Chapter 8

Assessing Pesticide Leaching at the Regional Scale: Uncertainty and Spatial Variability

The previous chapter presented a stochastic simulation of pesticide leaching potential, with organic matter content and atrazine DT50 as input parameters. The minimum number of Monte Carlo simulations was determined to ensure the robustness of the results. In this chapter, the methodology is applied with six parameters and their influence on the model results is examined by two techniques of sensitivity analysis.

8.1 Outline

A stochastic procedure similar to a second-order Monte Carlo analysis is used to assess pesticide leaching potential at the regional scale. The objective is to determine whether obtaining a spatially distributed output with this approach adds value compared with classical deterministic and stochastic assessments. Input parameters for GeoPEARL model are classified as georeferenced or non-georeferenced given the available information about their spatial distribution. Organic matter content and K_{sat} are classed as 'uncertain' georeferenced parameters. Pesticide half-life (DT50), sorption parameters and dispersion length are classed as spatially variable, non-georeferenced parameters. The methodology is applied to assess atrazine leaching potential in the Dyle river catchment (Belgium). The results demonstrate that the inclusion of the spatial variability of non-georeferenced parameters has

a significant effect on the amount of pesticide leaching. The 80^{th} percentile of pesticide leaching indicates higher leaching concentrations. Using an a posteriori sensitivity analysis based on a regression with cubic smoothing splines, atrazine DT50 is found to be the most important parameter. However, the splines model only accounts for about 60% of the total variance, suggesting the presence of interactions between parameters. In another sensitivity analysis, divergence and distances measures confirm the ranking of the parameters based on their influence on the modelling results. The consequences for pesticide leaching assessment are discussed in relation to the current procedures for pesticide registration and groundwater management[1].

8.2 Introduction

In Europe, the Water Framework Directive (EU, 2000) and its offshot the Groundwater Directive (EC, 2003) provide the member states with the major objectives and guidelines for groundwater management. The general objective is to insure adequate supply of good quality water, while preserving the hydrological, biological and chemical functions of ecosystems. In this respect, pesticide leaching to groundwater is an important issue because the regulatory limit of 0.1 μg/L is regularly exceeded across Europe (e.g. Tappe et al., 2002; IFEN, 2004; DGRNE, 2005).

Modelling pesticide leaching from the soil root zone allows the assessment of the risk of groundwater contamination by surface applied pesticides. For example, the EU registration directive EU/91/414 European Commission (1991) stipulates that modelled groundwater concentrations of pesticides may not exceed 0.1 μg/L for a single product. Leaching models are used in this context to assess groundwater concentrations. Working groups of the European commission such as FOCUS have standardised the leaching modelling procedures following a tiered approach (FOCUS, 2000, 2007). At the higher tiers, spatially distributed leaching models such as GeoPEARL (Tiktak et al., 2002, 2003), which couples a point scale leaching model (in this case PEARL) with spatial data derived from standard Geographical Information Systems can be used. Tiktak et al. (2004) demonstrated that

[1]This chapter is based on an article by Leterme B., Vanclooster M., van der Linden A.M.A., Tiktak A. and Rounsevell M.D.A.; in preparation.

a spatially distributed approach could be adopted at the national and pan-European level.

Two main issues arise from the application of pesticide leaching models at the regional scale. The first is the recognition that model predictions are inherently uncertain given the numerous sources of error in the modelling procedure (Dubus et al., 2003b). Even though deterministic models may be used to simulate pesticide leaching (given an appropriate upscaling or aggregation procedure), the need to quantify this uncertainty has lead to the development of probabilistic approaches to improve the value of risk assessment procedures as a decision-support tool (EUFRAM, 2005; Brown and Heuvelink, 2005).

The second issue results from the use of leaching models in spatially-distributed applications. Spatial predictions are sometimes required for groundwater vulnerability mapping, or to calculate over a certain area leaching percentiles, as these are often considered to be decision variables in operational risk assessment (Boesten et al., 1999; FOCUS, 2000; van der Linden et al., 2004). Therefore, the spatial variability of model inputs and outputs becomes critical when assessing pesticide leaching over a large area.

The combination of uncertainty and variability in risk assessment intuitively refers to stochastic analysis (EUFRAM, 2005). In this context, the variability of a quantity (also named stochastic uncertainty, or aleatory uncertainty) is defined as the inherent heterogeneity of this quantity over time, space, or some population of individuals (McKone, 1996; Counil et al., 2005; Cullen and Frey, 1999). Additional effort may yield a better estimate of the magnitude of variability, but it will not tend to reduce it (Ferson and Ginzburg, 1996). On the other hand, uncertainty (also called epistemic uncertainty) is caused by our incomplete knowledge of the system (Apel et al., 2004).

Monte Carlo (MC) analysis is probably the most commonly used stochastic technique for propagating uncertainty and variability in a modelled system. Second-order MC analysis is widely used in risk assessments, and most of the applications are found in eco-toxicological assessments (e.g. Wu and Tsang, 2004; Counil et al., 2005; Delignette-Muller et al., 2006). In these cases, uncertainty usually concerns the distribution of input parameters in the exposure model and variability is applied to the individuals of a popu-

lation (Counil et al., 2005).

McKone (1996) applied a second-order MC analysis to the modelling of contaminant fate in soils and compared the results of two different models. Soil and pesticide properties were classified as 'variable' and 'uncertain', respectively. In the present study, however, soil properties are considered to be 'uncertain' rather than 'variable' because the MC simulation is undertaken with a spatially distributed model. On the other hand, pesticide properties have been shown to have a certain spatial variability at different scales (Walker and Brown, 1983; Smith et al., 1987; Novak et al., 1997; Coquet, 2002; Charnay et al., 2005).

Studies examining the effect of spatial variability on pesticide leaching by stochastic simulation have suggested that spatial variability can significantly affect the leached fractions of pesticides (Jury and Gruber, 1989; van der Zee and Boesten, 1991). Earlier work focused mainly on the variability of soil properties within soil units, while pesticide properties were assumed constant (Carsel et al., 1988; Petach et al., 1991; Foussereau et al., 1993; Zhang et al., 1993).

MC simulation was also applied to non-georeferenced parameters. Zacharias et al. (1999) developed a stochastic framework at the field scale in which multiple realizations of a hypothetical field were undertaken with the same statistical distribution of soil properties. The MC simulation, however, considered all soil and pesticide parameters as non-georeferenced (i.e. the outputs can only be examined at the field-scale). Lindahl et al. (2005) combined georeferenced field management parameters (such as pesticide application dose) with a range of non-georeferenced parameters to study the contamination of surface water. They found that simulated values of pesticide loads reached concentrations similar to measurements as a result of summer outflows captured in the stochastic approach.

The present study applies an approach similar to second-order MC analysis to assess pesticide leaching at the regional scale. Six parameters are included in the uncertainty analysis, which differs from classical second-order MC simulations in using spatially distributed simulations. The central question is to determine the added value of this approach over classical deterministic and stochastic assessments. A secondary objective is to assess the relative sensitivity of the input parameters, in order to understand their

influence on the results uncertainty and spatial variability. Finally, the effect of adding spatial variability in pesticide properties is discussed in relation to the traditional procedures used for pesticide registration.

8.3 Materials and methods

The reader is referred to chapter 3 for a description of the study area.

8.3.1 GeoPEARL: model description and parameterisation

GeoPEARL couples the PEARL model (Tiktak et al., 2000) with spatial data derived from standard Geographical Information Systems. PEARL is a one-dimensional, dynamic, multi-layered model of the fate of pesticides and relevant transformation products in the soil-plant system. Soil water flow is described with Richards' equation and pesticide transport is simulated with the convection-dispersion equation.

Annual applications of atrazine (1 kg.ha^{-1}) on silage maize were simulated on all arable land, from 1980 to 2002. After six initialisation years, simulation output was taken as the annual average concentrations of atrazine at 1 m depth.

The parameterisation of soil properties (OM content and texture) was interpolated from soil profiles (Aardewerk database; Van Orshoven and Vandenbroucke, 1993) and a digital soil map (scale 1:25,000). Pedotransfer functions (PTFs) were used for the parameters not available in Aardewerk. Topsoil OM content was adjusted with a correction factor (see van Wesemael et al., 2004) to account for OM change since the 1950s (when the data were collected). An empirical relationship was fitted to the Aardewerk data to determine OM content with depth, while the 1:25,000 soil map was used to define average profiles with depth ('class matching' procedure; Van Orshoven, 1993).

Finally, due to the relatively small variability in OM and texture over the study area, it was possible to reduce the number of plots from 26606 to what will be defined as 100 'unique combinations', using a k-means clus-

ter analysis. This substantially reduced the run-time of the Monte Carlo analysis, without affecting the results.

More details on the parameterisation of soil properties are given in chapter 7 (section 7.3.1 and Figure 7.1).

8.3.2 Uncertainty analysis

The uncertainty analysis was based on a Monte Carlo (MC) approach, modified to account for the spatial variability of non-georeferenced parameters.

A previous MC analysis with only two parameters in the uncertainty analysis showed that the results are robust if 25 $\times P$ simulations are undertaken where P is the number of parameters (cf. chapter 7). Therefore, it was decided to include 6 parameters in the present MC analysis, in order to keep the computation time reasonable. The choice of the parameters followed the conclusions of Dubus et al. (2003a) in a previous sensitivity analysis performed on PESTLA (a predecessor of PEARL). For their 'Pesticide 1' (of which the properties were the closest to atrazine among the two compounds tested, with a K_{OM} of 20 L.kg^{-1} and a DT50 of 7.8 days), they found the Freundlich exponent, K_{OM} and DT50 to be the most sensitive pesticide parameters, and OM content and bulk density the most sensitive soil parameters. However, in GeoPEARL soil bulk density is calculated during model runs as a slave parameter of OM content (using the PTF of Bollen et al., 1995), and thus it was not possible to include this parameter in the uncertainty analysis. Other sensitive parameters were saturated water content, the parameter n in the van Genuchten equation of water retention, and K_{sat}. K_{sat} was selected for the uncertainty analysis because the low R^2 of its PTF gave low confidence in the values used in the deterministic simulation. Thus, the analysis presented here focused, *a priori* and limiting the selection to six parameters, on the uncertainty of OM content and K_{sat} in topsoil (georeferenced parameters); and DT50, dispersion length, Freundlich exponent and K_{OM} (non-georeferenced parameters).

8.3.3 Definition of the PDFs

A summary of the parameterisation of the inputs included in the uncertainty analysis is provided in Table 8.1. For all the parameters (except OM content), statistical distributions were fitted to experimental data. This method required the subsequent use of truncation (except for the uniform distribution) to prevent the sampling of unrealistic values at the extremes of the distributions. Truncation would not be necessary if sampling was made directly from experimental cumulative density functions. However, the main advantage of fitting statistical distributions is to avoid sampling artefacts that could result from discontinuities in the experimental data sets. Moreover, as Latin Hypercube Sampling is used to draw the parameter sets (cf. section 8.3.4), this potential problem could be further exacerbated. Another advantage is that the parameters of statistical distributions allow easier comparison or transfer to other case studies for which experimental data are not available.

OM content and K_{sat} are georeferenced parameters, because the interpolation using ordinary kriging led to a spatially distributed characterisation of OM content, which was further used to derive K_{sat} with a PTF. Following the cluster analysis, 100 values of OM content were assigned to the corresponding unique combinations. For each unique combination, the uncertainty distributions around these values were obtained using block kriging. In other words, the ordinary kriging (together with other variables) allowed the clusters delineation, while block kriging performed on each unique combination (or cluster) was used to estimate the value (and its variance) over this unique combination.

The uncertainty around the K_{sat} value was assessed from the standard error of the regression used by the PTF of Wösten et al. (2001). This lead to values of K_{sat} ranging approximately from 0.01 to 28.9 m.day^{-1}, which was regarded as too large to be realistic. Furthemore, considering that the R^2 of the K_{sat} PTF was poor (around 0.3), it was decided to truncate the normal distribution so that the possible values of K_{sat} became consistent with measurements made in the study area (Mallants, 1996; Javaux, 2004) and similar to the values found in the database of Wösten et al. (2001) for these soil types. Truncated at the 10$^{\text{th}}$ and 90$^{\text{th}}$ percentiles, K_{sat} values ranged from 0.33 to 1.58 m.day^{-1} (Table 8.1).

Table 8.1: Description of the parameters included in the uncertainty analysis.

Parameter	Distribution	Mean	Std. Dev.	Truncation	Range	Source
Georeferenced						
OM content (kg.kg^{-1})	Normal	n.a.†	n.a.	1-99%	-	Block-kriging
K_{sat} (m.day^{-1})	Normal	n.a.	2.25	10-90%	-	$\varepsilon_{K_{sat}}$ (Wösten et al., 2001)
Non-georeferenced						
DT50 (days)	Lognormal	8.97	0.93 (ln(days))	5-95%	1.94-41.60	Pussemier et al. (1997)
Dispersion length (cm)	Lognormal	5	0.87 (ln(cm))	5-95%	1.20-20.92	Vanderborght (pers. comm.)
Freundlich exp. (-)	Uniform	0.9	n.a.	-	0.8-1.0	Boesten (pers. comm.)
K_{OM} (L.kg^{-1})	Lognormal	49	0.70 (ln(L.kg^{-1}))	5-95%	15.51-154.97	Dorgelo (2006)

† Not applicable.

DT50, dispersion length, Freundlich exponent and K_{OM} are non-georeferenced parameters because the initial parameterisation of GeoPEARL assumed constant values. However, field and laboratory measurements have shown that these parameters can exhibit significant variability at different scales. For example, pesticide DT50 values show a large variability at the field or catchment scale (Walker and Brown, 1983; Smith et al., 1987; Charnay et al., 2005). Sorption coefficient (Smith et al., 1987; Novak et al., 1997; Coquet, 2002) and dispersivity length (Vanderborght et al., 2001) have also been shown to display considerable variability.

Data from a field study of Pussemier et al. (1997) were used to assess the distribution of DT50 values. These data consist of 33 laboratory measurements of the atrazine degradation rate in loam or sandy loam soils; most located in the Dyle catchment. DT50 of less than 10 days was found in more than 60% of the soil samples. Figure 7.4 (chapter 7) shows these data and the lognormal fit to them, together with the data of the Dutch registration dossier ($n = 27$; Dorgelo, 2006). The data of Pussemier et al. (1997) were chosen because Coquet et al. (2005) argued that whenever available, site-specific data should be preferred over databases to limit bias in pesticide leaching risk assessments at the catchment scale. The rapid dissipation observed by Pussemier et al. (1997) was linked to the adaptation of microbial communities resulting from repeated pretreatments with atrazine (intensive maize cropping). Such observations are excluded from the Dutch registration dossier if the effect is known to occur.

In the case of K_{OM}, however, site-specific data were not available. The distribution of K_{OM} values was based therefore on the lognormal fit to the data of the Dutch registration dossier ($n = 50$; Dorgelo, 2006). The input distributions of the dispersivity length and Freundlich exponent were based on parameters provided by Vanderborght (pooling column and field-scale data together; pers. comm.) and by Boesten (pers. comm.), respectively. Truncation levels for these parameters were set arbitrarily (cf. Table 8.1).

No correlation was simulated between the input parameters. In a deterministic configuration K_{sat} is correlated to OM content as a result of the use of a PTF for K_{sat} ($r = 0.77$). However, these parameters were not correlated in the MC simulations presented here due to a lack of data to assess their correlation and also because of the low R^2 of the PTF of Wösten et al. (2001). Dispersion length has been linked with effective flow rate

(Vanderborght et al., 2001), but not to hydraulic saturated conductivity.

8.3.4 Monte Carlo simulations

Sets of parameters were generated from the input distribution described in Table 8.1 with a Latin Hypercube Sampling (LHS) procedure. LHS uses a probabilistic sampling scheme that provides better coverage of the input distribution and has been shown to be more efficient than the random or stratified sampling in MC analysis Helton and Davis (2003).

For each of the 100 unique combinations, the input distributions of the georeferenced parameters were sampled 150 times (previous simulations with only two parameters showed that 25 $\times$ the number of parameters in the uncertainty analysis was sufficient to obtain robust results). Furthermore, for each of the 150 simulations, 100 values from the input distributions of the non-georeferenced parameters were drawn with LHS and randomly allocated to the 100 unique combinations. Thus a major difference between the georeferenced and non-georeferenced parameters lies in the way their PDFs were sampled in the MC analysis. A distinction was thereby made between variability and uncertainty of non-georeferenced parameters and uncertainty of georeferenced parameters, similar to the concepts of second-order MC analysis. The main difference with the latter technique lies in the spatially distributed nature of the simulations, which adds further constraints to the present sampling procedure.

A Matlab™ (version 7.0) routine was created for the generation of LHS input parameters and these replaced the default values in the GeoPEARL input files. A single GeoPEARL simulation with the MC procedure corresponds to 100 PEARL runs over the whole study area. The total number of model runs is therefore equal to $150 \times 100 = 15,000$ for the uncertainty analysis. Model runs were processed on a grid of 256 Central Processing Units (CPUs) using batch files.

8.3.5 Analysis of model outputs

The 80^{th} percentile of the annual average concentrations at 1 m depth (for a total of 17 simulation years) was taken as an indicator of atrazine leaching

potential. For a given location in the catchment, this indicator corresponds to the 80^{th} percentile of leaching due to variations in weather conditions (FOCUS, 2000) and could be mapped for any of the 150 MC simulations. Cumulative density functions of the minimum, median and maximum values of this indicator were drawn, reflecting the variability of leaching at the catchment scale. An indicator of leaching risk at the catchment scale was chosen as the 80^{th} percentile in space (Vanclooster et al., 2003).

Another indicator that is potentially relevant for decision makers is the area of the catchment where the regulatory limit of 0.1 μg/L is exceeded. This indicator is an aggregation of the pesticide leaching risk in the study area, and could be used for example to compare different catchments of similar sizes.

The results of the stochastic simulations were compared with a deterministic GeoPEARL simulation, which used the central values of the MC input distributions (i.e. non-georeferenced parameters are given a constant value across the study area).

The uncertainty in pesticide leaching risk has been characterised by the variance of its distribution, resulting from the 150 MC simulations. However, it may be interesting to know the sensitivity of the model response to the variation of the different inputs.

Therefore, sensitivity and possible interaction between the input parameters was tested using a first-order sensitivity index (also called top marginal variance or correlation ratio; e.g. Brus and Jansen, 2004). In this regression analysis, the output variable was approximated by the sum of cubic smoothing splines (Hastie and Tibshirani, 1991). This type of regression has the advantage of being able to replicate non-linearities in model response. The quality of this approximation was measured by adjusted R^2, i.e. the percentage of variance accounted for by the full spline model. Any difference between the adjusted R^2 and 100% is due either to interactions between the inputs that are not taken into account by additive models, or to a lack of flexibility in fitting the model response. The top marginal variance of an input is the variance reduction that would occur in the spline model, in the event of perfect new information about this input (i.e. no more uncertainty). The sensitivity analysis was performed with USAGE 2.0, a collection of GenStat algorithms for sensitivity and uncertainty analyses (Goedhart and Thissen,

2002; GenStat Committee, 2006). Again, minimum, mean and maximum values were reported for the different unique combinations of the study area.

In our case, the adjusted R^2 was found to have quite low values for most of the unique combinations. It was decided therefore to perform a more detailed sensitivity analysis, in order to have greater confidence in the conclusions drawn from the first-order sensitivity indices. For each parameter in turn, the complete MC analysis was repeated, but with this parameter kept constant (equal to the first moment of the input PDF). This approach is valid because no correlation was assumed between the parameters in the initial MC simulations. Any parameter may therefore be considered constant while the others are sampled through their input distributions for the sensitivity analysis.

For each of the 100 unique combinations, this resulted in six output distributions of the 80^{th} percentile of the annual average concentrations at 1 m depth. A PDF was fitted to these distributions using a Gaussian kernel estimator. The six distributions were then compared to the 'reference' distribution (i.e. the MC simulation with all six parameters uncertain/variable) by computing two measures of divergence/distance between the distributions. For probability distributions P and Q of a continuous variable, the Kullback-Leibler (KL; Kullback and Leibler, 1951) divergence of P from Q is defined as:

$$D_{KL}(P|Q) = \int_{-\infty}^{+\infty} p(x) \log \frac{p(x)}{q(x)} \, dx \tag{8.1}$$

where p and q denote the densities of P and Q. The KL divergence is not a measure of *distance* strictly speaking, because it is not symmetric ($D_{KL}(P|Q) \neq D_{KL}(Q|P)$).

The variational distance is defined as:

$$V(P|Q) = \int_{-\infty}^{+\infty} |p(x) - q(x)| \, dx \tag{8.2}$$

These two quantities, calculated for all 100 unique combinations, allowed the parameters to be ranked by increasing sensitivity with respect to the reference MC simulation. In other words, parameters that are highly sensitive

in the reference MC simulations should have high divergence/distance measures when they are kept constant in the MC analysis. This ranking was eventually used to either confirm or reject the conclusions from the spline regression analysis.

8.4 Results

8.4.1 Stochastic vs. deterministic simulations

Figure 8.1(a) presents a map of the results of the deterministic simulation, using central values of the input distributions for all parameters later included in the uncertainty analysis. Simulated values of the 80^{th} percentile of leaching due to weather conditions do not reach detectable concentrations. However, atrazine leaching is not uniform in the catchment, as for instance certain areas of higher leaching are visible (dark pixels in Figure 8.1(a)).

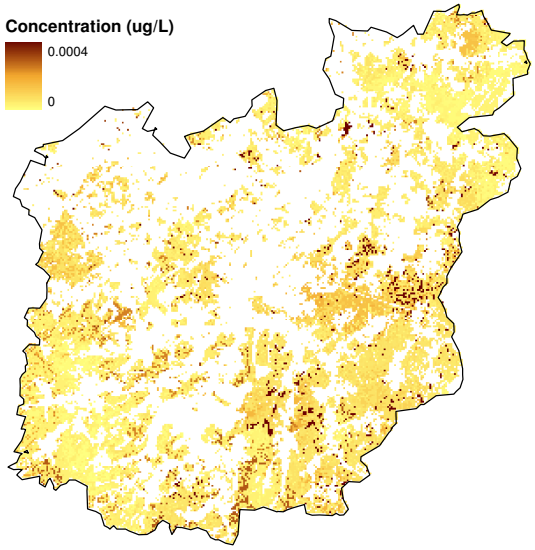
Figure 8.1(b) shows the spatial pattern of leaching in the MC analysis, by mapping (for each of the 100 unique combinations) the median simulated value of the 80^{th} percentile of annual average concentrations at 1 m depth. The location of higher concentration areas is similar between the stochastic and deterministic simulations, although the stochastic simulations appear to generate larger absolute values of leaching.

Figure 8.2 gives a scatter plot of the median value of the stochastic simulations vs. the deterministic run. The median of atrazine leaching in the MC analysis is not systematically higher than in the deterministic simulation. However, a majority of the 100 unique combinations are above the [1:1] line in Figure 8.2 and the output range of values has increased.

8.4.2 Leaching percentiles at the regional scale

Table 8.2 presents the main results of the MC analysis. Leaching in the deterministic simulation is negligible (80^{th} percentile in space equal to 3.10^{-5}) and the threshold of 0.1 μg/L is nowhere exceeded. For the stochastic simulations, the 80^{th} percentile in space has a median value of 0.1277 μg/L, i.e.

(a)



(b)

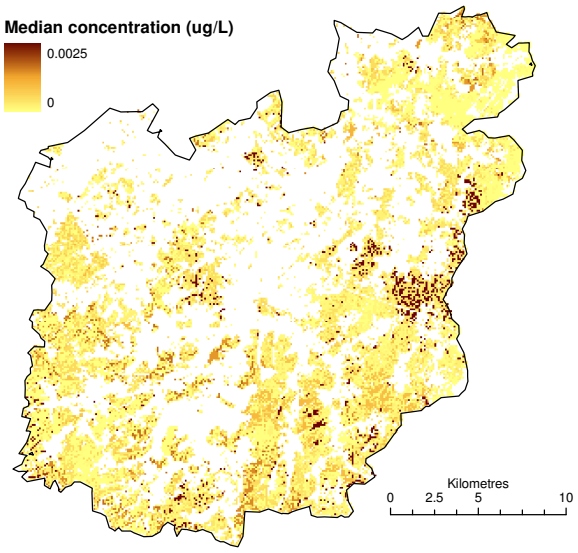


Figure 8.1: (a) 80^{th} percentile of the annual average concentrations of atrazine (μg/L) at 1 m depth for the deterministic GeoPEARL assessment. (b) Median simulated value of the 80^{th} percentile of the annual average concentrations of atrazine (μg/L) at 1 m depth, on a total of 150 MC simulations.

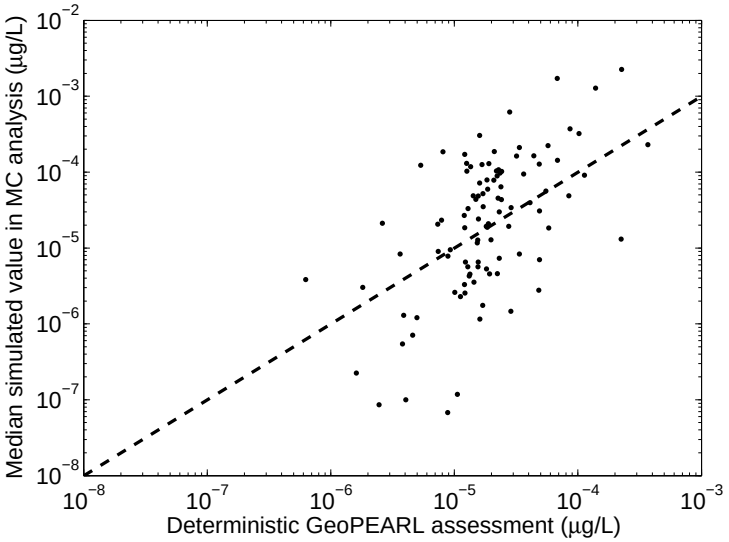


Figure 8.2: Scatter plot of the 80$^{\text{th}}$ percentile of the annual average concentrations of atrazine (μg/L) at 1 m depth: median simulated value in the MC simulations vs. deterministic GeoPEARL assessment.

above the regulatory limit of 0.1 μg/L. Another way of depicting the variability in leaching at the catchment scale is shown in Figure 8.3. Starting from the 70$^{\text{th}}$ percentile for clarity, the lower, median and upper CDFs of the 150 MC simulations illustrate both the uncertainty and the spatial variability of the risk assessment. It should be noted that the variable presented in Figure 8.3 is different from the variable shown in Figures 8.1(b) and 8.2. Figure 8.1(b) displays, for each unique combination, the median output of 150 MC simulations. The results presented in Figure 8.3 (and Table 8.2) look at the minimum, median or maximum value (out of 150 MC simulations) of the 80$^{\text{th}}$ percentile in space. Higher leaching areas are located in different parts of the catchment from one simulation to another, but the 80$^{\text{th}}$ percentile in space remains somewhat higher than the median value for a given unique combination. This explains why the values in Figure 8.3 and Table 8.2 are higher than in Figures 8.1(b) and 8.2.

The part of the study area with atrazine leaching above 0.1 μg/L is also presented in Table 8.2. This indicator is in fact another way of interpreting Figure 8.3, but in the context of groundwater protection management it bet-

ter captures the extent of potential leaching above the regulatory threshold. The indicator could also be used to compare different catchments or regions. Here, 20.9% of the arable part of the Dyle catchment has a potential atrazine leaching concentration above 0.1 μg/L at 1 m depth.

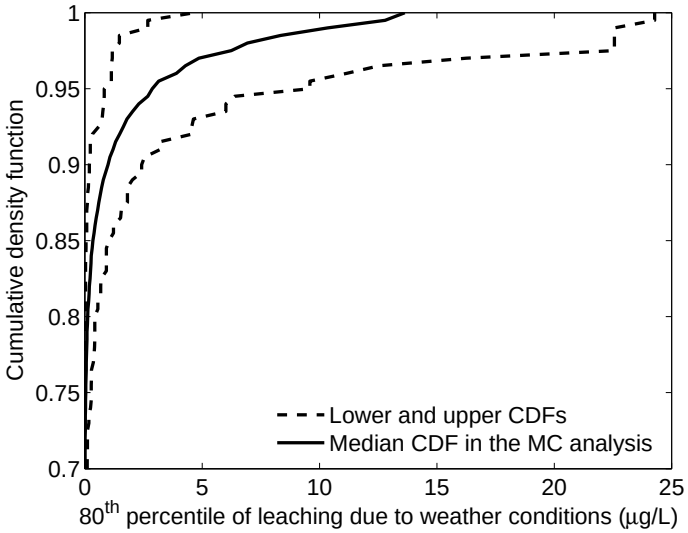


Figure 8.3: Lower, median and upper cumulative density functions of the results of the Monte Carlo simulations. Note that the y-axis starts at the 70^{th} percentile.

8.4.3 First-order sensitivity index

The relative contribution of the different parameters to the output variance was analysed in order to understand the large increase in simulated leaching variability that appeared in the stochastic simulations. Table 8.3 presents the variance decomposition obtained by fitting spline regression models to the MC results.

The validity of this regression-based sensitivity analysis appears to be quite low, as shown by the poor fit of the full spline model (mean adjusted $R^2 = 59\%$ with 5 effective degrees of freedom (*edf*); see Table 8.3). We initially tested the model with 2 effective degrees of freedom, but the mean adjusted R^2 was equal to just 53%. This could indicate either interaction

Table 8.2: Results of the deterministic and Monte Carlo simulations.

	Deterministic	Stochastic	
80^{th} percentile in space (μg/L)	3.10^{-5}	Min.	0.0267
		Median	0.1277
		Max.	0.4300
Part of the study area with > 0.1 μg/L (%)	0	Min.	12.7
		Median	20.9
		Max.	30.9

Table 8.3: Minimum, mean, and maximum (among 100 unique combinations) percentage of variance accounted for by the spline models ($edf = 5$) for the 80^{th} percentile of leaching due to weather conditions.

	Min.	Mean	Max.
Adjusted R^2	34	59	86
OM content	0	1	27
K_{sat}	0	2	15
DT50	22	51	83
Dispersion length	0	2	15
Freudlich exponent	0	2	14
K_{OM}	0	6	27

effects between the input parameters, or a lack of flexibility of the spline model. However, with 5 *edf*, adjusted R^2 was superior to 80% for six unique combinations only. This suggests the presence of interactions between the parameters, which significantly affects pesticide leaching. However, the results of the regression-based analysis confirmed the importance of DT50 in the MC analysis (Table 8.3). K_{OM} and OM content are suggested to have a significant part in the output variance, but this interpretation remains uncertain due to the low adjusted R^2.

8.4.4 Sensitivity analysis

An *a posteriori* sensitivity analysis was necessary to assess the validity of the information gained by the spline regressions. Table 8.4 presents the results of the differences generated by keeping the parameters constant in the MC analysis, one at a time. The Kullback-Leibler divergence and variational distance agree in the parameter rankings, which may be represented as follows (increasing sensitivity): K_{sat} < OM content << dispersion length < Freundlich exponent < K_{OM} << DT50.

Table 8.4: Minimum, median, and maximum (among the 100 unique combinations) of the Kullback-Leibler divergence and the variational distance between the results of the sensitivity analysis and the reference MC simulation.

	Kullback-Leibler divergence			Variational distance		
	Min.	Median	Max.	Min.	Median	Max.
OM content	<0.001	<0.001	0.014	0.002	0.008	0.026
K_{sat}	<0.001	<0.001	0.005	<0.001	<0.001	0.007
DT50	0.021	0.060	0.164	0.085	0.164	0.336
Dispersion length	<0.001	0.004	0.023	0.008	0.025	0.050
Freudlich exponent	0.002	0.016	0.094	0.012	0.039	0.077
K_{OM}	0.002	0.023	0.143	0.019	0.059	0.122

These results are consistent with, but also more detailed than, the parameter rankings obtained from the spline regression analysis. Furthemore, this concordance strongly supports the presence of interactions between the parameters, as suggested by the low adjusted R^2 of the spline regressions. The KL divergence and variational distance were also computed on all 150 MC simulations (instead of all 100 unique combinations), but the results (not shown) led to identical conclusions.

8.5 Discussion and conclusions

Six parameters were included in the present MC analysis and no correlation was assumed between them. The MC simulations showed that indicators such as the 80^{th} percentile of leaching in space were significantly affected by the uncertainty and spatial variability of soil and pesticide parameters. Two types of sensitivity analyses showed that the results were much more sensitive to (non-georeferenced) pesticide parameters than to (georeferenced) soil parameters. This does not necessarily reduce the value of spatially distributed simulations. In fact, the MC analysis was characterised by a lower variance in soil properties compared to pesticide properties, illustrated by, for example, the coefficients of variation of OM content (0.04 on average) and DT50 (1.17) distributions. Moreover, soil properties in the study area are relatively homogeneous (cf. chapter 3), with the exception of OM content for which spatial variability is observed (see Figure 7.2). Thus the conclusions about the relative importance of non-georeferenced (pesticide) and georeferenced (soil) parameters may vary greatly at a different scale or in other study areas with a greater soil variability.

The spatial pattern of the deterministic simulation reflected the distribution of topsoil OM content in the Dyle catchment (Figure 7.2; chapter 7). The spatial pattern of the median of the stochastic simulations was similar, even though OM content was found to be one of the least important parameters in the sensitivity analyses. This can probably be explained by interactions between OM content and pesticide parameters that were not taken into account in the spline regression models.

Among the pesticide properties, the variability of DT50 was predominant in explaining the results. Rapid transformation (low DT50) of atrazine, as observed in the data set of Pussemier et al. (1997), is certainly a key factor that accounts for the influence of this parameter. Values sampled in the lower part of the lognormal distribution produce very fast degradation, and the quantity of atrazine in solid and liquid phases is too low to generate significant leaching.

The importance of pesticide over soil parameters may be explained by the relatively small variability of soil properties in the Dyle catchment (restricted to arable land use). At a larger scale (national or European), the relative

importance of non-georeferenced parameters may be expected to decrease. It should also be noted that the conclusions derived from the uncertainty analysis only pertain to one substance—atrazine. For other compounds, the results could be very different. Furthermore, the approach is essentially a parameter uncertainty analysis (although uncertainty due to interpolation is also addressed for OM content). Model conceptual errors, such as the absence of preferential flow, have not been taken into account. This reflects the difficulty in separating the different sources of error in dynamic non-linear cases (Beven, 2005).

Leterme et al. (2006b, cf. chapter 7) performed a similar analysis with only two uncertain/variable parameters (OM content and DT50). Adding four new parameters increased extreme leaching concentrations by an order of magnitude, although at some point one would expect stabilisation when less sensitive parameters are introduced. This suggests that the variability of soil and pesticide properties could lead to unexpectedly high leaching events in extreme cases. However, no correlation between parameters was assumed in the absence of data supporting this, although certain sets of parameters producing extreme leaching events may be judged unrealistic (e.g. the influence of OM content on soil structure and K_{sat}).

Truncation thresholds on the input PDFs were set arbitrarily to avoid the generation of unrealistic sample values. However, this subjective choice can have important consequences for the results, as shown, for example, by Beulke et al. (2006). This was not investigated in the present chapter, but the influence of the PDF truncation level for DT50 was illustrated in chapter 7 (Leterme et al., 2006b).

The results showed that the inclusion of spatial variability in (pesticide) parameters in stochastic risk assessment has a significant impact on the amount of leaching, when compared to a deterministic simulation. Certain parameter sets sampled in the MC analysis created unfavourable conditions for atrazine sorption and degradation. These conditions are assumed to occur in the field mainly as a result of spatial variability of pesticide properties and this leads to higher leaching events. This study has fulfilled therefore its initial objective of showing the benefits of a stochastic approach based on second-order MC analysis, by clearly separating uncertainty from spatial variability in the uncertainty analysis. The approach allowed modelling of the spatial variability of non-georeferenced parameters and the results

showed the important consequences of this modelling paradigm for pesticide leaching potential.

In the context of groundwater management, this may have profound consequences for the perception of current procedures for the registration of new substances or groundwater vulnerability assessment. Registration procedures using spatially distributed simulations rely mainly on the variability of soil and climate properties. However, pesticide parameters such as DT50 and K_{OM} are usually assumed constant even though it is known that they show spatial variability at all scales. On the one hand, assuming constant pesticide parameters is desirable for the harmonisation of registration procedures, but on the other hand, the results of these procedures have ultimately to be confronted with 'real-world' expectations (monitoring data) regarding potential leaching concentrations (e.g. the regulatory limit of 0.1 μg/L). It seems therefore more logical to consider the variability of pesticide parameters in spatially distributed assessments.

Thus, there is a risk of a mismatch and misunderstanding for decision makers between the realistic scenarios of soil and climate spatial variability and unrealistic assumptions such as a constant DT50 at the regional scale. Any 'intrinsic' vulnerability assessment based on (spatially) constant pesticide properties may be completely invalidated by field (or groundwater) observations just because of the natural, spatial variability of DT50 or K_{OM}. Looking at the upper percentiles of the result CDFs, current registration procedures may not be sufficiently conservative if the spatial variability of DT50 and K_{OM} is considered.