$x = 0, 1, 2, 3, 4, 5, 6, 7, 10, 14, 20, 30, 61, 91, 122, 152, 183, 213, 244, 274, 305, 335, 365, 719$] is the *average temperature* (in°C) over the x days following application;
Ly [$y = -30, -20, -10, 10, 20, 30$] is the number of *days* before or after application until y mm of daily rain occur (*Ly* is referred to as the 'lag time'); $y < 0$ indicates that a rain event of y mm occurred before the date of pesticides application, and $y > 0$ indicates that the rain event occurred after application;
WRA_m_n [m = September, October, November; n = March, April] is the *cumulative daily rainfall* between the beginning of month m and the end of month n, or 'winter rain';
WRE_m_n [m = September, October, November; n = March, April] is the *cumulative daily recharge* between the beginning of month m and the end of month n, where recharge is defined as the difference between daily rainfall and potential evapotranspiration. Potential evapotranspiration was estimated using the Penman–Monteith method, based on measured weather data in the study area.

Predicted cumulative pesticide losses at 1 m depth and in drains, the climatic variables and other descriptive variables in the dataset (weighted average of percentage clay in the first two horizons, season of pesticide application) were organised by season–soil–pesticide scenarios and statistically analysed using classification trees and Pearson correlations. Modelling scenario data were aggregated into leaching and drainage datasets, and classification trees were used to explore multivariate relations among environmental and management factors. It was anticipated that classification trees would reveal which factors – among the overall suite of those considered – most influenced pesticide loss for the conditions of the study. Classification trees perform recursive, binary splits of data to reveal factors that best predict membership of a categorical dependent variable in data clusters.[25] Here, the dependent variable is the category of MACRO-predicted, cumulative pesticide loss for the 708 leaching and 885 drainage simulations, defined as ≤ 25 th percentile loss ('low'), the middle 50% of the data ('medium') and >75 th percentile loss ('large'). Classification results are expressed graphically as 'trees' with branches terminating in nodes that are considered homogeneous clusters of observations. The method employs exhaustive searches of the data and is an adaptation of algorithms used in classification-and-regression-tree analysis. It makes no assumption regarding the underlying distribution of the data, accepts both categorical and continuous predictor variables and automatically incorporates interactions among predictors. Version 7.1 of Statistica[26] was used on a subset of the climatic variables, plus percentage clay and season of pesticide application:

season [0,1], where spring = 0 and autumn = 1;
% clay (weighted average in the top two soil layers);
Rx [$x = -91, -61, -30, -14, 1, 14, 30, 61, 91, 122, 152, 183, 274, 365$], as defined above;
Ly [$y = -30, -10, 10, 30$], as defined above;
WRA_m_n [m = September, October, November; n = March, April], as defined above.

The subset of variables was intended to reduce the redundancy of weather information in the multivariate dataset. Percentage clay in the first two soil layers ('clay' in the following discussion) and time of application (spring versus autumn) were included in the analysis to gain a better understanding of interactions among soil and climatic factors (here, season is a surrogate for temperature).

Both Pearson and Spearman correlations were computed to determine the strength of monotonic relations between predicted pesticide loss and all climatic variables listed above, for each season–soil–pesticide scenario. It was anticipated that univariate correlations would yield insight into relations between pesticide loss and specific climatic factors for the various scenarios. Spearman rank correlations are resistant to the effects of outliers[27] and were therefore somewhat insensitive to extreme rainfall events, especially those occurring shortly after pesticide application. A major goal of the analysis was to assess model sensitivity (i.e. changes in predicted solute loss) to significant rainfall events shortly after application. Leaching in response to such events is a major water quality concern but has seldom been systematically evaluated for a broad range of conditions. Therefore, the present study emphasized Pearson correlations, which are used here less as classic measures of correlation and more as indicators of fast system response. Correlation coefficients were computed using SAS version 8.01.[28]

3 RESULTS AND DISCUSSION

The percentiles of predicted cumulative pesticide loss were about the same for the leaching and drainage scenarios (median = $0.012\,\mathrm{mg\,m^{-2}}$ and $0.011\,\mathrm{mg\,m^{-2}}$ respectively) (Table 1). Median pesticide losses expressed as percentage of the applied mass ($2\,\mathrm{mg\,m^{-2}}$) were 0.60% and 0.55% respectively. A Wilcoxon rank sum test indicated that differences in cumulative

Table 1. Statistics of predicted, total solute loss for aggregated MACRO output under leaching ($N = 708$) and drainage ($N = 885$) scenarios; percentage loss is based on a pesticide application rate of 2 mg m^{-2}

	Leaching		Drainage	
Statistic	Total pesticide loss (mg m^{-2})	Loss (%)	Total pesticide loss (mg m^{-2})	Loss (%)
0th percentile (minimum)	0.000001	0.000050	0.0000031	0.00016
25th percentile	0.00096	0.048	0.0010	0.050
50th percentile (median)	0.012	0.60	0.011	0.55
Mean	0.048	2.4	0.031	1.6
75th percentile	0.046	2.3	0.042	2.1
100th percentile (maximum)	0.58	29	0.28	14

pesticide loss for leaching and drainage were statistically insignificant ($P = 0.154$). Maximum cumulative pesticide loss was somewhat larger for leaching (0.58 mg m^{-2}) than for drainage scenarios (0.28 mg m^{-2}), which may reflect differences in soil properties and/or the hypothetical configuration of the drains. Three soils used in drainage scenarios have an organic carbon content of 1.9% or more, compared with two such soils in leaching scenarios, which will have produced stronger sorption in these drainage simulations. Also, leaching scenarios predicted pesticide loss at 1 m depth directly beneath the point of pesticide application. In contrast, drainage scenarios assumed interception of a fraction of water and dissolved pesticides. Based on actual practice in the soils studied, drain depth was varied from 0.6 to 0.8 m in MACRO simulations, with intervals of 2–30 m between drains. The shallowest drain depth and narrowest interval were specified for the two soils with the largest clay content (Hanslope and Denchworth).

3.1 Classification trees

MACRO simulations corresponding to season–soil–pesticide scenarios were aggregated to create two datasets (leaching and drainage) which were analysed with classification trees. The results indicated which variables have the most influence on cumulative pesticide loss in a multivariate context, among all variables considered, with Figs 1a and b showing the predictors explaining leaching and drainage losses respectively. The season of application (spring versus autumn) was the first variable explaining predicted pesticide loss from leaching (Fig. 1a). Subsequent explanatory variables were percentage clay and cumulative rain received in the year following pesticide application. Simulated pesticide loss was greater following autumn application on soils with a clay content of >10%. Hall soils had large predicted pesticide loss in autumn, regardless of precipitation amount (node 10 in Fig. 1a), which is somewhat surprising because this soil had a comparatively large sand content (69% in the first two layers and 81% overall). However, this soil also had a small subsoil organic carbon content, so there is less potential for sorption of pesticide at depth. Soils with a clay content of >16% (Ludford and Enborne) had large simulated pesticide loss when *R183* exceeded 390 mm, reflecting preferential flow effects on leaching in these more structured soils. For *R183* < 390 mm, medium pesticide loss was predicted to occur in these soils. In contrast, the left side of the classification tree indicates that low pesticide loss was predicted to occur when the temperature was relatively warm (i.e. spring application), soils had <10% clay or *R365* was <560 mm.

Soil texture was the first variable explaining simulated pesticide loss by drainage (Fig. 1b). Soils with ≤33% clay (Quorndon, Clifton, Brockhurst series) were estimated to have low to medium pesticide losses, and soils with greater amounts of clay (Hanslope, Denchworth) were estimated to have medium to large pesticide loss. Pesticide loss was predicted to be large in clay soils when *WRA_nov_apr* exceeded about 200 mm. In contrast, low pesticide loss was predicted to occur when soils contained <16% clay content and *R183* was <380 mm. Different variables further down the tree from the same parent node (texture) indicated interactions among season, clay, cumulative rain and winter rain. In particular, timing of application and amount of winter rainfall were important factors leading to large predicted pesticide loss in soils with high clay (node 11) (Fig. 1b).

The classification trees indicated that clay content was a dominant factor under both leaching and drainage scenarios; it was the basis of four split conditions for leaching data (Fig. 1a) and two split conditions for drainage data (Fig. 1b). The importance of clay and interactions with rainfall suggested that large simulated pesticide loss occurs in the more structured soils as a result of preferential flow, for conditions in north-western Europe. These types of loss were predicted to occur for both leaching (Ludford, Enborne soils) and drainage scenarios (Hanslope, Denchworth). The classification trees also indicated a seasonal (i.e. temperature) effect and provided threshold values of percentage clay and rainfall associated with the categorical levels of predicted pesticide loss. For both trees, the largest pesticide losses generally were predicted to occur in the autumn on more structured soils, but less rain was required for large pesticide loss in the case of drains. For example, node 11 of the drainage tree indicated that >200 mm of winter rainfall following pesticide application in the autumn on soils with greater than

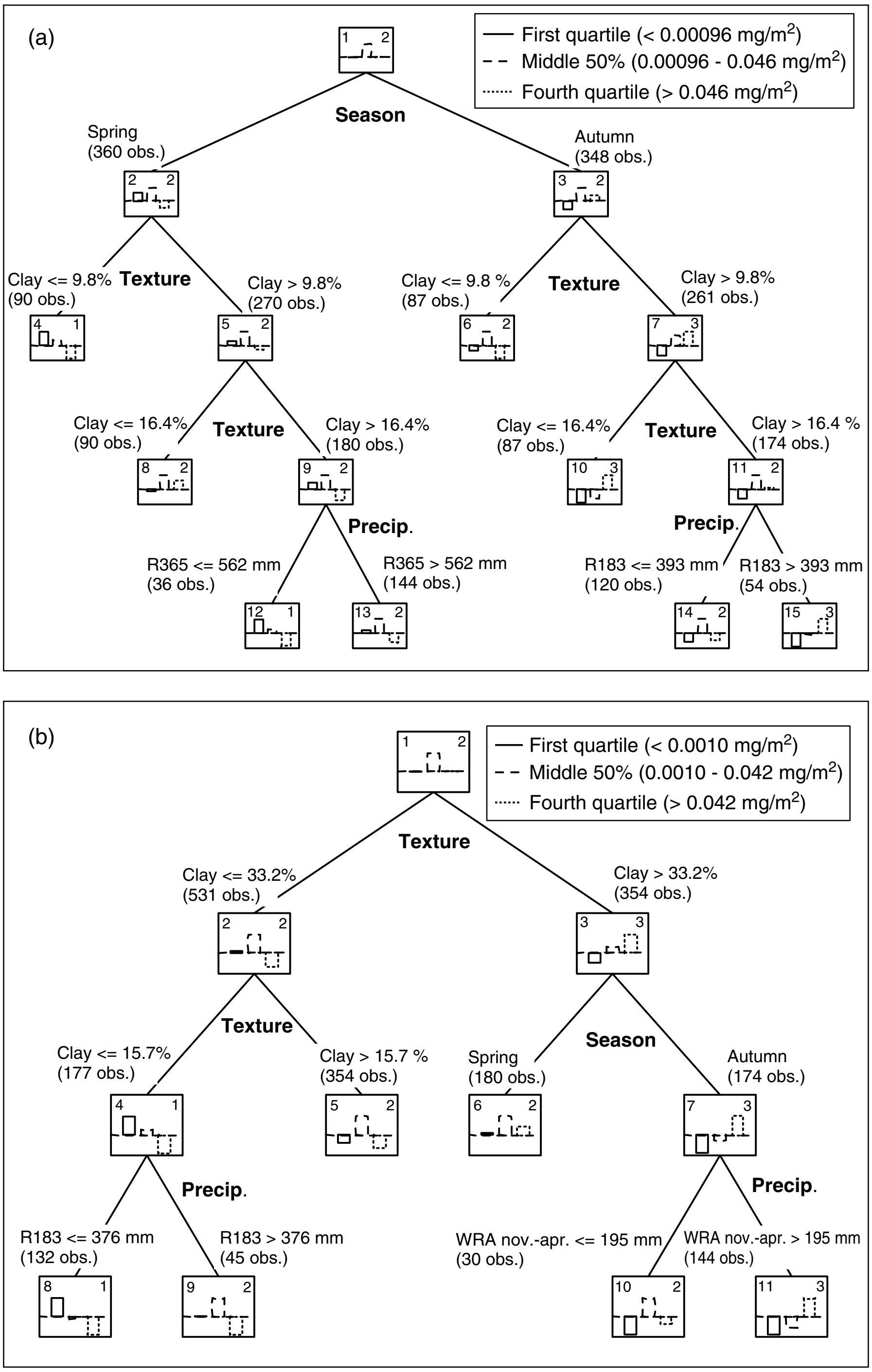

Figure 1. Classification tree analysis of cumulative solute loss for (a) leaching and (b) drainage scenarios. Tree nodes are indicated by boxes, with the node number in the upper left-hand corner of the box. The estimated contamination status of a node (1 = first-quartile pesticide loss, 2 = middle 50% of losses, 3 = fourth-quartile loss) is shown in the upper right-hand corner of the box and is based on the class with the largest number of observations at the node. The vertical bars indicate proportional changes in class members (MACRO predictions of pesticide loss) at a particular child node, compared with the parent node. The left-hand bar corresponds to the first-quartile pesticide loss, the middle bar corresponds to the middle 50% of the data and the right-hand bar corresponds to the fourth-quartile loss. For example, in 1b the bars indicate that node 3, which is estimated to have fourth-quartile pesticide loss, has a higher proportion of fourth-quartile members relative to the other two classes in comparison with the parent node (1).

33% clay produced large simulated pesticide loss to drains (Fig. 1b). Compared with the leaching result (clay >16%, *R183* >390 mm, node 15) (Fig. 1a), the smaller precipitation amount suggested the dominance of preferential flow pathways in drained soils with larger clay content, which is consistent with prior field studies.[29]

3.2 Pearson correlations

Pearson correlations between climatic variables and pesticide loss in leaching (Table 2) and drainage (Table 3) were computed for all 54 season–soil–pesticide combinations to show relations between predicted pesticide loss, climatic factors and soils. Initial analysis indicated that *WRA_m_n* was

Table 2. The top five Pearson correlations for climatic variables under each season–soil–pesticide scenario for leaching simulations. See the text for a detailed description of the variables. Clay and organic carbon (OC) contents corresponding to the first two soil layers are shown in parentheses next to each soil type. All correlations were significant at the 0.05 level, except as noted. In such cases, the attained significance level (P) is indicated in parentheses next to the variable name. The 75th percentile of predicted total solute loss corresponding to each scenario is shown in parentheses next to the pesticide name. Scenarios for which the 75th percentile solute loss exceeded the overall 75th percentile loss for all 708 MACRO leaching simulations (0.046 mg m^{-2}) have a bold red outline

Spring application						Autumn application					
Cuckney (clay = 9%; OC = 1.3%)											
Pesticide 1 (<0.01 mg/m²)		Pesticide 2 (<0.01 mg/m²)		Pesticide 3 (0.01 mg/m²)		Pesticide 1 (0.01 mg/m²)		Pesticide 2 (<0.01 mg/m²)		Pesticide 3 (0.02 mg/m²)	
T244	-0.758	R729	0.853	R1825	0.917	R244	0.775	WRA_oct_apr	0.917	R729	0.738
T213	-0.745	WRA_oct_apr	0.782	R1095	0.906	R152	0.759	WRA_oct_mar	0.909	R1825	0.728
T274	-0.727	WRA_nov_apr	0.762	L30	-0.889	R213	0.755	WRA_sep_apr	0.890	R1095	0.700
R729	0.711	R1095	0.753	R729	0.830	R183	0.753	WRA_nov_apr	0.889	R3650	0.675
T305	-0.683	R365	0.687	R3650	0.827	R274	0.750	R152	0.879	R7300	0.520
Ludford (clay = 22%; OC = 1.6%)											
Pesticide 1 (<0.01 mg/m²)		Pesticide 2 (<0.01 mg/m²)		Pesticide 3 (0.03 mg/m²)		Pesticide 1 (0.01 mg/m²)		Pesticide 2 (0.03 mg/m²)		Pesticide 3 (0.07 mg/m²)	
R10	0.494	WRA_nov_apr	0.862	WRA_oct_apr	0.973	R152	0.632	WRA_oct_mar	0.857	WRA_oct_mar	0.973
R61	0.487	WRA_nov_mar	0.822	WRA_nov_apr	0.971	WRA_nov_apr	0.623	WRA_sep_apr	0.856	WRA_sep_apr	0.969
C100	-0.474	WRA_oct_apr	0.813	WRA_sep_apr	0.925	WRA_oct_mar	0.620	WRA_nov_mar	0.846	WRA_oct_apr	0.966
R20	0.463	WRA_sep_apr	0.789	WRA_oct_mar	0.918	T61	-0.616	WRA_sep_mar	0.832	WRA_nov_apr	0.930
L20	-0.439	WRA_oct_mar	0.787	WRA_nov_mar	0.869	WRA_nov_mar	0.615	R152	0.830	R152	0.923
Hall (clay = 11%; OC = 1.9%)											
Pesticide 1 (0.01 mg/m²)		Pesticide 2 (0.03 mg/m²)		Pesticide 3 (0.21 mg/m²)		Pesticide 1 (0.16 mg/m²)		Pesticide 2 (0.20 mg/m²)		Pesticide 3 (0.43 mg/m²)	
R10	0.627	L20	-0.583	R729	0.860	T61	-0.631	R213	0.754	WRA_oct_mar	0.950
R20	0.597	R61	0.560	R365	0.724	T30	-0.616	WRA_nov_apr	0.753	WRA_nov_apr	0.942
R14	0.557	R91	0.536	R1095	0.716	T20	-0.579	R244	0.752	WRA_sep_apr	0.942
C50	-0.503	R10	0.532	WRA_nov_apr	0.710	T1	-0.578	R183	0.746	R213	0.941
R30	0.449	R183	0.513	WRA_oct_apr	0.679	T91	-0.571	WRA_oct_apr	0.744	R183	0.940
Enborne (clay = 40%; OC = 2.8%)											
Pesticide 1 (<0.01 mg/m²)		Pesticide 2 (0.01 mg/m²)		Pesticide 3 (0.07 mg/m²)		Pesticide 1 (0.06 mg/m²)		Pesticide 2 (0.06 mg/m²)		Pesticide 3 (0.14 mg/m²)	
R10	0.466	R335	0.852	WRA_oct_apr	0.978	T1	-0.708	WRA_nov_mar	0.860	WRA_oct_mar	0.972
R20	0.386	R365	0.847	WRA_nov_apr	0.959	T30	-0.674	WRA_sep_apr	0.855	WRA_oct_apr	0.963
R14	0.368	R305	0.840	WRA_oct_mar	0.938	T2	-0.672	WRA_oct_mar	0.853	WRA_sep_apr	0.956
T122 (P=0.065)	-0.341	WRA_oct_apr	0.836	WRA_sep_apr	0.937	T61	-0.666	WRA_nov_apr	0.850	WRA_nov_apr	0.949
T1 (P=0.076)	-0.329	WRA_nov_apr	0.803	WRA_nov_mar	0.872	T14	-0.660	WRA_oct_apr	0.831	R183	0.933

Color key

Winter rainfall	Short-term rainfall (≤ 91days)	Long-term rainfall (>91 days)	Cumulative rainfall	Lag times to rainfall	Short-term temperature (≤ 91days)	Long-term temperature (> 91days)

Table 3. The top five Pearson correlations for climatic variables under each season–soil–pesticide scenario for drainage simulations. See the text for a detailed description of the variables. Clay and organic carbon (OC) contents corresponding to the first two soil layers are shown in parentheses next to each soil type. All correlations were significant at the 0.05 level, except as noted. In such cases, the attained significance level (*P*) is indicated in parentheses next to the variable name. The 75th percentile of predicted total solute loss corresponding to each scenario is shown in parentheses next to the pesticide name. Scenarios for which the 75th percentile solute loss exceeded the overall 75th percentile loss for all 885 MACRO drainage simulations (0.042 mg m^{-2}) have a bold red outline

Spring application						Autumn application					
Quorndon (clay = 13%; OC = 1.4%)											
Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (<0.01 mg/m^2)		Pesticide 3 (<0.01 mg/m^2)		Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (<0.01 mg/m^2)		Pesticide 3 (0.01 mg/m^2)	
R305	0.825	WRA_sep_apr	0.854	R365	0.936	R152	0.826	WRA_sep_mar	0.781	WRA_oct_apr	0.959
R335	0.796	WRA_oct_mar	0.826	WRA_oct_apr	0.929	WRA_oct_mar	0.815	WRA_sep_apr	0.773	WRA_sep_apr	0.933
R365	0.770	WRA_nov_mar	0.824	WRA_nov_apr	0.906	WRA_oct_apr	0.799	WRA_oct_mar	0.747	WRA_nov_apr	0.920
R274	0.723	WRA_nov_apr	0.819	R335	0.904	WRA_sep_apr	0.795	WRA_nov_mar	0.736	WRA_oct_mar	0.914
R729	0.702	WRA_oct_apr	0.808	R305	0.857	WRA_nov_apr	0.782	R152	0.709	R152	0.859
Clifton (clay = 19%; OC = 2.1%)											
Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (<0.01 mg/m^2)		Pesticide 3 (0.02 mg/m^2)		Pesticide 1 (0.03 mg/m^2)		Pesticide 2 (0.02 mg/m^2)		Pesticide 3 (0.03 mg/m^2)	
R10	0.468	T365	-0.534	R1095	0.969	T61	-0.644	WRA_oct_apr	0.891	R1095	0.860
R20	0.394	T335	-0.511	R729	0.949	T91	-0.631	WRA_nov_apr	0.873	WRA_oct_apr	0.752
R14	0.362	T244	-0.499	R3650	0.806	WRA_nov_apr	0.622	WRA_oct_mar	0.866	R213	0.723
R6 (*P*=0.085)	0.320	T719	-0.488	R365	0.675	R152	0.620	WRA_sep_apr	0.852	R183	0.677
T152 (*P*=0.086)	-0.319	L-20	0.476	L30	-0.660	R305	0.613	R183	0.852	WRA_nov_apr	0.672
Brockhurst (clay = 26%; OC = 1.5%)											
Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (0.01 mg/m^2)		Pesticide 3 (0.04 mg/m^2)		Pesticide 1 (0.04 mg/m^2)		Pesticide 2 (0.04 mg/m^2)		Pesticide 3 (0.05 mg/m^2)	
R10	0.503	R10	0.492	R3650	0.929	T61	-0.698	R213	0.879	R213	0.854
R20	0.442	C100	-0.483	R1095	0.850	T30	-0.672	R183	0.874	R244	0.854
R14	0.420	R20	0.474	L30	-0.824	T91	-0.651	WRA_oct_apr	0.845	R1095	0.837
C50	-0.364	L20	-0.469	R729	0.770	T20	-0.629	R244	0.831	R274	0.831
T122 (*P*=0.058)	-0.350	C50	-0.451	R5475	0.767	T1	-0.629	WRA_oct_mar	0.828	R365	0.817
Hanslope (clay = 41%; OC = 1.9%)											
Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (0.01 mg/m^2)		Pesticide 3 (0.09 mg/m^2)		Pesticide 1 (0.10 mg/m^2)		Pesticide 2 (0.13 mg/m^2)		Pesticide 3 (0.19 mg/m^2)	
R10	0.491	R10	0.534	R729	0.850	T61	-0.696	WRA_nov_apr	0.809	WRA_oct_mar	0.955
R20	0.421	R20	0.478	WRA_nov_apr	0.848	T30	-0.665	WRA_sep_apr	0.805	WRA_sep_apr	0.946
R14	0.405	R61	0.470	R365	0.842	T1	-0.654	WRA_oct_mar	0.804	WRA_nov_apr	0.945
T122 (*P*=0.054)	-0.356	C100	-0.454	WRA_oct_apr	0.834	T20	-0.634	WRA_oct_apr	0.798	R213	0.944
T1 (*P*=0.057)	-0.352	R14	0.432	R335	0.790	T91	-0.624	WRA_nov_mar	0.795	WRA_oct_apr	0.943
Denchworth (clay = 56%; OC = 1.9%)											
Pesticide 1 (<0.01 mg/m^2)		Pesticide 2 (0.01 mg/m^2)		Pesticide 3 (0.07 mg/m^2)		Pesticide 1 (0.10 mg/m^2)		Pesticide 2 (0.11 mg/m^2)		Pesticide 3 (0.16 mg/m^2)	
R10	0.485	R10	0.518	WRA_nov_apr	0.872	T61	-0.687	WRA_oct_mar	0.831	WRA_oct_mar	0.963
R20	0.413	R20	0.466	WRA_oct_apr	0.844	T30	-0.643	WRA_sep_apr	0.831	WRA_sep_apr	0.953
R14	0.396	R61	0.455	R365	0.819	T1	-0.640	WRA_nov_apr	0.826	R183	0.949
T122 (*P*=0.055)	-0.354	C100	-0.453	R729	0.819	T91	-0.620	WRA_nov_mar	0.823	WRA_nov_apr	0.947
T1 (*P*=0.061)	-0.346	L20	-0.423	R335	0.769	T20	-0.612	WRA_oct_apr	0.816	WRA_oct_apr	0.947

Color key

Winter rainfall	Short-term rainfall (≤ 91days)	Long-term rainfall (>91 days)	Cumulative rainfall	Lag times to rainfall	Short-term temperatures (≤ 91days)	Long-term temperatures (>91 days)

highly correlated with *WRE_m_n* (Pearson's rho ≈1 for the same months *m_n*, for leaching data) and that the results were redundant if both were used. Also, the correlations were essentially the same regardless of which variable was used. Therefore, *WRE_m_n* was excluded from subsequent analysis, and the following discussion is based on *WRA_m_n* and the remaining variables described above. Tables 2 and 3 present soils in order of increasing susceptibility, based primarily on percentage clay in the first two layers. Susceptibility is generally predicted by MACRO to increase as percentage clay increases. The saturated hydraulic conductivity of the matrix is lower in clay soils than in sandy or loamy soils, which results in earlier and more frequent generation of macropore flow. Additionally, the model parameterisation reflects limited exchange of water and solutes between macropores and the soil matrix in strongly structured clay soils with massive aggregates. However, simulations with these data also suggest that the Hall soil (clay = 11%) is more susceptible than the Ludford soil (clay = 22%), which is explained in more detail below.

Tables 2 and 3 show the five climatic variables with the largest Pearson correlation coefficients for predicted leaching and drainage losses for specific season–soil–pesticide scenarios. A colour-coded scheme is used to improve the readability of the results. All of the correlations are significant at the 0.05 level, except as noted. For variables with $P > 0.05$, the attained significance level is shown in parentheses next to the variable name. To indicate which of the scenarios had large predicted pesticide loss, those having 75th percentile loss greater than the overall 75th percentile loss (0.046 mg m^{-2} for all 708 leaching simulations and 0.042 mg m^{-2} for all 885 drainage simulations) have a bold red outline in Tables 2 and 3. This facilitates comparison of Pearson correlation results with levels of pesticide loss (low, medium, large) estimated by the classification trees.

In general, 75th percentile predicted pesticide loss increased with decreasing temperature (as indicated by the season of pesticide application), increasing clay content and increasing pesticide persistence, for both leaching (Table 2) and drainage (Table 3) scenarios. Thus, scenarios with large predicted pesticide loss are found in the lower right portion of each table. These relations are supported by the classification tree analysis, which found that large predicted pesticide loss occurred on clay soils receiving large rainfall amounts after autumn application (Fig. 1). An exception to this overall pattern was observed for the Hall soil, which had the largest pesticide loss (up to 0.43 mg m^{-2}) of any of the individual scenarios shown in Table 2. The Hall soil has less organic carbon at depth (0.3% at 50–70 cm) than soils having larger clay content (e.g. Ludford with 0.5% organic carbon at 50–75 cm), which reduces the sorption coefficient in MACRO. The sorption coefficient (K_d) of non-ionic compounds is calculated from the organic carbon partition coefficient (K_{oc}) and the fraction of organic carbon (f_{oc}) according to: $K_d = K_{oc}f_{oc}$. The simulated, increased susceptibility of the Hall soil to leaching was corroborated by classification tree analysis (Fig. 1a). Soils with 10–16% clay (i.e. Hall, large pesticide loss, node 10) were as susceptible in the autumn, regardless of precipitation amount, as those having more clay and with *R183* > 390 mm (Ludford and Enborne, large pesticide loss, node 15).

None of the rainfall statistics describing the rainfall patterns and magnitude shortly before application was found to play a predominant role in simulated pesticide loss. Prior experiments offer conflicting evidence of the importance of antecedent water content and related processes. Some studies found no significant relation between initial soil moisture content and the leaching of isoproturon or its concentration in soil pore water.[30] Additionally, variations in soil moisture content were found to have no significant effect on losses of isoproturon, chlorotoluron and linuron to drains in field experiments conducted on Denchworth heavy clay soils.[31] However, other studies have found that the water content of the soil at the time of application may have a significant effect on the transport of pesticides. Processes invoked to explain these differences include diffusion and sequestration in micropores and/or organic matrices,[32] and the increased accessibility of sorption sites as organic matter becomes more hydrophilic with increasing moisture.[33] With the exception of diffusion into micropores, these processes are not represented in the model simulations carried out in the present study.

In addition to the general relations mentioned above, inspection of Tables 2 and 3 reveals patterns that suggest the relative importance of climatic factors to simulated pesticide losses by leaching and drainage. For leaching predictions, the main climatic statistic determining the extent of losses for pesticide 3 – the pesticide displaying the strongest sorption – was winter rainfall between October/November and March/April immediately following pesticide application, irrespective of the application scenario considered (spring and autumn) (yellow variables in Table 2). Correlations between simulated pesticide loss and winter rainfall typically were >0.80, and the maximum correlation coefficient was 0.98 ($P < 0.0001$) (spring application, Enborne soil, pesticide 3). This result is consistent with a lysimeter study that related rainfall plus irrigation from November to May with water flows and isoproturon and bromide losses from sandy loam and clay loam soils in the UK.[34] The study found that flows and losses increased with increasing water input, particularly for the sandy loam. An exception to the overall dominance of winter rainfall in the present study was predicted for the more sandy soil (Cuckney series), where an influence of long-term rainfall statistics (cumulative rainfall typically from 5 months to 5 years) was identified (light blue in Table 2). The specific behaviour predicted for

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the Cuckney soil can be related primarily to the leaching patterns of pesticide 3 that span ca 15 years (data not shown). MACRO predicts that leaching via the soil matrix (micropores) increases as rainfall increases. The increased moisture content of the micropores also causes macropore flow to start sooner, which can result in increased pesticide loss if the concentration is sufficiently large in layers where macropore flow is generated. However, care should be taken in the interpretation of the long-term simulation results, as the effects of sorption 'ageing', which is commonly observed in experiments, are not accounted for in the modelling.

For pesticide 1, which has the lowest K_{oc} (20 L kg^{-1}) of the three compounds, an effect of winter rainfall following application was still apparent for the Ludford soil in the autumn (yellow variables), while predicted leaching losses for the more susceptible Hall and Enborne soils were negatively correlated with short-term air temperatures (1 day to 3 month average temperatures; medium orange variables), especially after autumn application. This specific behaviour of pesticide 1 is consistent with the transfer of a rapidly degrading compound moving quickly down the profile through preferential pathways. For spring applications, simulated losses of pesticide 1 could be linked to a number of statistics describing the rainfall conditions after application, including the cumulative rainfall over the 10–61 days following application (*R10* to *R61*; medium blue), the number of days until the profile receives a significant rainfall event (e.g. *L20*, the number of days from application to a 20 mm daily rainfall event; green) or the number of days after application until a cumulative rainfall volume of 50 or 100 mm is reached (*C50* or *C100*; purple). In contrast to winter rain statistics, these correlation coefficients were all <0.80 (absolute value basis). For all but two of the leaching simulations shown, however, these correlations were significant at the 0.05 level (Table 2). The small but significant correlations (0.368–0.627) associated with the short-term rainfall variables (*R10* to *R61*) are attributable to pesticide 1 losses which were consistently 0.01 mg m^{-2} or less in the spring. Because pesticide 1 was predicted to disappear rapidly from the soil profile, simulated losses are smaller and perhaps less amenable to correlation with the weather variables. However, the influence of short-term rainfall on a mobile, rapidly degrading compound is plausible. MACRO simulates increased pesticide leaching via macropores when rain occurs soon after application, because most of the pesticide is still at the soil surface and is routed directly into macropores for rapid transport to depth. These relations are corroborated by several field studies in which positive relations between early rainfall and pesticide loss were observed.[29,35–37] One such study[36] also observed a negative correlation between total loss and elapsed time until accumulation of 25 mm rain, which is similar to the present results for *L20* and *L30* following spring application of pesticide.

Simulated losses from the Cuckney soil (where flow is predicted to occur primarily in the soil matrix) displayed more long-term behaviour, with an influence of average temperatures computed over a period from 7 to 10 months (light orange). Results for pesticide 2 were found to be intermediate between those described above for pesticide 1 and pesticide 3. For autumn applications, the influence of winter rainfall following application on simulated losses of pesticide 2 was widespread among the various soils considered (yellow). In contrast, predicted losses of pesticide 2 following spring applications were determined by winter rainfall, but also by long-term rainfall (light blue), rainfall volumes shortly after application (medium blue) and the time to extreme rainfall events (green).

In contrast to the results obtained for leaching, a stronger influence of the more dynamic aspects of the meteorological conditions shortly after application was apparent for simulated drainage losses, especially for simulations involving pesticides 1 and 2 (Table 3). The influence of rainfall and temperature conditions shortly after application (medium blue and medium orange) was clear for pesticide 1 in all of the soils except the Quorndon. A similar behaviour was noted for pesticide 2 in more clayey soils. Lag time influenced simulated losses of pesticides 2 and 3 following spring application on more structured soils. The dominance of short-term rainfall is consistent with field studies in which the largest pesticide concentration in drain water was found in the first drainage event following application, indicating preferential flow,[35] and also with a review of more than 30 studies of pesticide transfer to drains in North America.[29] In the latter study, preferential flow resulting from rainfall soon after pesticide application was identified as a dominant transport mechanism. In the present study, winter rainfall after application was predicted to be related to pesticide loss (yellow), but its influence was mainly limited to the transfer of pesticides 2 and 3 following autumn application and to transfers for the less structured Quorndon soil for spring application. As before, correlations with winter rainfall typically were >0.80; the maximum correlation with winter rainfall was 0.96 ($P < 0.0001$) (autumn application, Denchworth soil, pesticide 3).

3.3 Transferability of results to a different climate

Models are a cost-effective and efficient means of evaluating large numbers of agroenvironmental scenarios in situations where collection of field data is impractical. In the present study, 1593 MACRO simulations were conducted, based on multiple pesticides, soil types, application dates and 100 years of synthetic rainfall data. As all models have limitations, the results obtained here are model and weather dependent. An independent climatic dataset from Zaragosa, Spain, was tested with Pearson correlations to see if climatic factors identified as influential with the Oxford data (winter rain, short-term rain and temperature and time lag until significant rainfall) are important elsewhere in Europe. The objective was to identify areas of overlap as well as of dissimilarity, to aid in the selection of variables for a separate analysis to develop climatic zones for all of Europe.[38] The comparative simulation study included a repeat of all leaching modelling trials and conditions except for the weather information. For leaching scenarios at Zaragosa, short-term rain effects were noted for pesticides 1 and 2 on the more structured soils (Hall and Enborne) (data not shown), which is very similar to the Oxford results. However, temperature effects were more widespread at Zaragosa, and the influence of winter rain was reduced. Temperature was moderately to strongly correlated (i.e. correlation coefficients were less than about -0.5 and -0.8 respectively) with pesticide loss for all soils except the Hall, for both spring and autumn applications. This effect was seen primarily for the more mobile pesticides (1 and 2), but also for pesticide 3 on the more structured soils (Ludford and Enborne). Winter rain was important at Zaragosa mainly for pesticides 2 and 3 applied to the Hall, which is susceptible to leaching. The reduced influence of winter rain at Zaragosa apparently is related to climatic differences between the two sites. Oxford has up to 30% more daily rain events of 10 mm or less, and the frequent daily events promote leaching. The cumulative effect of the increased frequency of rain is manifested as a strong, positive correlation between winter rain and pesticide loss for a number of scenarios (yellow cells in Table 2). In contrast, Zaragosa is somewhat warmer and drier, and the predominant variable is temperature, which is negatively correlated with pesticide loss for several scenarios. Average annual temperature is 9.4 °C at Oxford and 14.5 °C at Zaragosa.

4 CONCLUSIONS

An extensive modelling study involving multiple soils, timing of applied pesticides and variable precipitation patterns was undertaken to identify meteorological drivers that most influence pesticide loss by leaching and to drains. The results were corroborated to a large extent by field studies reported in the literature. Climatic factors influencing pesticide loss are specific to soil–pesticide combinations to some extent, but general rules can nevertheless be drawn:

- Pearson correlation coefficients and 75th percentile values of predicted cumulative pesticide loss indicated that loss generally increased with increasing clay content, increasing rainfall of variable duration, decreasing temperature (as indicated by climate variables and the season of pesticide application) and increasing pesticide persistence, for both leaching and drainage scenarios. Weather interacts strongly with soil type, such that short-term climatic variables generally are more influential in soils with high clay content. However, the influence of these variables and the timing of extreme events in relation to pesticide application were greater for drainage scenarios than for leaching. These results reflect the rapid transport of pesticides to drains via macropores in soils with high clay content.
- Classification trees corroborated correlation results in that large pesticide loss was predicted to occur on clay soils receiving large rainfall amounts after autumn application, for both leaching and drainage scenarios. This suggests that the fate and transport processes are similar for leaching and drainage over the range of depths studied here (0.6–1 m). Leaching below 1 m, however, would be expected to be less in drained soils because of slowly permeable or impermeable substrates and therefore interception of percolate by the drains. The classification trees also indicated threshold levels of rain and clay content that resulted in large pesticide loss. Knowledge of system thresholds can help managers identify specific areas prone to leaching.
- An exception to the overall pattern of large pesticide loss on clay soils was observed for the Hall soil, which comprises 69% sand and 11% clay in the first two layers. The Hall soil had the largest simulated pesticide loss of any of the individual season–soil–pesticide scenarios. Pesticide loss in this case is attributable primarily to matrix flow in coarse soil, rather than to macropore flow. The Hall has less organic carbon at depth, which means that MACRO predicts weaker sorption of pesticides.
- Pesticide losses by leaching and drainage show considerable temporal variability owing to random weather patterns. All of the climatic variables considered here (cumulative rainfall in a time period, number of days until a specified amount of rainfall, etc.) were referenced to pesticide application date. Thus, the timing of rainfall and extreme events in relation to application date were of prime importance.
- For leaching scenarios, Pearson correlations indicated an overall strong influence of winter rainfall at Oxford following pesticide application in spring or autumn, especially for less mobile and more persistent compounds. For more mobile compounds with limited persistence, short-term rainfall and temperature effects were noted. Rain occurring within 10 days markedly influenced leaching of pesticide 1 ($K_{oc} = 20\,\mathrm{L\,kg^{-1}}$, $DT_{50} = 8$ days) on seven out of nine soils considered.
- Repetition of leaching simulations with data from Zaragosa, Spain, which has a drier and warmer climate, indicated that certain of these results are transferable to other regions. Short-term rain effects at Zaragosa were very similar to the Oxford results. However, temperature effects were more widespread at Zaragosa, and winter rain was less influential. These results underscore the importance of selecting

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factors representative of diverse conditions for use in a separate analysis aiming to develop climatic zones for all of Europe.

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REFERENCES

1 Karpouzas DG and Singh BK, Microbial degradation of organophosphorus xenobiotics: metabolic pathways and molecular basis. *Adv Microb Physiol* **51**:119–185 (2006).

2 Matamoros DE, van Griensven A, van Biesen L and Vanrolleghem PA, Development of a geographical information system for pesticide assessment on an Ecuadorian watershed. *Water Sci Technol* **52**:259–265 (2005).

3 Sinkevich MG, Walter MT, Lembo AJ, Richards BK, Peranginangin N, Aburime SA, *et al*, A GIS-based ground water contamination risk assessment tool for pesticides. *Ground Water Mon Remed* **25**:82–91 (2005).

4 Groundwater scenarios in the EU review of active substances. Report of the FOCUS working group on groundwater scenarios, EC document reference SANCO/321/2000 rev. 2 (2000).

5 Surface water scenarios in the EU evaluation process under 91/414/EEC. Report of the FOCUS working group on surface water scenarios, EC document reference SANCO/4802/2001 rev. 2 (2001).

6 Leaching models and EU registration. Report of the FOCUS working group on leaching models, EC document reference 4952/VI/95 (1995).

7 Soil persistence models and EU registration. Final report of the FOCUS soil modelling working group (1997).

8 Mangels G, *The Development of Muscrat (Multiple Scenario Risk Assessment Tool) – a Software Tool for Conducting Surface Water Exposure Assessments* (2001). [Online]. Available: http://www.waterborne-env.com/modeling/muscrat_documentation.pdf [25 March 2008].

9 Dubus IG, Brown CD and Beulke S, Sensitivity analyses for four leaching models *Pest Manag Sci* **59**:962–982 (2003).

10 Boesten J, Sensitivity analysis of a mathematical model for pesticide leaching to groundwater. *Pestic Sci* **31**:375–388 (1991).

11 Jarvis NJ, *The MACRO Model (Version 4.3) – Technical Description* (2006). [Online]. Available: http://www-mv.slu.se/bgf/Macrohtm/macro43b/TechMacro43.pdf [25 March 2008].

12 Flury M, Experimental evidence of transport of pesticides through field soils – a review. *J Environ Qual* **25**:25–45 (1996).

13 Jarvis NJ, The MACRO model (Version 3.1) – Technical description and sample simulations. Monograph, Reports and Dissertations No. 19, Swedish University of Agricultural Sciences, Uppsala, Sweden (1994).

14 Armstrong A, Aden K, Amraoui N, Diekkruger B, Jarvis N, Mouvet C, *et al*, Comparison of the performance of pesticide-leaching models on a cracking clay soil: results using the Brimstone Farm dataset. *Agric Water Manag* **44**:85–104 (2000).

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

16 Brown CD, Bellamy PB and Dubus IG, Prediction of pesticide concentrations found in rivers in the UK. *Pest Manag Sci* **58**:363–373 (2002).

17 Brown CD, Dubus IG, Fogg P, Spirlet M and Gustin C, Exposure to sulfosulfuron in agricultural drainage ditches: field monitoring and scenario-based modelling. *Pest Manag Sci* **60**:765–776 (2004).

18 Holman IP, Dubus IG, Hollis JM and Brown CD, 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. *Sci Total Envir* **318**:73–88 (2004).

19 Larsson MH and Jarvis NJ, Evaluation of a dual-porosity model to predict field-scale solute transport in a macroporous clay soil. *J Hydrol* **215**:153–171 (1999).

20 Merdun H and Quisenberry VL, Simulation of water and solute transport with MACRO model in Cecil loamy sand soil. *Aus J Soil Res* **42**:939–951 (2004).

21 Reichenberger S, *Field-scale Risk Assessment for Diffuse-source Pesticide Inputs into German Surface Waters*, ISBN 3-931789-41-1, ISSN 0949–8230. Justus Liebig University, Giessen, Germany (2005).

22 Scorza RP, Jr, Jarvis NJ, Boesten JJTI, van der Zee SEATM and Roulier S, Testing MACRO (version 5.1) for pesticide leaching in a Dutch clay soil. *Pest Manag Sci* **63**:1011–1025 (2007).

23 Tiktak A, Application of pesticide leaching models to the Vredepeel dataset II. *Agric Water Manag* **44**:119–134 (2000).

24 Fowler HJ, Kilsby CG, O'Connell PE and Burton A, A weather-type conditioned multi-site stochastic rainfall model for the generation of scenarios of climatic variability and change. *J Hydrol* **308**:50–66 (2005).

25 *StatSoft Electronic Textbook*. [Online]. StatSoft. Available: http://www.statsoft.com/textbook/stathome.html [25 March 2008].

26 *StatSoft, Inc.* [Online]. Available: http://www.statsoft.com/ [25 March 2008].

27 Helsel DR and Hirsch RM, *Statistical Methods in Water Resources*. *Studies in Environmental Science* 49. Elsevier, New York, NY, 522 pp. (1992).

28 *SAS Institute Inc.* [Online]. Available: http://www.sas.com/index.html [25 March 2008].

29 Kladivko EJ, Brown LC and Baker JL, Pesticide transport to subsurface tile drains in humid regions of North America. *Crit Rev Environ Sci Technol* **31**:1–62 (2001).

30 Beulke S, Brown CD, Fryer CJ and van Beinum W, Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils. *Chemosphere* **57**:481–490 (2004).

31 Brown CD, Fryer CJ and Walker A, Influence of topsoil tilth and soil moisture status on losses of pesticide to drains from a heavy clay soil. *Pest Manag Sci* **57**:1127–1134 (2001).

32 Rocha WSD, Regitano JB and Alleoni LRF, 2,4-D residues in aggregates of tropical soils as a function of water content. *Soil Sci Soc Am J* **70**:2008–2016 (2006).

33 Ochsner TE, Stephens BM, Koskinen WC and Kookana RS, Sorption of a hydrophilic pesticide: effects of soil water content. *Soil Sci Soc Am J* **70**:1991–1997 (2006).

34 Beulke S, Brown CD, Fryer CJ and Walker A, Lysimeter study to investigate the effect of rainfall patterns on leaching of isoproturon. *Pest Manag Sci* **58**:45–53 (2002).

35 Scorza RP, Jr, Smelt JH, Boesten J, Hendriks RFA and van der Zee S, Preferential flow of bromide, bentazone and imidacloprid in a Dutch clay soil. *J Environ Qual* **33**:1473–1486 (2004).

36 Walker A, Rodriguez-Cruz MS and Mitchell MJ, Influence of ageing of residues on the availability of herbicides for leaching. *Environ Pollut* **133**:43–51 (2005).

37 Worrall F, Parker A, Rae JE and Johnson AC, A study of suspended and colloidal matter in the leachate from lysimeters and its role in pesticide transport. *J Environ Qual* **28**:595–604 (1999).

38 Blenkinsop S, Fowler HJ, Dubus IG, Nolan BT and Hollis JM, Developing climatic scenarios for pesticide fate modelling in Europe. *Environ Pollut* 2007. doi:10.1016/j.envpol.2007.10.021.