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Evaluation of probabilistic modelling approaches against data on leaching of isoproturon through undisturbed lysimeters

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Abstract

This study evaluated probabilistic modelling approaches against data on leaching of isoproturon through two contrasting soil types. Leaching through undisturbed lysimeters from a sandy loam (Wick series) and a moderately structured clay loam (Hodnet series) was investigated in seven replicates. The variability of soil properties and of sorption and degradation of isoproturon was estimated by taking 6-14 samples within the areas of lysimeter extraction in the field. Normal distributions were assigned to Koc and DT50 and a large number of values for these two parameters were sampled from each distribution. Parameter values were used to simulate movement of isoproturon through the lysimeters with the preferential flow model MACRO. Uncertainty in output

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distributions was compared with the variability of measured data. A constrained probabilistic assessment varying only degradation and sorption properties was sufficient to match the observed variability in cumulative leaching from the coarse-textured Wick soil (CV = 79%). Variation of pesticide properties alone could not match observed variability in cumulative leaching from the structured Hodnet soil (CV = 61%) and variability in a number of soil properties was incorporated. For both soils, constrained probabilistic approaches where only the top few most sensitive model inputs were varied were sufficient to match or exceed observed variability.

Keywords: Pesticide, groundwater, preferential flow, probabilistic modelling, MACRO

1. Introduction

Mathematical models are used to evaluate the potential for leaching of pesticides to groundwater within regulatory procedures. Traditionally, deterministic approaches have been applied where a single combination of model input parameters is used to predict a single time series of concentrations in leachate. The parameter combination is often selected to represent realistic worst-case conditions, but the likelihood of this combination occurring under real environmental and usage conditions is not assessed. Deterministic procedures do not account for the uncertainty in the modelling which arises from various sources (Dubus et al., 2003), such as the spatial and temporal variability in factors influencing pesticide behaviour (Rao and Wagenet, 1985) or the uncertainty associated with the measurement, calculation or estimation of input parameters (Loague and Green, 1991). Although deterministic assessments may be appropriate for lower tiers of the regulatory process, it is increasingly recognised that the uncertainty in model input parameters should be taken into account in regulatory decision making at higher tiers (Laskowski, 1999; Solomon, 1999). This can be achieved by running a deterministic model many times for a large number of different input values or modelling scenarios followed by a statistical analysis of the model output. This would allow evaluating the uncertainty in model predictions and estimating the confidence that should be assigned to modelling results. An end result of such probabilistic assessments is the likelihood and frequency of exceeding a threshold environmental concentration. An increasing number of studies incorporating uncertainty in pesticide risk assessments have been reported in the literature (Di and Aylmore, 1997; Li *et al.*, 1998; Laskowski, 1999; Zacharias *et al.*, 1999; Carbone et al., 2002).

The wide range of factors that influence pesticide fate such as soil type, hydrogeology, climate, cropping, usage patterns and physico-chemical pesticide properties makes probabilistic assessments highly complex. One of the factors causing variability in pesticide leaching to depth is the heterogeneity of soil and pesticide properties (Rao and Wagenet, 1985; Flury *et al.*, 1998). Pesticide degradation and sorption were found to vary in space and time in a number of studies (Walker and Brown, 1985; Beck *et al.*, 1996; Vischetti *et al.*, 1997). This is mainly due to the variability in soil physical, chemical and biological factors which influence degradation and sorption processes (Parkin, 1993). A particularly large variability in soil hydrological properties which influence water movement and associated solute leaching is found for soils which are prone to preferential flow. Preferential flow refers to a situation where water infiltrating a soil does not equilibrate with the resident soil water, but flows rapidly to depth. For example, shrinkage cracks, earthworm channels or root holes may operate as flow pathways in which water moves rapidly downwards and by-passes the denser soil matrix. Preferential flow pathways are not permanent structures and they are not evenly distributed across the field. Rather, they vary greatly in time and space (Ogden *et al.*, 1999).

The aim of this study was to evaluate probabilistic modelling approaches against data on leaching of isoproturon through two contrasting soil types. Leaching through undisturbed lysimeters from a sandy loam (Wick series) and a moderately structured clay loam (Hodnet series) was investigated in seven replicated lysimeters. Measured soil properties, pesticide sorption and degradation values were analysed statistically and the data were used to simulate movement of isoproturon with the preferential flow model MACRO. This model was selected to exemplify the approach, which is itself generic and broadly applicable. Distributions for pesticide loss predicted by the model were compared to observed data.

2. Lysimeter experiment

2.1 Experimental methodology

A two-year lysimeter experiment was undertaken which investigated the leaching of isoproturon through two undisturbed soils. Materials and methods, experimental data and modelling results for the first study period are presented in detail elsewhere (Beulke *et al.*, 2002). The methodology used in the second experimental season is summarised below.

Leaching of isoproturon through undisturbed lysimeters from a sandy loam (Wick series) and a moderately structured clay loam (Hodnet series) was investigated in seven replicates. Matrix flow is expected to be the dominant process in the sandy Wick soil, although potential preferential pathways in the form of vertical worm channels were observed in the field. The structured clay loam was selected to represent a soil type where preferential flow is clearly an important process. Average values for the main properties of the Wick and Hodnet soil are given in Table 1.

Undisturbed soil cores (25 cm diameter, 50 cm length) were extracted in October 1998 from arable fields in Warwickshire, UK and transferred to a lysimeter facility in Silsoe, Bedfordshire. The study was started on 15 December 1998. There was no leaching from mid April 1999 onwards. The last sample was taken on 14 April 1999 (120 days after application) and results will be presented up to this date. The study was terminated on 15 May when no additional significant leaching was expected due to increasing evapotranspiration in the warmer summer months. The rainfall volume received for each treatment was adjusted to match a target range by covering lysimeters during particularly wet periods and/or adding artificial irrigation where necessary. Total input of rainfall + irrigation from mid December to mid May was 260 mm.

Radiolabelled isoproturon was applied to the lysimeters in mid December 1998. For each lysimeter, [^{14}C] ring-labelled isoproturon (radioactive purity >99%, specific activity 2.56 GBq mmole^{-1}) was mixed approximately 1:30 with non-labelled isoproturon and dissolved in 60:40 water:methanol (3.0 ml) to give a dose equivalent to 2.5 kg a.s. ha^{-1}. The specific activity of the applied mixture was 76.7 MBq mmole^{-1} and the activity applied per lysimeter was 4.01 MBq. The isoproturon solution was applied to the lysimeters using a pipette and followed by two methanol rinses. Flow from each lysimeter was collected at regular intervals over the winter, measured for volume and subsamples analysed for amount of radioactivity.

Soil samples were taken from up to 50-cm depth from the area of lysimeter extraction in the field to characterise the variability in soil characteristics. In autumn 1997, samples were taken at 10 locations within 1 m of the points of lysimeter extraction. Soil was sampled in 10-cm increments up to 30-cm depth and analysed for organic carbon content. Additional analyses of organic carbon contents were carried out for six samples from 30-40 and 40-50 cm depth. Bulk density and water release characteristics were determined for samples taken at six points from 0-50 cm depth in 10-cm increments. Particle size distribution, pH and saturated hydraulic conductivity were measured at up to 2 sampling points in the field. In autumn 1998, samples were taken from the same field within 0.5 m of the point of extraction of each of the fourteen lysimeters. Samples from 0-30 cm were analysed for organic carbon content and pH. Bulk density and selected points of the water release curve (0, -1 and –5 kPa) were determined for samples taken from 10-15 cm to characterise topsoil properties.

Sorption and degradation of isoproturon was investigated in samples taken at the time of lysimeter extraction from 10 different locations within the same fields. In order to characterise degradation, soil samples were treated with isoproturon (15 mg a.s. kg^{-1} soil) and incubated in the laboratory at a temperature of 15^{o}C and a soil moisture content equivalent to a matric potential of –33 kPa (18.2% w/w, Wick; 30.0% w/w, Hodnet). Soil residues were measured at intervals and first-order DT50 values were derived from these data. DT50 values indicate the time required for 50% loss of the initially applied pesticide. Sorption was determined by equilibrating soil samples with an aqueous solution at a single initial concentration of the pesticide (10 mg a.s. kg^{-1} soil). The relationship between sorbed amounts and those present in solution was calculated. The methodology for degradation and sorption studies is described in more detail by Beulke *et al.* (2002).

2.2 Experimental results

2.2.1 Variability in soil and pesticide properties

Coefficients of variation for soil properties measured in the first experimental season are given in Table 2.

Ten soil samples were taken in the first experimental season from 0-10 cm, 10-20 cm and 20-30 cm depth within the areas of lysimeter extraction and analysed for organic carbon contents. A further set of six samples was taken from 30-40 cm and 40-50 cm depth. Results showed a considerable variability of organic carbon contents within the areas of lysimeter extraction. Coefficients of variation for the sandy Wick soil ranged from 8.3 to 18.8% depending on the soil depth (Table 2). Similar results were found for the Hodnet clay loam where coefficients of variation for organic carbon contents ranged from 9.4 to 18.2%. Water contents at a range of water tensions were determined for samples from the Wick and Hodnet soils. Samples were taken at six points within the area of lysimeter extraction in 10-cm increments up to 50 cm depth. Coefficients of variation were between 1.8 and 15.0% for the Wick soil and between 2.2 and 16.1% for the Hodnet soil.

In the second experimental season, the variability of soil properties was investigated by taking topsoil samples close to the point of lysimeter extraction (14 samples per soil type). Coefficients of variation for the Wick soil were 11.5% for organic carbon contents, 9.8% for bulk density, 6.8% for the water content at saturation and 6.2% for the water content at -5 kPa. Variability in the Hodnet soil was somewhat smaller with coefficients of variation of 7.5% for organic carbon contents, 4.5% for bulk density, 3.2% for the water content at saturation and 5.2% for the water content at -5 kPa.

Sorption and degradation of isoproturon was determined for 10 samples taken from each site at the time of lysimeter extraction. Figure 1 shows Box-and-Whisker plots of Kd values (sorption coefficients) and DT50 values at 15°C and -33 kPa for the two soils.

Kd values in the Wick soil ranged from 1.1 to 1.5 ml g^{-1}. The herbicide was more strongly sorbed in the Hodnet soil with Kd values between 1.7 and 2.1 ml g^{-1}. A large variability in the degradation of isoproturon was found for the Hodnet soil where DT50 values in the ten samples ranged from 8.5 to 25.5 days. Degradation in the Wick soil varied to a lesser extent (DT50 values 7.5 to 17.6 days).

2.2.2 Variability in pesticide leaching

A characterisation of radioactivity in leachate from the lysimeters was only possible for a small proportion of samples and the measured radioactivity was fully assigned to isoproturon for the purposes of this modelling study. Any breakdown products which may have contributed to the observed levels of radioactivity were ignored. The data on isoproturon presented below should thus not be taken as absolute values, but rather as parent equivalents.

Figure 2 shows concentration profiles of isoproturon in leachate from each of the seven replicate lysimeters of the Wick series. Breakthrough curves for most cores were relatively smooth except for one lysimeter where the concentration profile was of irregular shape and large concentrations were measured shortly after application, suggesting an influence of preferential flow. Matrix flow was expected to be the dominant process in the sandy Wick soil, but potential preferential pathways in the form of vertical worm channels were found during extraction of the soil cores. A dye (Brilliant blue) was leached through selected lysimeters at the end of the experiment and a large stained pore down to the bottom of the core was found in the lysimeter which exhibited an irregular flow pattern. This supports the assumption that the large initial concentrations of isoproturon observed in leachate from this lysimeter result from preferential flow.

Concentration profiles for the Hodnet soil clearly showed preferential movement of the pesticide for two of the seven replicates with isoproturon detected early in the season and at a maximum concentration of 17.2 $\mu g\ l^{-1}$ (Figure 2). Breakthrough curves were smoother for the remaining five replicates. Soils of the Hodnet series are structured and prone to preferential flow. Hydraulic properties which determine the relative importance of preferential flow are spatially variable in this soil type. This is likely to be the main reason for the relatively large variability between replicate lysimeters. Differences in pesticide degradation and sorption may have contributed to the observed differences in leaching through the seven cores.

Figure 3 shows Box-and-Whisker plots for cumulative losses of isoproturon from the sandy loam (Wick series) and the clay loam (Hodnet series) 120 days after application

(DAA). Total losses from the Wick lysimeters ranged from 0.025 to 0.204 mg/m^2 with a coefficient of variation of 79%. Losses from the seven Hodnet soil cores were between 0.035 and 0.393 mg/m^2 with a coefficient of variation of 61%.

3. Probabilistic Modelling

Soil and pesticide properties were initially averaged across the field and used as input for the preferential flow model MACRO (Jarvis, 1994) to simulate isoproturon concentrations in leachate from the two series of lysimeters. Version 4.1b of the model (August 1998) was used in this study. MACRO divides the soil pore system into the soil matrix where flow is relatively slow and driven by convection and dispersion (micropore domain) and a region with preferential flow pathways which deliver water and solutes rapidly to depth (macropore domain). By varying the input parameters, the MACRO model can be set up to simulate a soil dominated by preferential flow, a soil with no preferential flow at all or any combination of flow types between these two extremes. The main application of MACRO is to simulate flow through structured clay soils where rapid movement of water and solutes through cracks and fissures is important. The model can also be applied to intermediate loam soils where earthworm and root channels may deliver water and solutes rapidly to depth. MACRO has been evaluated against a number of datasets on leaching of pesticides or non-interactive solutes (Bergström, 1996; Brown *et al.*, 1998; Larsson and Jarvis, 1999). Although discrepancies from measured data are occasionally observed, the results are generally promising. Water and pesticide movement through structured heterogeneous clay soils can be difficult to simulate consistently with MACRO (Vink et al., 1997; Armstrong *et al.*, 2000; Beulke *et al.*, 2001). However, similar results were found for the other models tested (CRACK-NP, LEACHP, PESTLA, PLM, SIMULAT, SWAT, VARLEACH).

This is due to the large spatial and temporal variability of influencing factors in such soils and the inability of the models to represent all relevant controlling processes at the present time. The simulation of water and pesticide movement through intermediate soils is less challenging. MACRO showed a better match to data from a range of intermediate soils than models which do not consider preferential flow in work by Brown et al. (1999).

Pesticide and soil properties are variable in space and time. Their spatial variability was investigated in this study by taking samples close to the points of lysimeter extraction. Existing probabilistic approaches allow incorporation of this variability into the modelling and quantification of the uncertainty in model output arising from the uncertainty and variability in model input. The potential applicability of such approaches within regulatory risk assessments was evaluated.

The following general approach was adopted. The parameterisation of MACRO was based on measured information where possible. No calibration of the model was undertaken. Variables for probabilistic modelling were *a priori* selected on the basis of results from model sensitivity analyses. Probability density functions representing the variability of pesticide and soil properties were assigned on the basis of expert judgement and experimental information. A large number of values for key input parameters was generated and these were used to simulate the leaching of isoproturon through the Wick and Hodnet lysimeters. MACRO was run for each combination of input parameters. The resulting distributions of model output (cumulative isoproturon load 120 DAA) were compared with measured losses of isoproturon and with those simulated on the basis of a deterministic approach using a single set of average input parameters.

In this study, Latin Hypercube sampling from distributions of model input parameters was used in combination with the MACRO model. This aimed at demonstrating a technique which allows to incorporate uncertainty and variability into pesticide fate modelling. The MACRO model was used as an example, but the technique can be applied equally well to any other pesticide leaching model.

3.1 Selection of variables for probabilistic modelling

Results from model sensitivity analyses for MACRO (Dubus and Brown, 2002) guided the selection of variables for probabilistic modelling. The authors investigated the sensitivity of input parameters for MACRO and three other pesticide leaching models for transport of two pesticides through the Wick and Hodnet soil. Results for a pesticide with a DT50 value of 60 days at 8^{o}C, a Koc value of 100 ml g^{-1} and a Freundlich exponent of 0.9 are shown in Figure 4. For comparison, average degradation and sorption characteristics of isoproturon in the Hodnet soil are: DT50 =18 days at 15^{o}C; Koc = 98 ml g^{-1}. In Figure 4, the fifteen parameters with the strongest influence on simulated pesticide losses are ranked using a relative sensitivity index (MAROV) and also grouped into broad classes of parameters. The larger the MAROV value for a given parameter, the greater its sensitivity. The calculation of MAROV indices is described in detail by Dubus and Brown (2002).

For the Wick soil, MACRO was found to be most sensitive to changes in sorption parameters (FREUND, ZKD) and degradation rates (DEG). In the Hodnet soil, leaching of the pesticide was more sensitive to changes in hydraulic parameters than to changes in the degradation rate or the sorption coefficient (Figure 4). TPORV (total porosity), ZN (macropore tortuosity), XMPOR (boundary water content), KSM (boundary hydraulic conductivity) and ASCALE (aggregate half-width) were the soil hydraulic parameters with the strongest influence on leaching through this structured soil.

On the basis of these results, probabilistic modelling of isoproturon leaching through the Wick soil incorporated the variability of the DT50 and/or Kd values of isoproturon. Two probabilistic modelling exercises were carried out for the Hodnet soil. Initially, only DT50 and/or Kd values of isoproturon were varied. Thereafter, those hydraulic parameters for which measurements were available (TPORV and XMPOR) were varied either on their own or in combination with pesticide parameters.

3.2 Probabilistic modelling incorporating the variability in pesticide properties

3.2.1 Attribution of statistical distributions to pesticide properties and statistical sampling

Ten soil samples were taken in the field within the area where lysimeters were extracted and degradation and sorption of isoproturon was determined in each sample. Although this was useful for providing a first estimation of the variability of isoproturon behaviour within this area, the sample size was too small to allow a robust attribution of a distribution to the data. Only speculations could therefore be made. Basic statistics were computed and Kolmogorov-Smirnov (KS) tests were carried out to test for normality of the distributions. Results suggested that out of the four populations examined, only one had the potential to follow a normal law (DT50 values for the Wick soil). The three remaining datasets (Kd in the Wick and Hodnet soils, DT50 values for the Hodnet soil) were log-transformed and resulting data were tested for normality by graphical means and using a KS test. These tests were negative. Other types of distributions were not tested because the small number of observations would not have allowed any confidence to be assigned to the results. A pragmatic approach was followed instead. Sorption and degradation properties have been found to be either normally (Elabd *et al.*, 1986) or log-normally (Novak *et al.*, 1997) distributed in the field. It was decided to assign a normal distribution to pesticide properties in this probabilistic modelling exercise, although a log-normal distribution could have also been selected. The normal distribution is intuitively easier to parameterise than its log-transformed version. The arbitrary adoption of a normal distribution implies that the most frequent value of a specific parameter is considered to be the mean of the population and that data are assumed to be symmetrical on each side of this value.

Probability density functions of the normal law are fully characterised by their mean and standard deviation. The mean and standard deviation were taken as those observed in the field for each input parameter. A total of 100 values were randomly sampled from the statistical distributions. Sampling was restricted to the range defined by the mean ± 1.96 x standard deviation in order to avoid the sampling of unrealistic values. For a normal distribution, 95% of the values fall within this range.

Measured DT50 values were corrected for moisture effects on degradation prior to their use as model input. This was necessary because the reference moisture in MACRO is fixed to the water content at the boundary between the micropores and macropores (XMPOR). The DT50 values for the Wick and Hodnet soil measured at -33 kPa were adjusted to XMPOR using the equation implemented in the model (Jarvis, 1994). This resulted in DT50 values for the Wick soil of 6.0-14.0 days with an average of 9.3 days. DT50 values at XMPOR for the Hodnet soil ranged from of 8.2 to 24.7 days (average = 18.0 days). Parameters for the statistical distributions are presented in Table 3.

Random sampling into statistical distributions was performed using the UNCSAM package (Janssen *et al.*, 1994) and a Latin Hypercube Sampling (LHS) scheme. LHS is a stratified Monte Carlo sampling technique which allows the number of model runs to be kept to a minimum (Helton, 1993). The SENSAN package (Doherty *et al.*, 2002) was used to automatically generate input files for MACRO using the sampled values, run the model and record the appropriate model output.

Three separate cases were considered:

1. The first case accounted for the variability of DT50 values alone. A total of 100 DT50 values were sampled from each of the distributions for the Wick and the Hodnet soil. Sampled DT50 values were then combined with average Kd values for each of the two soils. MACRO simulations were performed for each of the 100 combinations and the total load of isoproturon leached until 120 DAA was recorded.
2. An additional modelling exercise was carried out to account for only the variability of sorption coefficients of isoproturon. One hundred sorption coefficients were sampled within the limits given in Table 3 and these were combined with the average DT50 value for each of the two soils.
3. In the third case, the variability of DT50 values and sorption coefficients was considered simultaneously and 100 combinations of DT50 and Kd values were sampled and used as model input.

3.2.2 Results

Box-and-Whisker plots of measured cumulative isoproturon losses between 0 and 120 DAA are compared with those of simulated losses following variation of pesticide input parameters for MACRO in Figure 5 (Wick soil) and Figure 6 (Hodnet soil). Isoproturon loads derived from deterministic modelling with MACRO on the basis of average pesticide properties are indicated for comparison.

The use of a range of DT50 values for the Wick soil caused a large variability of simulated isoproturon loads with a coefficient of variation of 38% (Figure 5). The variability in sorption coefficients resulted in a skewed distribution of isoproturon loads and the coefficient of variation of the model output was again 38%. Isoproturon loads for the Wick soil covered a larger range when DT50 values and sorption coefficients were varied simultaneously (CV = 58%). The range of simulated pesticide losses from the Wick soil agreed relatively well with the range of data measured for the seven replicate lysimeters (Figure 5). The simulated mean and median were, however, larger than the measured values. Coefficients of variation for the observed losses of isoproturon (79%) were larger than those for the probabilistic modelling exercises (38-58%). It should be noted, however, that only seven measured values were available compared with 100 model simulations.

Probabilistic modelling for the Wick soil showed that the incorporation of uncertainty in pesticide degradation and sorption parameters will result in a considerable variability in simulated pesticide behaviour. Results suggest that for this soil type the variability in model output will encompass a relatively large proportion of the variability at the site. The contribution of additional factors not considered in this probabilistic analysis can, however, not be excluded. It should also be noted that experimental information on pesticide leaching was available for seven soil cores only.

The average simulated loss of isoproturon from the Hodnet lysimeters for the three probabilistic modelling studies agreed well to the mean loss from the seven lysimeters (Figure 6). There was a relatively large difference between the variability in simulated leaching (CV = 15-24%) and that of measured data (CV = 61%). This suggests that the incorporation of variability in the considered pesticide properties alone may not be appropriate to fully represent the variability in isoproturon leaching for this soil type. The variability in physical properties found at the site may be an additional important factor. This hypothesis was tested through additional probabilistic analyses for the Hodnet soil to consider some of the uncertainty associated with soil hydraulic properties.

3.3 Probabilistic modelling incorporating the variability in soil and pesticide properties

3.3.1 Attribution of statistical distributions to soil properties and statistical sampling

The five soil parameters with the strongest influence on leaching of a pesticide through the Hodnet soil were TPORV, ZN, XMPOR, KSM and ASCALE in a sensitivity analysis for MACRO by Dubus and Brown (2002; Figure 4). Probabilistic modelling of isoproturon leaching through the Hodnet soil incorporated the variability of those hydraulic parameters for which measurements were available (total porosity TPORV and boundary water content XMPOR). Soil parameters were varied on their own or in combination with the DT50 value and Kd value of isoproturon.

The average porosity for each soil layer was derived from data measured in the first experimental season (six water release curves were available per 9-cm or 10-cm soil layer). A normal distribution was arbitrarily assigned to TPORV. The standard deviation was set such that 95% of the data (mean ± 1.96 x standard deviation) fell between the minima and maxima given in Table 4. This corresponded to a coefficient of variation for TPORV of 5.1%. It should be noted that the selection of the distribution influences the results of the probabilistic exercise. An equal number of values will be sampled either side of the mean if a normal distribution is chosen. In contrast, lognormal distributions are skewed. There was a negligible difference in the goodness of fit of a normal or log-normal distribution to the 6 datapoints as indicated by the KS test. However, the sample size was too small to allow a robust attribution of a distribution to the data in this study.

XMPOR could not be varied independently because this would have resulted in unrealistic combinations of total porosity and boundary water content. Instead, it was assumed that the proportion of the total pore volume assigned to the micropore region was normally distributed. These proportions were derived from measured water release curves (water content at XMPOR / water content at 0 kPa). It was further assumed that 95% of the values for this proportion fall between the boundaries given in Table 4. The random sampling of values for TPORV and its proportion assigned to the micropore region (see below) resulted in coefficients of variation for XMPOR in the five soil layers of 5.1 - 5.4%.

The total range of possible values for each parameter was divided into sections of equal probability and 350 combinations of TPORV and the fraction of total porosity assigned to XMPOR were sampled using Latin Hypercube Sampling. MACRO simulations were carried out for each of these parameter combinations. Pesticide properties remained constant for this modelling exercise. In an additional exercise, TPORV, XMPOR and pesticide sorption and degradation parameters were varied simultaneously. The distributions of pesticide parameters described in Section 3.2 were used for this purpose.

3.3.2 Results

Figure 7 compares Box-and-Whisker plots of cumulative isoproturon losses measured for the Hodnet lysimeters with plots of simulated losses following variation of total porosity (TPORV) and the boundary water content (XMPOR), alone or in combination with pesticide parameters. Simulated leaching of isoproturon varied to a relatively large extent when the variability in TPORV and XMPOR was taken into account (Figure 7). The range of simulated pesticide losses from the Hodnet soil arising from the variability of TPORV and XMPOR (0.022 mg m^{-2} to 0.573 mg m^{-2}) agreed relatively well with the range of data measured for the seven replicate lysimeters. The coefficient of variation (52%) was somewhat smaller than the observed variability (CV = 61%). The maximum simulated isoproturon loss increased to 0.819 mg m^{-2} when pesticide properties were included in the probabilistic modelling exercise. The coefficient of variation of isoproturon loads (63%) resulting from the variability in soil and pesticide properties was somewhat larger than that attributed to variability in hydraulic properties alone and agreed well to the observed variability.

The results confirm that simulations of pesticide leaching through structured soils are sensitive to changes in TPORV and XMPOR. These parameters are uncertain and have a large influence on model predictions in structured soils and should, therefore, be included in probabilistic modelling for such soils. This is expected to result in a large variability in predicted pesticide leaching.

Soil properties which showed the strongest influence on simulated pesticide losses from the Hodnet soil in sensitivity analyses by Dubus and Brown (2002) were selected for this study. The variability of simulated isoproturon losses arising from the variation of these parameters was similar to the variability in results for the seven replicate Hodnet lysimeters. It should be noted, however, that the range and distribution of model output strongly depends on the assignment of plausible ranges and distributions to each of the input parameters.

4. General discussion

The two soils studied within the current investigations were selected to contrast in their properties and this led to large differences in the results obtained. Movement of water and solute through the coarse-textured Wick soil appears to have been dominated by matrix flow, although a contribution from preferential flow was apparent in some of the soil cores. Here, a simple approach involving the variation of the DT50 and Kd values for isoproturon was sufficient to account for the observed variability in cumulative leaching. The Hodnet soil is more structured and preferential flow had a significant influence on pesticide movement. The variation assigned to selected pesticide properties in this study could not match observed variability in cumulative leaching and it was necessary to incorporate variability in soil properties.

Simplified investigations were undertaken where only the top few most sensitive model inputs were varied. For both soils, such constrained probabilistic approaches were sufficient to match or exceed the variability observed between the seven replicate lysimeters. This seems promising although it should be noted that the variability at the site may not be fully characterised by this relatively small number of replicates.

The results suggest that full probabilistic treatments accounting for all input parameters and possible sources of uncertainty as well as uncertainties inherent in model assumptions may significantly over-estimate variability. Exclusion of part of the uncertainty from the modelling process does not mean that it does not exist, but rather that modelling is likely to be less stable than reality and that more useable results may be obtained through a constrained approach. There are several reasons for the discrepancy between variability in modelling results and that observed in the field. Uncertainty in model input is not only caused by environmental variability (*e.g.* soil properties, climate, crop growth), but also by uncertainties related to experimental, analytical and estimation procedures used to obtain model parameters (*e.g.* determination of degradation parameters; Dubus *et al.*, 2003).

The parameters needing to be varied to match observed behaviour for both soils were correctly identified by the sensitivity analysis undertaken for MACRO (Dubus and Brown, 2002). This gives credence to results from the two studies and highlights the importance of using sensitivity analysis within the design of probabilistic approaches.

Probabilistic modelling which considers the uncertainty in a small number of selected parameters relies on the assumption that the model is capable of describing the situation at hand. The simulation of the leaching of pesticides in soils prone to preferential flow represents a significant challenge to modellers. For these soils, the consideration of uncertainty in the few most sensitive parameters might not be enough to account for the uncertainty in the modelling. This issue needs to be investigated further.

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Table 1: Soil properties

	Wick series[a]				Hodnet series				
	0-10 cm	10-20 cm	20-29 cm	40-50 cm	0-10 cm	10-20 cm	20-29 cm	30-40 cm	40-50 cm
Sand (%)	63.7	65.0	67.5	68.9	38.6	39.7	26.8	35.3	27.6
Silt (%)	22.3	21.9	19.5	23.2	36.5	35.4	44. 7	37.6	43.1
Clay (%)	13.4	13.2	13.09	7.83	24.9	24.9	28.6	27.1	29.3
Organic carbon (%)	1.3	1.3	1.2	0.5	1.9	2.0	1.8	0.8	0.5
Bulk density (g cm^{-3})	1.36	1.28	1.37	1.54	1.25	1.30	1.42	1.57	1.57
pH (H_2O)	6.9	6.9	7.0	7.0	6.7	6.3	6.3	6.1	6.4
Water content at 0 kPa (vol. %)	42.6	41.5	39.5	36.6	46.0	44.9	43.0	37.7	37.5
Water content at -5 kPa (vol. %)	28.3	27.1	28.2	25.8	36.3	38.2	38.5	34.0	32.8
Water content at -1500 kPa (vol. %)	8.9	8.2	8.9	7.6	16.4	17.0	18.3	21.1	19.3

[a] No measurements were carried out for 29-40 cm depth. The top soil horizon extended to 35-cm depth.

Table 2: Coefficients of variation (%) for soil properties measured in the first experimental season (1997/98)

	Wick series[a]				Hodnet series				
	0-10 cm	10-20 cm	20-29 cm	40-50 cm	0-10 cm	10-20 cm	20-29 cm	30-40 cm	40-50 cm
Organic carbon	10.9	8.3	8.9	18.8	9.4	18.0	9.5	18.2	13.2
Bulk density	3.6	4.6	5.1	3.3	4.6	6.0	4.4	6.5	3.4
Water content at 0 kPa	2.4	4.4	8.1	6.8	1.8	1.8	2.0	3.5	3.2
Water content at -5 kPa	4.6	4.2	8.7	7.7	5.4	4.8	2.8	5.4	7.8
Water content at -1500 kPa	1.8	4.0	6.2	15.0	10.1	9.9	8.7	12.7	15.8

[a] No measurements were carried out for 29-40 cm depth. The top soil horizon extended to 35-cm depth.

Table 3: Parameterisation of normal distributions assigned to DT50 values and Kd values for the Wick and Hodnet soil

	Wick DT50 (days)	Wick Kd (ml g^{-1})	Hodnet DT50 (days)	Hodnet Kd (ml g^{-1})
Mean	9.3	1.32	18.0	1.86
Standard deviation	2.6	0.15	5.5	0.12
CV (%)	27.4	11.5	30.8	6.5
Lower boundary (2.5th percentile)	4.3	1.02	7.2	1.62
Upper boundary (97.5th percentile)	14.3	1.61	28.9	2.10

Table 4: Characteristics of the distributions assigned to TPORV (% vol.) and XMPOR (fraction of TPORV) for the Hodnet soil and boundaries of the interval for random sampling

	Depth (cm)	0-10	10-20	20-29	29-39	39-50
TPORV	Mean	46.0	44.9	43.0	37.7	37.5
	Standard deviation	2.4	2.3	2.2	1.9	1.9
	Lower boundary (2.5th percentile)	41.4	40.3	38.7	33.9	33.7
	Upper boundary (97.5th percentile)	50.6	49.4	47.3	41.5	41.2
XMPOR	Mean	0.85	0.91	0.95	0.94	0.93
	Standard deviation	2.0	2.1	2.1	1.8	1.8
	Lower boundary (2.5th percentile)	0.81	0.86	0.90	0.89	0.87
	Upper boundary (97.5th percentile)	0.90	0.95	0.97	0.99	0.98

Figure 1: Box-and-Whisker plots for Kd values and DT50 values of isoproturon in 10 samples from the Wick and Hodnet soil

Figure 2: Concentrations of isoproturon in leachate from the Wick and Hodnet soil lysimeters (seven replicates per soil)

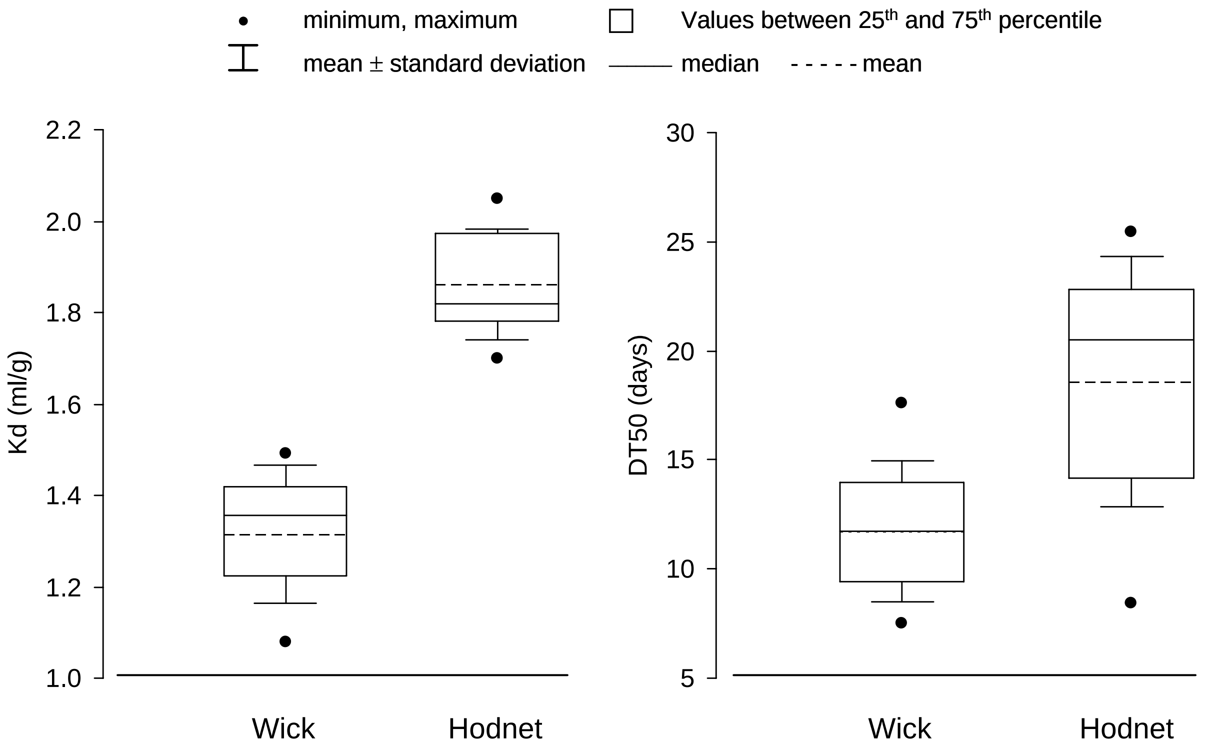
Figure 3: Box-and-Whisker plots for cumulative isoproturon losses from the Wick and Hodnet soil lysimeters (symbols as in Figure 1)

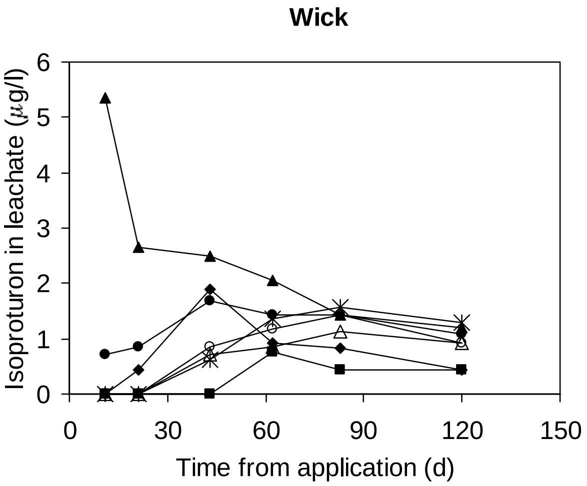
Figure 4: MAROV indices (-) for the fifteen most sensitive input parameters for MACRO for loss via leaching from the Wick and Hodnet soil of a pesticide with Koc = 100 ml g^{-1} and DT50 = 60 days at 8^{o}C. The larger the MAROV index the greater the sensitivity of MACRO to this particular parameter (from Dubus and Brown. 2002).

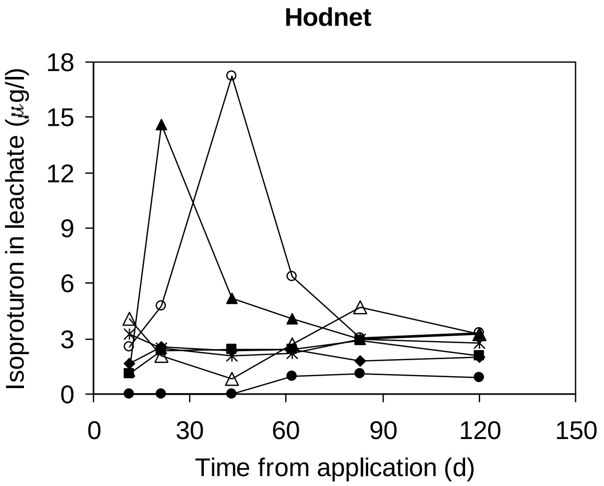
Figure 5: Box-and-Whisker plots for measured isoproturon losses from the Wick lysimeters and for those simulated following variation of pesticide input parameters for MACRO (symbols as in Figure 1; ■= isoproturon load simulated with average parameters)

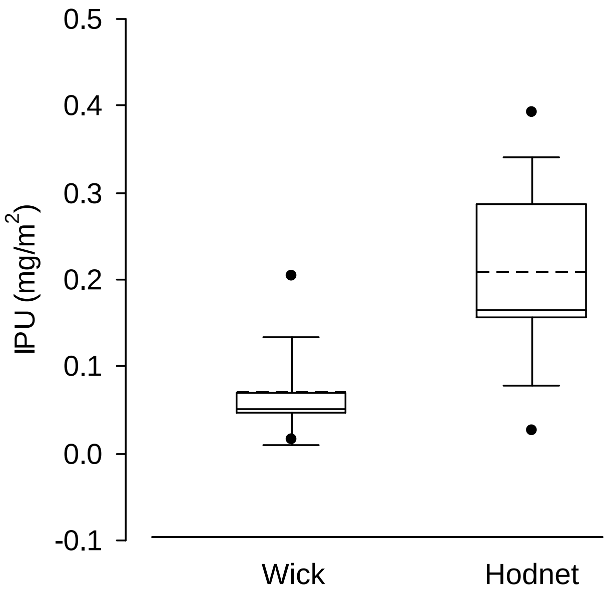
Figure 6: Box-and-Whisker plots for measured isoproturon losses from the Hodnet lysimeters and for those simulated following variation of pesticide input parameters for MACRO (symbols as in Figure 1; ■= isoproturon load simulated with average parameters)

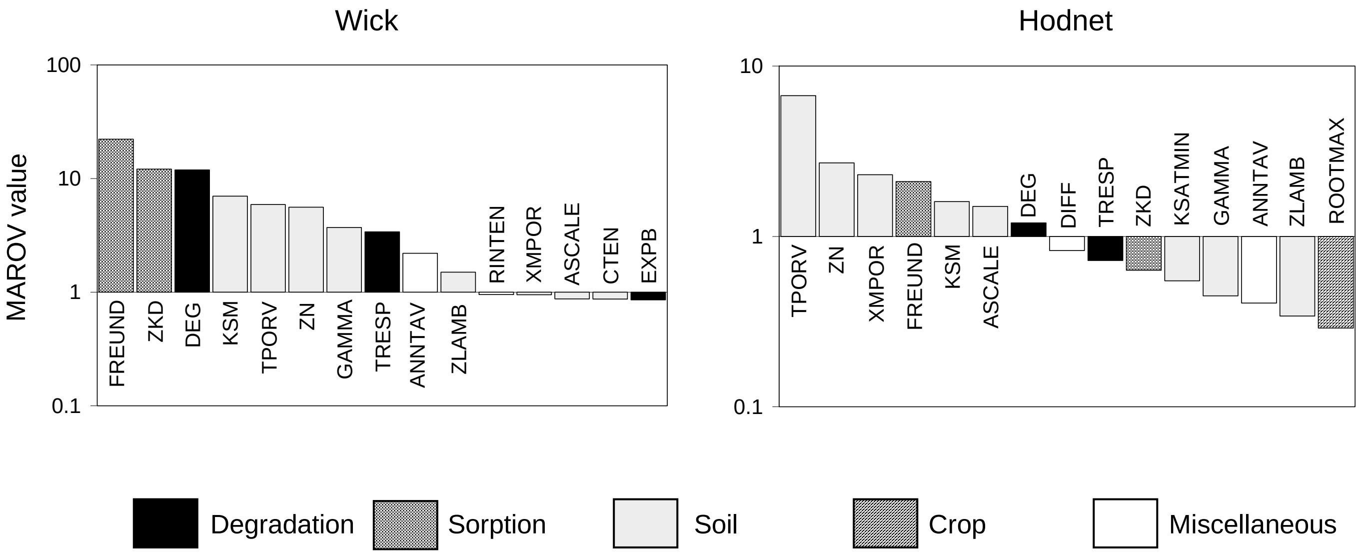
Figure 7: Box-and-Whisker plots for measured isoproturon losses from the Hodnet lysimeters and for those simulated following variation of input parameters for MACRO (symbols as in Figure 1)

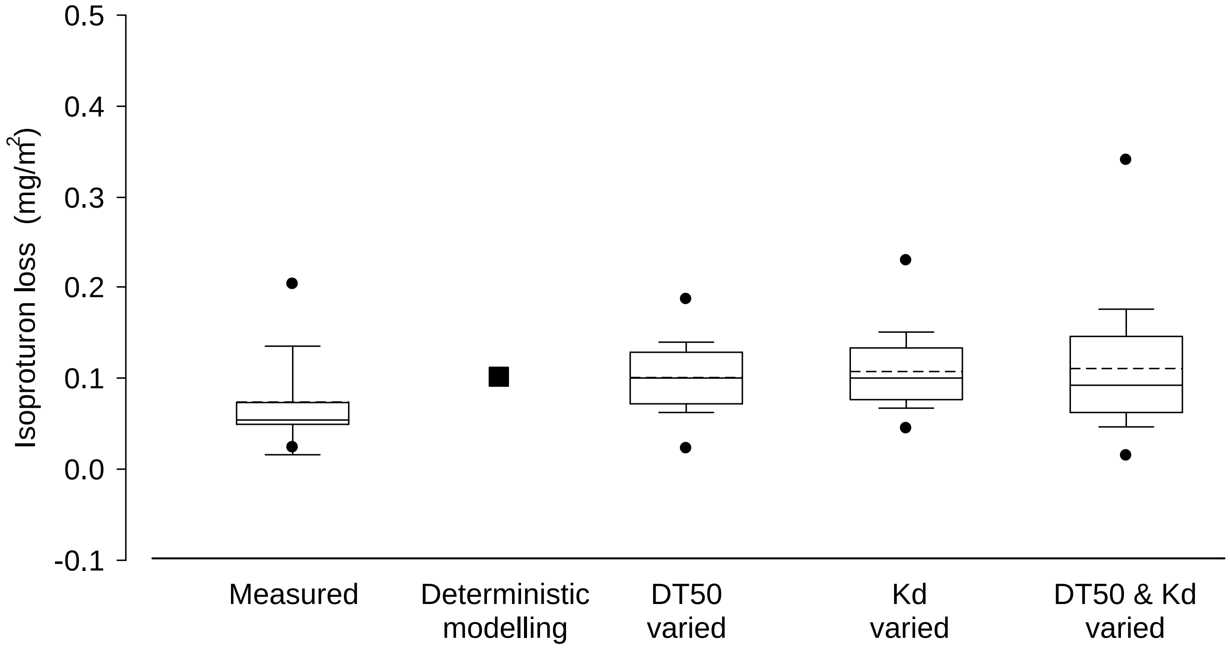

● minimum, maximum
Values between 25th and 75th percentile
mean ± standard deviation
median
- - - - - mean
Kd (ml/g)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
Wick
Hodnet
DT50 (days)
30
25
20
15
10
5
Wick
Hodnet

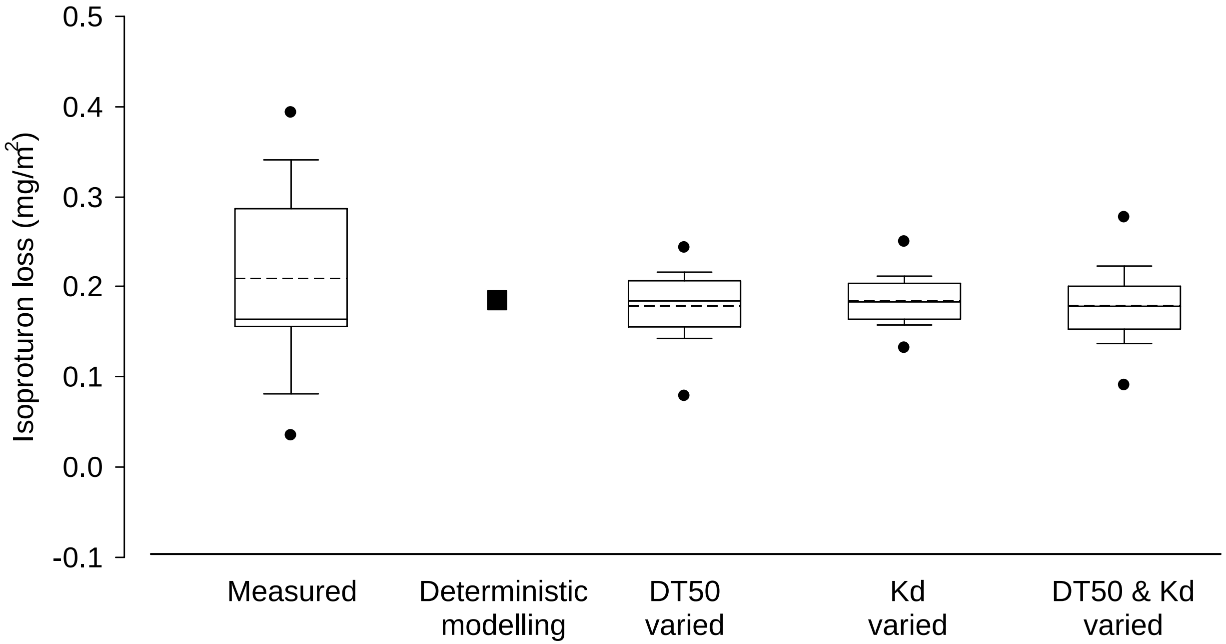

Wick
Isoproturon in leachate (µg/l)
6
5
4
3
2
1
0
0
30
60
90
120
150
Time from application (d)

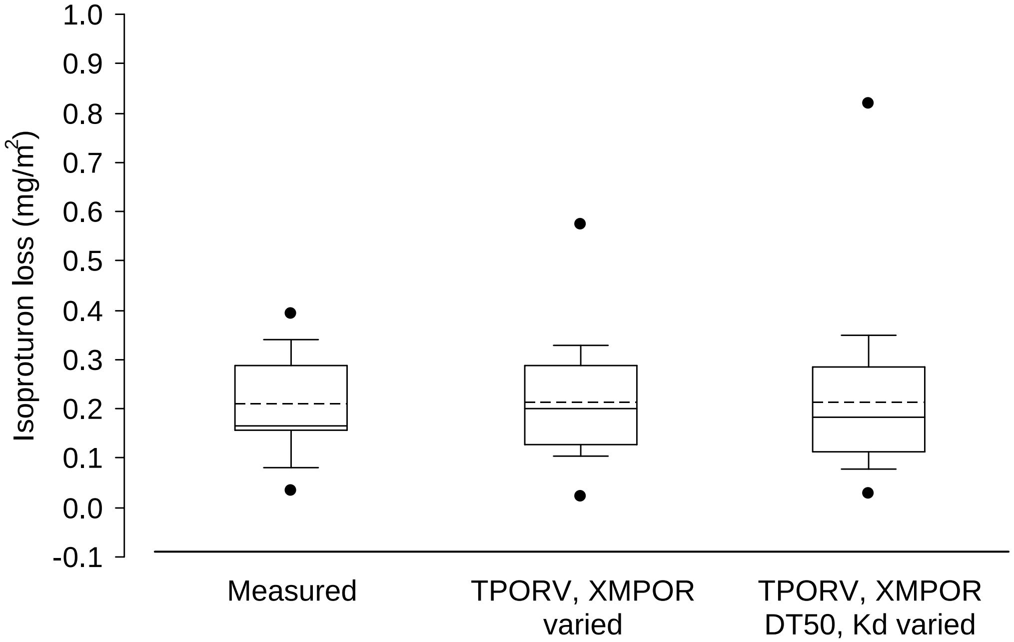

Hodnet
Isoproturon in leachate (µg/l)
18
15
12
9
6
3
0
0
30
60
90
120
150
Time from application (d)


IPU (mg/m^2)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
Wick
Hodnet


Wick
Hodnet
MAROV value
100
10
1
0.1
FREUND
ZKD
DEG
KSM
TPORV
ZN
GAMMA
TRESP
ANNTAV
ZLAMB
RINTEN
XMPOR
ASCALE
CTEN
EXPB
10
1
0.1
TPORV
ZN
XMPOR
FREUND
KSM
ASCALE
DEG
DIFF
TRESP
ZKD
KSATMIN
GAMMA
ANNTAV
ZLAMB
ROOTMAX
Degradation
Sorption
Soil
Crop
Miscellaneous


Isoproturon loss (mg/m^2)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
Measured
Deterministic modelling
DT50 varied
Kd varied
DT50 & Kd varied


Isoproturon loss (mg/m^2)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
Measured
Deterministic modelling
DT50 varied
Kd varied
DT50 & Kd varied


Isoproturon loss (mg/m^2)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
Measured
TPORV, XMPOR varied
TPORV, XMPOR DT50, Kd varied

Evaluation of probabilistic modelling approaches against data on leaching of isoproturon through undisturbed lysimeters

Beulke, Sabine

2004-11-15

Sabine Beulke, Colin D. Brown, Igor G. Dubus, Christopher J. Fryer and Allan Walker, Evaluation of probabilistic modelling approaches against data on leaching of isoproturon through undisturbed lysimeters, Ecological Modelling, Volume 179, Issue 1, 15 November 2004, Pages 131-144