ELSEVIER

Sources of uncertainty in pesticide fate modelling

Igor G. Dubus*, Colin D. Brown, Sabine Beulke

Cranfield Centre for EcoChemistry, Cranfield University, Silsoe, Beds MK45 4DT, UK

Abstract

There is worldwide interest in the application of probabilistic approaches to pesticide fate models to account for uncertainty in exposure assessments. The first steps in conducting a probabilistic analysis of any system are: (i) to identify where the uncertainties come from; and (ii) to pinpoint those uncertainties that are likely to affect most of the predictions made. This article aims at addressing those two points within the context of exposure assessment for pesticides through a review of the different sources of uncertainty in pesticide fate modelling. The extensive listing of sources of uncertainty clearly demonstrates that pesticide fate modelling is laced with uncertainty. More importantly, the review suggests that the probabilistic approaches, which are typically being deployed to account for uncertainty in the pesticide fate modelling, such as Monte Carlo modelling, ignore a number of key sources of uncertainty, which are likely to have a significant effect on the prediction of environmental concentrations for pesticides (e.g. model error, modeller subjectivity). Future research should concentrate on quantifying the impact these uncertainties have on exposure assessments and on developing procedures that enable their integration within probabilistic assessments.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Uncertainty; Sensitivity; Monte carlo; Probabilistic; Pesticide; Model; Leaching

1. Introduction

Probabilistic approaches to environmental risk assessment for pesticides and other chemicals are currently receiving a vast amount of interest, especially in the US (ECOFRAM, 1999; Solomon et al., 2000) and in Europe (Jager et al., 2001; EUPRA, 2001). The application of probabilistic techniques to the assessment of exposure is traditionally expected to yield a number of benefits including: (i) the quantification of the uncertainty associated with model predictions; (ii) the identification of the factors which most influence model predictions; (iii) the promotion of critical examination of the data and exposure models; and (iv) the generation of meaningful outputs for subsequent decision-making (EUPRA, 2001). The overall aim of any probabilistic exercise is to account for 'uncertainty'. Uncertainty is a capacious term used to encompass a multiplicity of concepts (Morgan and Henrion, 1990) and has different meaning in various disciplines (Mowrer, 2000). Terminology that has been related to uncertainty within the context of contaminant modelling

*Corresponding author. *Present address*: BRGM, 3, Avenue Claude Guillemin, 45000 Orléans, France. Tel.: +33-238-644-750; fax: +33-238-643-446.

E-mail address: i.dubus@brgm.fr (I.G. Dubus).

includes: variation, variability, ambiguity, heterogeneity, approximation, inexactness, vagueness, inaccuracy, subjectivity, imprecision, misclassification, misinterpretation, error, faults, mistakes and artefacts. Within the context of this article, the term uncertainty is used in its widest sense and is meant to represent the combination of factors of various origins leading to a lack of confidence with regard to the description of the system under study. The terminology used encompasses both stochastic variability and incertitude.

The very first step in any assessment of uncertainty is to compile a list of the different sources of uncertainty (Warren-Hicks and Moore, 1998). Listing uncertainties is useful in that it provides a means to: (i) explicitly acknowledge the different uncertainties which will either be integrated in the modelling or not; (ii) identify those uncertainties which are difficult to integrate into uncertainty analyses carried out using traditional methods (e.g. Monte Carlo or first order uncertainty analyses); and (iii) draw attention to the confidence that should be assigned to the results of probabilistic modelling. Although uncertainty analyses and probabilistic modelling exercises within the context of pesticide fate modelling have been reported in the literature (e.g. Carsel et al., 1988; Fontaine et al., 1992; Nofziger et al., 1994; Maund et al., 2001; Carbone et al., 2002), sources of uncertainty have never been discussed in detail.

This article reviews the sources of uncertainty associated with pesticide fate modelling. For illustration, emphasis is put on simulation of pesticide leaching through soil, but the analysis and discussions are relevant to other pesticide fate models and the broader field of environmental modelling. Contributions to the overall uncertainty are presented in a practical classification which follows the different steps in the modelling process: (i) the acquisition of basic (primary) data in the field or in the laboratory; (ii) the derivation of model input parameters from basic data or by other means; and (iii) the modelling itself. Sources of uncertainty that are rarely acknowledged, but which may have a significant influence on estimations of environmental concentrations, are also discussed.

2. Uncertainty in the primary data

The primary data are defined here as the basic physical, chemical and environmental properties determined either in the field or in the laboratory which are either directly fed into a model or used to derive input parameters for the model. Depending on the amount of information available to the modeller, primary data might include site characteristics (e.g. longitude, latitude, elevation), soil properties (e.g. organic carbon content, particle size distribution, water retention data), weather conditions (e.g. rainfall, minimum and maximum temperatures, humidity and radiation data), pesticide properties (e.g. solubility, Henry's constant, laboratory data on sorption and degradation) or results of field experiments (e.g. soil residues at different depths, pesticide loss by run-off, pesticide concentrations in leaching or drainage waters). Uncertainty in the primary data will arise from the spatial and temporal variability of environmental variables, from sampling procedures in the field and from analysis in the laboratory. These sources of uncertainty are discussed below.

2.1. Spatial and temporal variability of environmental variables

A large number of articles have reported on the spatial variability of pesticide residues or leaching in the field (Rao and Wagenet, 1985; Vischetti et al., 1997) or in lysimeters (Flury et al., 1998; Simmonds and Nortcliff, 1998). This has been attributed to some extent to the variability in space of environmental properties which in turn influence predictions of pesticide leaching models, such as physical (Bosch and West, 1998), chemical (Wood et al., 1987) and biological (Parkin, 1993; Soulas and Lagacherie, 2001) data. Temporal variability has been the subject of much less research. Causes of spatial variability are traditionally classified into intrinsic or extrinsic factors. Taking the agricultural soil system as an example, intrinsic variability is due to natural conditions in soils whilst extrinsic variability is that imposed on a field as part of crop production practices. Examples of soil characteristics that exhibit intrinsic variations are texture and mineralogy whilst tillage, fertilizer and

pesticide applications, harvesting and removal of crop residues all contribute to the development of an extrinsic variability.

Spatial dependency of measurements in the field occurs when samples collected close to one another are more similar than samples collected at greater distances (Cambardella et al., 1994). Although the application of classical statistics to instances where spatial dependence is present is valid (Brus and de Gruijter, 1997), the use of geostatistics designed to exploit non-random and correlated data (Yost et al., 1993) is often preferred (Hamlett et al., 1986). Geostatistical analyses have been performed to study the spatial variability of pesticide sorption (Cambardella et al., 1994; Novak et al., 1997; Jacques et al., 1999) and degradation (Price et al., 2001) in the field. Webster and Oliver (2001) provide a description of geostatistical techniques. Describing uncertainty using geostatistics is not an activity exempt from uncertainty itself as variogram uncertainty may be large (Jansen, 1998) and spatial interpolation may be undertaken using different techniques.

The capacity of soils for sorption and degradation play an important role within the context of pesticide fate modelling (Boesten and van der Linden, 1991; Dubus et al., 2003). Spatial variability in pesticide sorption has been reported for a range of geographical entities, including individual fields showing some homogeneity in terms of soil series (Lennartz, 1999; Elabd et al., 1986; Jacques et al., 1999), fields or contiguous fields made of different soil series (Jaynes et al., 1995; Novak et al., 1997; Oliveira et al., 1999), catchments (Coquet and Barriuso, 2002) and a large number of soils contrasting in their geographical origin (Barriuso and Calvet, 1992; Ahmad et al., 2001a; Dubus et al., 2001). Variability in the sorption distribution coefficient K_d can generally be reduced by normalising it to the organic carbon content (Hamaker and Thompson, 1972), but the variability of the resulting K_{oc} often remains considerable (Fig. 1). Some authors consider that the use of K_{oc} reduces the variability in K_d and that variability in K_{oc} is generally due to experimental errors and variations in the nature of the organic matter (Gerstl, 2000) although others have observed that normalisation of K_d to organic car-
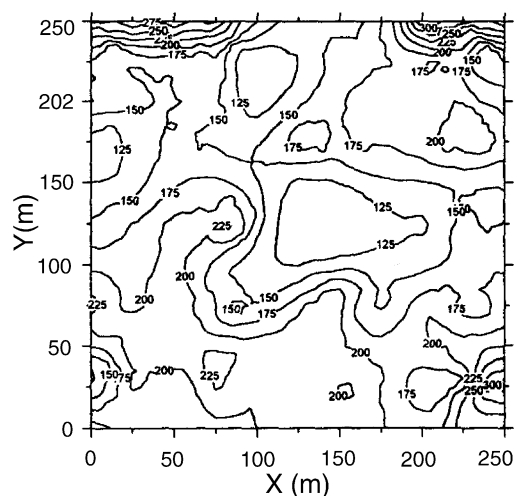

Fig. 1. Distribution of K_{oc} for atrazine within a 6.25-ha field. The contour map was generated from 2601 block-kriged estimates of K_{oc} for atrazine based on a 5 by 5 m grid pattern using block estimates (reproduced from Novak et al., 1997, with permission).

bon failed to reduce variability compared to that of K_d (Elabd et al., 1986; Beck et al., 1996). In terms of shape of distribution describing spatial variability, both normality (Coquet and Barriuso, 2002; Wood et al., 1987; Elabd et al., 1986; Lennartz, 1999) and log–normality (Novak et al., 1997; Jaynes et al., 1995) of K_d have been reported. In most of the modelling studies accounting for the variability in the sorption distribution coefficient K_d, a normal distribution was hypothesised (Nofziger et al., 1994; Franke and Teutsch, 1994; van der Zee and Boesten, 1993; Di and Aylmore, 1997) although uniform (Soutter and Pannatier, 1996; Warren-Hicks et al., 2002) and log–normal (Dubus and Brown, 2002) distributions have also been used. The practical implementation of Monte Carlo modelling for sorption has been handled differently by various authors. Nofziger et al. (1994) considered that K_{oc} was normally distributed and then derived K_d by multiplying K_{oc} by fixed values of organic carbon. In contrast, some studies derive K_d on the basis of fixed values of K_{oc} and a distribution of organic carbon values (Lafrance and Banton, 1995; Zacharias et al., 1999). Disregarding one of the two

components of the variability in Kd is likely to have noticeable effects on results of the probabilistic modelling (Coquet and Barriuso, 2002).

The spatial variability of degradation has received less attention. Walker et al. (2002) investigated the variation in degradation of isoproturon at the field level and reported DT50 values varying from 6 to 30 days. Spatial differences in degradation were found to occur over a range of a few metres or even less. Vischetti et al. (1997) reported CVs of 11–110% for DT50 for metamitron and chloridazon in three Italian field soils. Walker and Brown (1983) investigated the variability of DT50 for metribuzin and simazine for 10 different plots in three fields (CV of 7 and 21% for simazine and metribuzin, respectively) and the within-field variability (20 samples per plot; CV 23 and 25% for simazine and metribuzin, respectively). Walker et al. (2001) suggested that the variability in the degradation of isoproturon was related to microbial biomass and diversity, which appeared to be influenced by pH at the field scale. Rao and Davidson (1982) reviewed the data on degradation for 31 pesticides. The coefficient of variation for topsoil metabolism or dissipation was usually greater than 40% and averaged 73% (Cohen et al., 1995). Wolt et al. (2001) consider that a log–normal distribution should be used to describe the variability in degradation data because physicochemical properties of the soil environment that may impact half-life, such as aggregate and particle size distribution, exchangeable cations and diffusion coefficients are log–normally distributed. Warren-Hicks et al. (2002) reported a beta distribution for describing the spatial variability of chemical degradation rates at three sites although it should be noted that the beta distribution is very flexible and can take a very diverse set of shapes (Vose, 2000).

Relatively large variabilities have been reported for residues of pesticides in the field. Uncertainty in pesticide residues observed shortly after application might be due in part to the variability associated with the spraying of the pesticide (Vischetti et al., 2001). These authors reported CVs of 9.5–31% for concentrations of four herbicides sampled using spray traps and CVs of 30–61% for concentrations in soil 1–2 h after spraying. Larger CVs for application rates have been report-

ed by others (Vischetti et al., 1998; Walker and Brown, 1983; Smith and Parrish, 1993). Residues of various contaminants in the environment have often been found to be log–normally distributed and Ott (1990) provided a theoretical justification of the ubiquity of this skewed distribution in the description of environmental concentrations of pollutants.

Issues of spatial variability are not limited to pesticide and soil properties as rainfall data may also be significantly variable (Krajewski et al., 1998). Variability in rainfall will directly affect the water balance in pesticide fate models. The assumption usually made of spatial uniformity in rainfall at the small watershed scale did not hold for a 4.4-ha catchment characterised by convective storms (Goodrich et al., 1995) and a large uncertainty in the model outputs can be expected if this rainfall variability is not accounted for in the modelling (Chaubey et al., 1999).

2.2. Sampling procedures and measurement error

The term 'measurement error' refers to the uncertainty originating from the sampling in the field and the determination of physical or chemical properties of the samples. Differences in sampling procedures for pesticide residues between organisations and individuals is likely to contribute to the overall uncertainty in the determination of persistence of pesticides in the field. Walker and Brown (1981) compared the degradation of metamitron, atrazine and propyzamide in fresh soil with that in soil stored for seven months either at 5 °C, frozen, or sieved and air-dried. They found considerable differences in degradation rates both between the pretreatments, and between stored and fresh soil for metamitron and atrazine. Procedures for the preparation of sediment and soil samples (storage, subsampling, sieving, drying/rewetting, homogenisation) and the subsequent addition of organic compounds (addition method, carrier solvents, mixing) are largely variable between the individuals and this may introduce unintentional bias in the experimental studies (Northcott and Jones, 2000). As well as a 'random error', laboratory measurements may be subject to a 'systematic error', which results from bias in the

measuring apparatus and experimental procedure. Systematic errors arise, for example, because a measurement device is imperfectly calibrated, consistently used incorrectly or an incorrect multiplier or scaling factor is used in the computations (Millstein, 1994). Uncertainty may also arise from the use of laboratory or field materials, which have been demonstrated to interact with pesticides such as ceramic porous cups (Beltran et al., 1995), walls of PVC lysimeters (Koskinen et al., 1999), flasks and tubes (Topp and Smith, 1992) or filtering devices (Mouvet and Jücker, 1997; Clausen, 2000; Ahmad et al., 2001b).

Uncertainty in the modelling may originate from the use of input data obtained using different laboratory approaches. A typical example is the derivation of sorption and degradation data for a compound through either batch and incubation experiments or column studies. Degradation has often been found to be faster in column experiments than in incubation procedures (Comfort et al., 1992; Estrella et al., 1993). This has been attributed to the downward movement of degrading microorganisms through the soil profile (Shaw and Burns, 1998) and to the decreasing substrate concentrations in the incubation experiments compared with constant influent substrate concentrations in column experiments (Estrella et al., 1993). Fitting a mathematical model to column breakthrough curves is generally expected to result in sorption values similar to those which can be obtained in the batch experiments (Wauchope et al., 2002) provided small infiltration rates are used (Johnson and Farmer, 1993), an adequate fitting model is adopted (Singh et al., 1996) and batch experiments do not implement high solution to soil ratios and short equilibration times (Johnson et al., 2000).

With regard to rainfall, Krajewski et al. (1998) compared rainfall measurement from a tipping bucket and an optical gauge at the same location and reported significant differences between the two measuring devices, especially at the beginning of rainfall events. Specific factors that may influence the reliability of rainfall data include differences in the measurement height, the presence of a building or natural feature, which may influence the distribution of wind at the point of measure-

ment (Verschoor et al., 2001), losses by evaporation, the absence of heating systems to enable the measurement of snowfall, differences in collector shapes, the non-instantaneous character of buckets when being emptied, the presence of impurities deposited in buckets and inadequate calibration (Viton, 1970; Krajewski et al., 1998).

3. Uncertainty in the derivation of model input parameters

Process simulation models are by their very nature complex and it is not easy to make them simple to use (Garen et al., 1999). A 'good' model should strike a balance between complexity (which can be grossly estimated by the number of model parameters) and accuracy (goodness of fit between simulated and measured) (Beck et al., 1997). Although the use of experimental data for a direct parameterisation of a pesticide leaching model is recommended, these data are not always available and most input parameters will require manipulation of the data by the modeller. For instance, units of the model input may be different from that of the field or laboratory measurement or the model might need surrogate parameters, which reduce primary data to a few summary variables. Examples include the use of DT50 values (surrogate for the degradation data), sorption distribution coefficients (surrogate for the sorption isotherm data) and parameters of the van Genuchten or Brooks and Corey equations (surrogate for the water release and hydraulic conductivity curves). The difficulty in using experimental data directly in the modelling holds particularly for the more complex models that may include conceptual theories for which parameters are difficult to derive. In these instances, the modeller might decide to (i) leave the parameters at their default values, (ii) make an educated guess using expert judgement, (iii) extract values from existing databases or (iv) derive the values from empirical functions presented in the literature. Each procedure may introduce uncertainty into the modelling, depending on the sensitivity of the model.

3.1. Derivation of parameters from primary data

As seen before, uncertainty in degradation can originate from spatial and temporal variability of

Table 1
Variability in DT50 and DT90 values introduced by the fitting of different equations to four degradation datasets (different compounds). Only those fittings with $r^2 > 0.7$ were considered. Adapted from Leake et al. (1995)

	Number of fittings	Range (days)	Coefficient of variation (%)
	DT50 values		
Dataset 1	8	16–38	35.1
Dataset 2	7	95–110	5.4
Dataset 3	9	95–180	24.0
Dataset 4	9	64–180	41.3
	DT90 values		
Dataset 1	8	32–120	42.3
Dataset 2	6	336–380	4.2
Dataset 3	9	317–411	8.1
Dataset 4	9	241–698	33.9

degradation in the field, from storage and preparation of soil samples and from slight differences in experimental conditions in the laboratory. Additional uncertainties in the modelling originate from the derivation of values for input parameters. A typical example is the variability in DT50 values arising from their derivation from laboratory data. Leake et al. (1995) calculated laboratory DT50 values for four pesticides by applying six decay equations using six curve-fitting programs. Calculated DT50 values were found to be strongly affected by the equation and package used (Table 1). Other sources of uncertainty in the derivation of DT50 values include: (i) the application of first-order kinetics to data which do not follow this decay pattern; (ii) the use of linear transformation of the data as opposed to a direct nonlinear estimation (Beulke and Brown, 2001); and (iii) modeller subjectivity (Boesten, 2000). Averaging procedures can also introduce significant uncertainty. Leaching concentrations predicted using the average of four sorption values were 2–30 times smaller than the average of four separate simulations with the individual sorption values (Beulke et al., 2001). Degradation data are generally log–normally distributed (Wolt et al., 2001), so the median of a population of data points may be very different from its mean. Aspects of interaction between model non-linearity and error are discussed in Addiscott and Tuck (2001) using examples based on a solute leaching model. The difference between 'evaluate first' and 'interpolate first' also raises concern with regard to the uncertainty in large-scale spatial simulations, particularly where there is an implicit assumption that using spatially averaged parameters is equivalent to applying spatial averaging to the model output (Heuvelink and Pebesma, 1999; Addiscott and Tuck, 2001). Discrepancies can also be introduced in the modelling if different statistics summarising sorption and degradation are used.

3.2. Procedures to derive input parameters using limited information

3.2.1. Use of pedotransfer functions
Soil hydrological properties are subject to a large spatial variability and are strongly dependent on the measurement technique (Vereecken, 1992). In order to help with the model parameterisation, empirical equations, known as pedotransfer functions (PTFs; Bouma, 1989), have been established which express relationships between basic soil properties and parameters which are difficult to measure. Typical examples are the derivation of retention data or parameters of retention curve equations (Tietje and Hennings, 1993) and the derivation of saturated hydraulic conductivities (Pachepsky et al., 1999). PTFs suffer from a number of shortcomings, which introduce additional uncertainty in the model parameterisation. First, the uncertainty in the databases used to derive relationships is likely to transfer to the derivation of values using these relationships. Secondly, PTFs usually have a domain of validity, which is often unknown to the end-user and thus ignored. In

addition, the differences between values estimated with different PTFs results in variability in estimated parameters (Tietje and Tapkenhinrichs, 1993). Tiktak et al. (1999) performed an uncertainty analysis of a model describing the deposition of cadmium in the Netherlands and found that the largest source of uncertainty in coarse-textured soils was introduced by an empirical relationship to estimate cadmium sorption in the soils. The use of PTFs for estimating soil hydraulic conductivity was identified as a key problem for obtaining reliable LEACHM predictions (Inskeep et al., 1996). Satisfaction with the accuracy of PTFs is dependent on the intended use of the relationships (Pachepsky et al., 1999). For instance, PTFs were used to derive hydraulic properties for the MACRO model and were considered sufficiently accurate for registration purposes (Jarvis et al., 2000). An alternative to estimating the hydrological parameters using PTFs is to use soil databases, which provide measured values for water retention and hydraulic conductivity curves for specific classes of soil (e.g. Wösten et al., 1994; Hollis et al., 1993). Again, the use of such generic data are likely to introduce some uncertainty in the modelling, although the procedure is useful for performing regional assessments and for parameterisation of a model under conditions of limited data.

3.2.2. Use of spatially referenced data

Applications in pesticide fate modelling may draw on GIS (geographical information systems) technology and spatial data for (i) deriving local environmental properties for a given site through the use of spatial databases (e.g. Hallet et al., 1995) or (ii) performing spatially distributed pesticide exposure assessments at different scales (see Cryer et al. (2001), Shukla et al. (2000), Verro et al. (2002) and Bach et al. (2001) for recent applications at the scales of catchment, county, region and country, respectively). Although the end products of GIS applications (typically large, attractive multicoloured maps or tables) give an impression of reliability and accuracy on which clear cut decisions can be robustly based (Mowrer, 2000), they may be subject to significant uncertainties. Hardly any GIS in use can present the

user with information about the confidence limits that should be associated with the end product (Heuvelink, 1998), while the uncertainty in GIS applications is recognised from a research point of view (Goodchild and Gopal, 1989; Heuvelink, 1998; Zhang and Goodchild, 2002).

Data stored in GIS may be acquired through digitisation or scanning of the existing maps or by interpolation from point observations. The acquisition of data from existing maps through digitisation means that the variability/uncertainty in the maps is propagated to the digitised version. The digitisation process itself will introduce additional uncertainty in the data (Burrough and McDonnell, 1998). Although maps usually display data with a number of homogeneous zones separated with crisp boundaries, these boundaries, such as the limit between two soil series, are often gradual and mapping units are rarely truly homogeneous in the real world (Heuvelink, 1998). This may lead to misclassification of location in map units or positional errors of class boundaries (Tarantola et al., 2002). In addition, the representation of spatial attributes in the form of uniform grid cells (the problem of 'mixed pixels'; Burrough and McDonnell, 1998) will carry some uncertainty. Each grid cell typically contains a single value of an attribute, so the information presented (typically a mean value) does not reflect the variability in the attribute displayed unless multi-layered maps are used. In vector-raster conversion, the mixed pixel problem leads to the dilemma of whether to classify a cell according to the class covering the geographic reference point (e.g. the centre of the cell) or according to the dominant class occurring in the cell.

The acquisition of data through interpolation from point observations involves extrapolations and generalisation assumptions, and thus there is a risk of a particular point in space being misclassified. Some of this uncertainty can be accounted for using geostatistics (Webster and Oliver, 2001). The point data are themselves uncertain since they are subject to positional and measurement error. Data will carry additional uncertainty if their sampling location is assessed using global positioning (Mowrer, 2000) or if they have been acquired through remote sensing techniques (Friedl

et al., 2001). Although some of the physical, chemical and biological variables measured in the field will vary in time over different scales (e.g. days, season, year, decade), the geographically referenced data will only represent a single occurrence or state in time.

As for a numerical model, uncertainty in the data stored in the GIS may be propagated to the spatial outputs produced through manipulation of the data within the GIS, depending on the sensitivity of the calculations applied to the data. Additional uncertainty may be introduced when data from sources of different quality are combined, when multiple classification classes are integrated (Stine and Hunsaker, 2001) or when the data are transformed from vector to raster (Burrough, 1986). It is important to realise that the outcome of a GIS exercise at a given scale may be influenced by the spatial resolution of the data (Tarantola et al., 2002) and that model predictions may be affected (Finke et al., 1999). Recommendations are available on the estimation of the risk of pesticide leaching at the regional scale using GIS (Loague et al., 1996).

3.3. Other sources of uncertainty in the derivation of input parameters

Additional uncertainty factors associated with the derivation of input parameters from primary data include the treatment of replicates and outliers in a dataset, the selection of a representative variable (i.e. arithmetic or geometric mean, median), the use of inadequate units or the rounding of values. Millstein (1994) considers that a simultaneous and proportional increase in the precision of all variables will help to control error arising from loss of significant digits in a computation with one numerical division. Particular attention has to be paid to units of parameters since discrepancies in units between pesticide leaching models are common. Another source of uncertainty arises from the lack of detailed information provided in scientific reports, which are used to support the model parameterisation. Examples include the reporting of pH values of soil samples without the specification of the background electrolyte and the reporting of the particle size distribution as sand, silt,

clay without any reference to particle-size limits (Nemes et al., 1999). Whereas FAO and some national systems (e.g. USA, France), define the boundary between sand and silt fractions at 50 μm, others (e.g. UK, Germany) set the division at 60 or 63 μm (Wösten et al., 1999).

4. Other uncertainties related to the modelling

Modelling the fate of pesticides represents a challenge to any modeller since the behaviour of the compound in soil is influenced by a large number of physical, chemical and biological processes, some of them probably unknown. The multiplicity of factors affecting the fate of pesticides leads to the introduction of uncertainty in the modelling through model error (also referred to as structural error or model inadequacy), the inability of the model to represent reality accurately even when adequate model inputs are being used. Other sources of uncertainty inherent in the use of pesticide leaching models which are often overlooked are the influence of the choice of a particular model, subjectivity introduced by the modeller, linguistic imprecision and the inappropriate use of concepts implemented in the models. These are discussed below. Sources of uncertainty which were considered to be outside the scope of the present review include: human error (through unstable or biased experimental procedures, interpretation, typing error or the simple variation between people; Stine and Hunsaker, 2001) and uncertainty resulting from the upscaling of models to a scale larger than that for which they were developed (Gaunt et al., 1997).

4.1. Inability of the model to describe experimental observations

The fact that a model is unable to simulate experimental observations even when an appropriate set of model inputs is used has been termed as structural error, conceptual error, uncertainty in the conceptual model, model inadequacy and model error (Beck et al., 1997). Although model error can be due to errors in translation (the process of converting a scientific concept into a set of equations or computer code; Addiscott and Tuck,
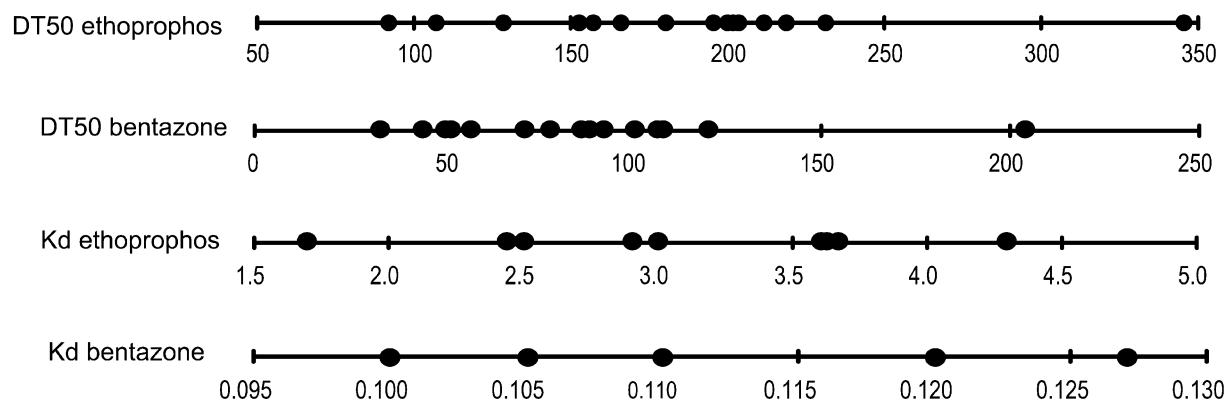
Fig. 2. Variability in the selection of DT50 and Kd values for ethoprophos and bentazone by a range of modellers. Selection was based on the same degradation and sorption datasets for all individuals (adapted from Boesten, 2000).

2001), these 'errors' will most often originate from the non-inclusion or inappropriate representation of significant processes in the model. The error is typically revealed through evaluation exercises where the model is tested against experimental data. Excellent fit for simulations of field leaching data have rarely been reported in the literature and this is not surpirsing given the complexity of the system to be described.

4.2. Selection of a pesticide fate model

Choosing an appropriate model can be a difficult and confusing task, especially for the non-expert (Del Re and Trevisan, 1995; Garen et al., 1999). PRZM is the primary model used in the United States to assess the fate of a pesticide in the unsaturated zone whereas four models (PRZM, PELMO, PEARL and MACRO) are mainly used in the European Union. Most of these models have their own specificities and comparison studies have demonstrated that large differences between the models can sometimes be obtained (Vink et al., 1997). Model selection can be a significant source of uncertainty in pesticide fate modelling. Pollock et al. (2002) compared the variation in predictions from four pesticide leaching models to that obtained by varying a number of input parameters in a Monte Carlo exercise. These authors concluded that the variability in results due to model selection could be more significant than that due

to input parameter variation, although it should be noted that only a small variation (CV 10%) was assigned to the input parameters. In theory, the selection of a particular model from those recommended for pesticide registration should result from balance between considerations regarding the model (i.e. model capabilities, data required, extent of validation, ease of use and documentation; Russell et al., 1994), the objectives of the modelling exercise (e.g. predictive simulation, simulation of field data, calibration), and the availability of data for model parameterisation (Di and Aylmore, 1997), but external factors such as known preferences of national registration authorities also come into play (Travis, 2000).

4.3. Modeller subjectivity

Brown et al. (1996) first reported a ring test in which pesticide leaching in a sandy loam soil was simulated by five modellers using three pesticide fate models. Other recent studies with a larger number of models and datasets have confirmed the user-dependent variability of model outputs (e.g. Tiktak, 2000; Boesten and Gottesbüren, 2000). Boesten (2000) reported a ring test exercise in which 18 pesticide fate modellers received raw data from the laboratory degradation studies and were asked to derive DT50 values (at 10 °C) and sorption distribution coefficients for ethoprophos and bentazone, respectively. Calculated DT50 val-

ues ranged from 92 to 346 days (mean 191 days, CV 29%) and from 33 to 204 days (mean 83 days, CV 46%) for the two compounds (Fig. 2). Variation in sorption distribution coefficients was smaller with CVs of 21 and 13% for the two pesticides. Variability in the derivation of environmental properties was attributed, in decreasing importance, to the expert judgement introduced in establishing the relationship between transformation rate and soil temperature, the inclusion/exclusion of data for incubation times larger than 100–200 days and the use of different fitting procedures. Uncertainty in degradation and sorption properties is almost always propagated through the modelling (Dubus et al., 2003). Boesten (2000) suggested that the subjective influence of the model user was much greater than the variability introduced by the use of different models. The uncertainty introduced by the modeller subjectivity could be reduced through detailed guidance on model parameterisation (Brown et al., 1996) and discussion of procedures for deriving input parameters (Boesten, 2000).

4.4. Inadequate use of concepts implemented in models

Perhaps one of the largest sources of error in modelling is the use of concepts, which do not apply to a particular modelling situation. Examples of pitfalls are the inadequate use of the Koc (or Kom) approach and the parameterisation of pesticide decay. Sorption is often characterised by the Koc and the sorption distribution coefficient normalised to organic carbon is defined as:

$$Koc = \frac{Kd}{OC} \times 100 \qquad (1)$$

where Kd is the linear sorption distribution coefficient determined in the batch equilibrium experiments, usually expressed in l/kg, and OC is the organic carbon content, expressed in percent.

The Koc was introduced to reflect the linear relationship between Kd and OC, which was established for non-ionic compounds (Hamaker and Thompson, 1972) because this variable has the virtue of being broadly independent of any partic-

ular soil (Hamaker, 1975). Nevertheless, the Koc concept tends to be used by modellers for all molecules regardless of their ionisation status. The Koc approach is usually invalid for ionisable compounds (Wauchope et al., 2002) since there is often no clear influence of organic matter on sorption (Shimizu et al., 1992; Ukrainczyk and Ajwa, 1996). Another pitfall relates to the parameterisation of degradation. Most pesticide leaching models use first-order kinetics to describe the degradation of pesticides in soil. If a first-order model is selected in the model, then it is a necessity that DT50 values (or degradation rates) derived by first-order kinetics are used, even if other equations fit the data better (Beulke and Brown, 2001). Inputing DT50 values in a model that was derived with another equation is a common mistake since the modeller can be provided with DT50 values without further information on the way these were derived. The inadequate application of model concepts is likely to contribute significantly to the overall uncertainty of the modelling and should obviously be avoided. Adequate documentation, on-screen help, version control and the provision of training are all possible ways to address this.

4.5. Linguistic imprecision

Linguistic imprecision was identified as a source of uncertainty by Morgan and Henrion (1990), as we often refer to events or quantities with imprecise language. Equally, we may describe two different concepts using the same term. Sorption data originating from batch equilibrium studies are often described using the non-linear Freundlich equation:

$$X = Kf \, C^{1/n} \qquad (2)$$

where X is the amount adsorbed, C is the concentration of pesticide in solution, and Kf and $1/n$ are coefficients (referred to as the Freundlich distribution coefficient and exponent, respectively).

It is common practice to normalise the Kf coefficient to organic matter and to report this new variable as Koc. As pointed out earlier, the initial

definition of the Koc refers to the linear distribution coefficient (Eq. (1)). Therefore, there is possible confusion on the term Koc, which could represent either the linear or Freundlich distribution coefficient normalised to organic carbon. Differences in the values for the two different Koc will be maximum for the compounds that exhibit strong non-linear sorption.

The term 'field capacity' refers to a specific point on the water retention curve to which a wetted, freely-draining profile is considered to drain within a defined period. Uncertainty in the modelling might arise because the reference tension varies between countries: -5 kPa in the UK, -10 kPa in the Netherlands, -33 kPa in the US, for instance. Similarly, different leaching models implement different definitions (-5 kPa in MACRO, -33 kPa in PRZM, -10 kPa in PESTLA) and the model user can introduce significant uncertainty if he/she does not select the appropriate tension.

4.6. Model calibration

Model calibration is a cornerstone in pesticide fate modelling (Dubus et al., 2002). It is sometimes considered that calibration can help to reduce the uncertainty in the modelling through the derivation of input parameters that improves the simulation of experimental data, but this might not always be the case (Beck, 1987). The calibration might be ill-posed (Carrera and Neuman, 1986) and uncertainty will originate from the fact that multiple combinations of input parameters will provide a similar fit to the experimental data (equifinality; Beven and Binley, 1992). Predictive uncertainty arising from the lack of a unique solution to the calibration problem can be accounted for using dedicated procedures such as the Generalized Likelihood Uncertainty Estimation (Beven, 2001), the Pareto Optimal Set procedure (Yapo et al., 1998) or the non-linear predictive analyser of the PEST inverse modelling package (Doherty, 2002). Although these approaches will provide a confidence interval for each optimised parameter and for subsequent extrapolations on the basis of these parameters, the uncertainty estimates provided will be dependent on subjective choices

made, such as the selection of an objective function or the limit from which you consider that the model is not calibrated anymore (Beven, 2001). 'Parameter lumping' may also prevent a decrease in uncertainty following calibration (Dubus et al., 2002). This occurs when there is enough flexibility in the modelling system to allow for changes in specific parameters to compensate for inaccuracies, uncertainties and limitations associated with experimental data, modelling and calibration procedures. Lumped parameters can only be obtained by calibration and will have lost their physical, chemical or biological definition (Jansen, 1998). In cases where lumping occurs, calibration will result in an increase in parameter uncertainty, although this may not be transparent to the modeller.

5. Discussion and implications

5.1. Contribution of individual sources of uncertainty to the overall uncertainty in pesticide fate modelling

The listing of sources of uncertainty clearly shows that pesticide fate modelling is laced with uncertainty. A priority should therefore be to estimate the magnitude of the uncertainties listed above and whether they transfer into uncertainty in the estimation of exposure. This task is made difficult because only a few uncertainties are easily quantified, many or most are quantified with difficulty and several may not be quantifiable at all (Oreskes, 1998). In addition, parameter uncertainty may be transferred differently through the modelling, from suppression to large exaggeration (Addiscott and Tuck, 2001) depending on the sensitivity of the model. For these reasons, very few attempts to differentiate between the contributions of the different sources of uncertainty to the overall uncertainty in exposure modelling have been reported (Zhang et al., 1993; Nofziger et al., 1994; Loague et al., 1996). Zhang et al. (1993) investigated the influence of the uncertainty in model input parameters and year-to-year rainfall variability on predictions of the pesticide leaching model Chemical Movement in Layered Soils using first-order second moment analysis and Monte Carlo simulation. Both sources of uncertainty were

found to have comparable effects on the magnitude of the uncertainty in model predictions and the combined variabilities appeared to magnify the overall uncertainty. Nofziger et al. (1994) considered the influence of the uncertainty in weather, soil and pesticide properties on predictions for bentazone leaching. Uncertainty contributions were found to vary between the two years simulated and the overall uncertainty in predictions when combining the three classes of uncertainty was 28 orders of magnitude. Loague (1994) investigated the influence of reductions in data uncertainties on the overall uncertainty levels predicted in a number of uncertainty analyses. A useful step in gaining an understanding of the uncertainty in pesticide fate modelling resulting from the uncertainty in model input parameters is to assess the extent of the latter. Such an approach was recently undertaken by an IUPAC working group, which derived information on the uncertainty in sorption in the form of 'rules of thumb' (Wauchope et al., 2002). The authors considered that (i) the batch experiment probably varies from the true average Kd in the field of the same soil by a factor of two; (ii) the variability in Kd in the field is to be attributed to variation of the organic matter content in the field and of the organic matter itself and typically has a CV of approximately 50%; (iii) a Kd determined for different soils will vary by approximately one order of magnitude; (iv) a CV of 30–60% is common in multi-soil studies and reflects the variability in the sorption capacity of the organic matter and in the measurement of the organic carbon content; and (v) Koc values reported for different studies with multiple soils are expected to vary by an order of magnitude. The application of a similar approach for other key model input parameters would be useful. A number of sensitivity analyses have demonstrated that predictions of pesticide fate models for leaching will mainly be influenced by sorption and degradation parameters (Boesten, 1991; Soutter and Musy, 1998; Dubus et al., 2003), although a number of models have also shown large sensitivities to hydrological parameters (Dubus and Brown, 2002; Wolt et al., 2002).

Model error is one of the most basic forms of error in modelling, but is notoriously difficult to estimate. In chemistry, the analytical bias can be estimated independently by the use of certified reference materials (Ramsey, 1998) or by comparing a given method to others (Heber et al., 1998). An attempt to transpose this general evaluation approach to environmental fate modelling has occasionally been made through the comparison of results of simple models against those obtained with codes that are more complex to assess the model error. For instance, Loague et al. (1996) compared the results of the simple 'Attenuation factor' index method with the more conceptually rigorous PRZM model. However, the procedure is limited since relative agreement with a complex model does not guarantee agreement with behaviour in the field. For these reasons, model error is traditionally assessed by comparing model predictions against experimental data (model evaluation). The inherent capability of models to describe field data can be assessed by simulating the experimental data using information on the study site but without knowledge of the pesticide concentrations found at the site ('predictive' or 'blind' simulation). It is increasingly recognised that pesticide leaching models cannot accurately simulate field data in predictive mode, partly because of variability and uncertainty aspects (Vanclooster et al., 2000). The most popular technique for evaluating model error has therefore been to calibrate the model against the data to be simulated although issues are being introduced through the use of calibration (Dubus et al., 2002). Whether calibration is used or not, the testing of the model is likely to be as much an evaluation of the capabilities of the modeller as of those of the model. User-subjectivity has been shown to contribute to the modelling uncertainty to such an extent that it may prevent the evaluation of model concepts (Tiktak, 2000).

5.2. The uncertainty iceberg

Techniques used to propagate uncertainty in pesticide fate modelling include differential analysis (Loague, 1991; Loague et al., 1996; Li et al.,

1998; Freissinet et al., 1999; Diaz-Diaz et al., 1999), Fourier amplitude sensitivity test (Fontaine et al., 1992), Monte Carlo analysis (Carsel et al., 1988; Zhang et al., 1993; Nofziger et al., 1994; Soutter and Pannatier, 1996; Soutter and Musy, 1998, 1999; Zacharias et al., 1999; Ma et al., 2000; Trevisan et al., 2001; Dubus and Brown, 2002; Carbone et al., 2002; Pollock et al., 2002) and fuzzy logic (Freissinet et al., 1998, 1999). These uncertainty analyses have investigated the effects of input uncertainty on model predictions and generally assume implicitly that (i) the major sources of uncertainty are those associated with model input parameters; (ii) the model is structurally correct; (iii) modeller subjectivity is minimal; and (iv) an adequate parameterisation of a model is possible. Jansen (1998) noted that in the best case, these uncertainty analyses could only provide an optimistic estimate of prediction error, since model errors cannot be fully captured by such analyses and because of restrictions in the sources of uncertainty considered. The contribution of sources of uncertainty other than those in model input parameters is largely unknown and further research is clearly required in this area. It can be strongly suspected that random variability is simply swamped by other kinds of uncertainties (Bailar, 1988, reported by Costanza et al., 1992). As noted earlier, model error is notoriously difficult to estimate and cannot be easily implemented in traditional uncertainty assessment techniques. Modeller subjectivity can be assessed by asking different individuals to simulate the same modelling situation (Brown et al., 1996; Boesten, 2000).

Somewhat perversely, the selection and implementation of techniques designed to account for uncertainties are themselves subject to significant uncertainty. For instance, overall results from Monte Carlo based probabilistic assessments will be influenced by the selection of input parameters to be included in the analysis (Nofziger et al., 1994), the type (Mosleh, 1986; Brattin et al., 1996) and parameterisation (Brattin et al., 1996) of probability distribution functions attributed to input parameters, the absence or presence of correlation between variables (Iman and Conover, 1982), the extent of the correlations considered (Smith et al., 1992), the sampling scheme used (Saltelli et al.,
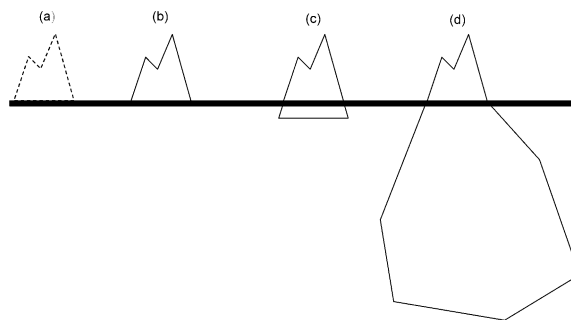

Fig. 3. The uncertainty iceberg. Although uncertainty in pesticide fate modelling has been ignored in the past (a), there has been a number of attempts to quantify uncertainty over the last 10 years (b). The challenge is now to ascertain whether the uncertainty, which is accounted for represents a large (c) or small (d) proportion of the overall uncertainty in pesticide fate modelling.

2000) and the seed number used in the sampling (Dubus and Janssen, 2003).

It is generally considered important to differentiate in quantitative risk analyses between stochastic variability ('Type A' uncertainty) and uncertainty due to the lack of knowledge (incertitude or 'Type B' uncertainty) (IAEA, 1989; Hoffman and Hammonds, 1994; US EPA, 1996). This is because variability is an inherent and irreducible property of the scenario being evaluated, while incertitude is not an inherent property and can (at least in theory) be reduced by collecting additional data or information or performing additional analysis (Brattin et al., 1996). The approach typically results in a two-dimensional (also known as 'nested' or 'double loop') Monte Carlo analysis, being carried out where the contribution of each of these broad classes is assessed. Typical applications of two-dimensional Monte Carlo analyses reported in the literature have only focused on a limited number of sources of uncertainty and may have ignored significant others (Kelly and Campbell, 2000). Results might therefore underestimate uncertainty and convey a false sense of accuracy.

A simple but useful representation of the challenges facing the pesticide fate modelling community and those who base part of their

decision-making on the results of pesticide leaching models is presented in Fig. 3. In the past (iceberg (a)), the uncertainty associated with pesticide fate modelling was largely ignored by modellers and decision-makers, and the uncertainty iceberg was largely concealed. The last 10 years have seen an increasing recognition of variability in the natural environment and procedures to account for uncertainties in model input, such as Monte Carlo analysis, have been recommended and applied (iceberg (b)). A listing of the sources of uncertainty in pesticide fate modelling reveals that many are not accounted for by traditional approaches to uncertainty analysis and that the underwater section of the uncertainty iceberg may be much larger than anticipated (icebergs (c) and (d)). More research is urgently required to estimate the ratio emerged/submerged matter currently implemented in probabilistic modelling exercises. As noted by Cornell (1972); reported by Melching (1995), it is important that we avoid the tendency to model only those probabilistic aspects that we think we know how to analyse.

6. Conclusions

Research on uncertainty is concerned with the identification of uncertainty, its description and with predicting its effects on the outputs of the analysis. The present article has demonstrated that the errors and uncertainties accumulate in pesticide fate modelling in various forms and disguises. Further research is clearly required to (i) assess the magnitude of the different sources of uncertainties affecting pesticide fate modelling; and (ii) integrate into probabilistic modelling exercises those significant sources of uncertainty that are not currently considered (e.g. model error, modeller subjectivity). There is no doubt that assessing the uncertainty in inputs of soil and water models and model error is a difficult task. Working towards a better quantification of uncertainties and their reduction should be a common effort across the whole community of people who have a direct or indirect input into the study of the fate of pesticides, from individuals involved in designing soil sampling strategies in the field right through to the modellers and eventually to decision-makers.

Deterministic models implicitly assume that data on which the parameterisation is based are error-free and parameters and model structures are considered as completely known (Tarantola et al., 2002). Although there have been some attempts at putting variability at the heart of the modelling itself (Jury and Gruber, 1989; Gustafson and Holden, 1990; van der Zee and Boesten, 1991; Wu et al., 1997), deterministic models are likely to remain the main tools for simulating the fate of pesticides for the foreseeable future. Accounting for uncertainty in pesticide fate modelling is still in its infancy, but progress in this domain is crucial if robust estimates of uncertainty in model predictions are to be obtained. Uncertainty will limit the use of a model for making regulatory decisions unless the uncertainty is figured into the decision making process (Jury et al., 1987; Greig-Smith, 1992; Costanza et al., 1992). Disclosure of the sources and magnitude of the uncertainty is needed for the decision maker to understand how confident he or she can be about the decisions that are being made.

References

Addiscott TM, Tuck G. Non-linearity in modelling soil processes. Eur J Soil Sci 2001;52:129–138.

Ahmad R, Kookana RS, Alston AM, Bromilow RH. Differences in sorption behaviour of carbaryl and phosalone in soils from Australia, Pakistan and the United Kingdom. Aust J Soil Res 2001a;39:893–908.

Ahmad R, Kookana RS, Alston AM. Syringe filtration as a source of error in pesticide residue analysis in environmental samples. B Environ Contam Tox 2001b;66:313–318.

Bach M, Huber A, Frede HG. Modeling pesticide losses from diffuse sources in Germany. Water Sci Technol 2001;44:189–196.

Bailar JC III. Scientific inferences and environmental problems. The uses of statistical thinking. Chapel Hill: Institute for Environmental Studies, University of North Carolina, 1988.

Barriuso E, Calvet R. Soil type and herbicides adsorption. Int J Environ An Ch 1992;46:117–128.

Beck MB. Water quality modelling: a review of the analysis of uncertainty. Water Resour Res 1987;23:1393–1442.

Beck AJ, Harris GL, Howse KR, Johnston AE, Jones KC. Spatial and temporal variation of isoproturon residues and associated sorption/desorption parameters at the field scale. Chemosphere 1996;33:1283–1295.

Beck MB, Ravetz JR, Mulkey LA, Barnwell TO. On the problem of model validation for predictive exposure assessments. Stoch Hydrol Hydraul 1997;11:229–254.

Beltran J, Hernandez F, Lopez FJ, Morell I. Study of sorption processes of selected pesticides on soils and ceramic porous cups used for soil solution sampling. Int J Environ An Ch 1995;58:287–303.

Beulke S, Brown CD. Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. Biol Fert Soils 2001;33:558–564.

Beulke S, Brown CD, Dubus IG. Characterisation of sorption for the modelling of pesticide fate. In: Walker A. (Ed.) Pesticide behaviour in soils and water. BCPC Symposium Proceedings No. 78, Farnham, UK, 2001, pp. 51–56.

Beven K. Rainfall-runoff modelling: the primer. Chichester, UK: John Wiley and Sons Ltd, 2001. p. 360

Beven K, Binley A. The future of distributed models–model calibration and uncertainty prediction. Hydrol Process 1992;6:279–298.

Boesten JJTI. Sensitivity analysis of a mathematical model for pesticide leaching to groundwater. Pestic Sci 1991;31:375–388.

Boesten JJTI. Modeller subjectivity in estimating pesticide parameters for leaching models using the same laboratory dataset. Agr Water Manage 2000;44:389–409.

Boesten JJTI, van der Linden AMA. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J Environ Qual 1991;20:425–435.

Boesten JJTI, Gottesbüren B. Testing PESTLA using two modellers for bentazone and ethoprophos in a sandy soil. Agr Water Manage 2000;44:283–305.

Bosch DD, West LT. Hydraulic conductivity variability for two sandy soils. Soil Sci Soc Am J 1998;62:90–98.

Bouma J. Using soil survey data for quantitative land evaluation. Adv Soil Sci 1989;9:177–213.

Brattin WJ, Barry TM, Chiu N. Monte Carlo modeling with uncertain probability density functions. Hum Ecol Risk Assess 1996;2:820–840.

Brown CD, Baer U, Günther P, Trevisan M, Walker A. Ring test with the models LEACHP, PRZM-2 and VARLEACH: variability between model users in prediction of pesticide leaching using a standard data set. Pestic Sci 1996;47:249–258.

Brus DJ, de Gruijter JJ. Random sampling or geostatistical modelling? Choosing between design-based and model-based sampling strategies for soil (with discussion). Geoderma 1997;80:1–59.

Burrough PA. Principles of geographical information systems for land resources assessment. Oxford, UK: Clarendon Press, 1986. p. 193

Burrough PA, McDonnell RA. Principles of geographical information systems. Oxford, UK: Oxford University Press, 1998. p. 333

Cambardella CA, Moorman TB, Novak JM, Parkin TB, Karlen DN, Turco RF, Konopka AE. Field-scale variability of soil properties in Central Iowa soils. Soil Sci Soc Am J 1994;58:1501–1511.

Carbone JP, Havens PL, Warren-Hicks W. Validation of pesticide root zone model 3.12: employing uncertainty analysis. Environ Toxicol Chem 2002;21:1578–1590.

Carrera J, Neuman SP. Estimation of aquifer parameters under transient and steady state conditions. 2. Uniqueness, stability and solution algorithms. Water Resour Res 1986;22:211–227.

Carsel RF, Parrish RS, Jones RL, Hansen JL, Lamb RL. Characterizing the uncertainty of pesticide leaching in agricultural soils. J Contam Hydrol 1988;2:111–124.

Chaubey I, Haan CT, Salisbury JM, Grunwald S. Quantifying model output uncertainty due to spatial variability of rainfall. J Am Water Resour As 1999;35:1113–1123.

Clausen L. Retention of pesticides in filter membranes. J Environ Qual 2000;29:654–657.

Cohen SZ, Wauchope RD, Klein AW, Eadsforth CV, Graney R. Offsite transport of pesticides in water: mathematical models of pesticide leaching and runoff. Pure Appl Chem 1995;67:2109–2148.

Comfort S, Inskeep WP, Macur RE. Degradation and transport of dicamba in a clay soil. J Environ Qual 1992;21:653–658.

Coquet Y, Barriuso E. Spatial variability of pesticide adsorption within the topsoil of a small agricultural catchment. Agronomie 2002;22:389–398.

Cornell CA. First-order analysis of model and parameter uncertainty. In: Proceedings of the International Symposium on Uncertainties in Hydrology and Water Resources Systems, University of Arizona, Tucson, Arizona, 1972, pp. 1245–1272.

Costanza R, Funtowicz SO, Ravetz JR. Assessing and communicating data quality in policy relevant research. Environ Manage 1992;16:121–131.

Cryer SA, Fouch MA, Peacock AL, Havens PL. Characterizing agrochemical patterns and effective BMPs for surface waters using mechanistic modeling and GIS. Environ Model Assess 2001;6:195–208.

Del Re AAM, Trevisan M. Selection criteria of xenobiotic leaching models in soil. Eur J Agron 1995;4:465–472.

Di HJ, Aylmore LAG. Modeling the probabilities of ground-water contamination by pesticides. Soil Sci Soc Am J 1997;61:17–23.

Diaz-Diaz R, Loague K, Notario JS. An assessment of agro-chemical leaching potentials for Tenerife. J Contam Hydrol 1999;36:1–30.

Doherty J. PEST–model independent parameter estimation. Corinda, Australia: Watermark Computing, 2002. p. 122

Dubus IG, Barriuso E, Calvet R. Sorption of weak organic acids in soils: clofencet, 2,4-D and salicylic acid. Chemo-sphere 2001;45:767–774.

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

Dubus IG, Janssen PHM. Issues of replicability in Monte Carlo modelling: a case study with a pesticide leaching model. Environmental Toxicology and Chemistry, 2003 (in press).

Dubus IG, Beulke S, Brown CD. Calibration of pesticide leaching models: critical review and guidance for reporting. Pest Manag Sci 2002;58:745–758.

Dubus IG, Brown CD, Beulke S. Sensitivity analyses for four pesticide leaching models. Pest Manag Sci, 2003 (in press).

ECOFRAM. http://www.epa.gov/oppefed1/ecorisk/, 1999.

Elabd H, Jury WA, Cliath MM. Spatial variability of pesticide adsorption parameters. Environ Sci Technol 1986;20:256–260.

Estrella MR, Brusseau ML, Maier RS, Pepper IL, Wierenga PJ, Miller PM. Biodegradation, sorption and transport of 2,4-dichlorophenoxyacetic acid in saturated and unsaturated soils. Appl Environ Microb 1993;59:4266–4273.

EUPRA. Probabilistic risk assessment for pesticides in Europe. Implementation and research needs. Report from the Euro-pean Workshop on Probabilistic Risk Assessment for the Environmental Impacts of Plant Protection Products, The Netherlands, 2001, 109.

Finke PA, Wladis D, Kros J, Pebesma EJ, Reinds GJ. Quan-tification and simulation of errors in categorical data for uncertainty analysis of soil acidification modelling. Geoder-ma 1999;93:177–194.

Fontaine DD, Havens PL, Blau GE, Tillotson PM. The role of sensitivity analysis in groundwater risk modelling for pes-ticides. Weed Technol 1992;6:716–724.

Flury M, Yates MV, Jury WA, Anderson DL. Variability of solute transport in field lysimeters. In: Führ F, Hance R.J., Plimmer J.R., Nelson J.O. (Eds.), The lysimeter concept. ACS Symposium series 699, 1998, pp. 65–75.

Franke HJ, Teutsch HJ. Stochastic simulation of the regional pesticide transport including the unsaturated and the satu-rated zone. Ecol Model 1994;75:529–539.

Freissinet C, Erlich M, Vauclin M. A fuzzy logic-based approach to assess imprecisions of soil water contamination modelling. Soil Till Res 1998;47:11–17.

Freissinet C, Vauclin M, Erlich M. Comparison of first-order analysis and fuzzy set approach for the evaluation of imprecision in a pesticide groundwater pollution screening model. J Contam Hydrol 1999;37:21–43.

Friedl MA, McGwire KC, McIver DK. An overview of uncertainty in optical remotely sensed data for ecological applications. In: Hunsaker CT, Goodchild MF, Friedl MA, Case TJ, editors. Spatial uncertainty in ecology. New York: Springer-Verlag, 2001. p. 258–283.

Garen D, Woodward D, Geter F. A user agency's view of hydrologic, soil erosion and water quality modelling. Catena 1999;37:277–289.

Gaunt JL, Riley J, Stein A, Penning de Vries FWT. Require-ments for effective modelling strategy. Agr Syst 1997;54:153–168.

Gerstl Z. An update on the Koc concept in regard to regional scale management. Crop Prot 2000;19:643–648.

Goodchild M, Gopal S. Accuracy of spatial databases. London, UK: Taylor and Francis, 1989. p. 290

Goodrich DC, Faures JM, Woolhiser DA, Lane LJ, Sorooshian S. Measurement and analysis of small-scale convective storm rainfall variability. J Hydrol 1995;173:283–308.

Greig-Smith PW. A European perspective on ecological risk assessment, illustrated by pesticide registration procedures in the United Kingdom. Environ Toxicol Chem 1992;11:1673–1689.

Gustafson DI, Holden LR. Nonlinear pesticide dissipation in soil: a new model based on spatial variability. Environ Sci Technol 1990;24:1032–1038.

Hallet SH, Thanigasalam P, Hollis JM. SEISMIC: a desktop information system for assessing the fate and behaviour of pesticides in the environment. Comput Electron Agr 1995;13:227–242.

Hamaker JW, Thompson JM. Adsorption. In: Goring CA, Hamaker JW, editors. Organic chemicals in the soil envi-ronment. New York: Marcel Dekker, 1972. p. 49–143.

Hamaker JW. The interpretation of soil leaching experiments. In: Haque R, Freed VH, editors. Environmental dynamics of pesticides. New York: Plenum Press, 1975. p. 115–133.

Hamlett JM, Horton R, Cressie NAC. Resistant and exploratory techniques for use in semivariogram analyze. Soil Sci Soc Am J 1986;50:868–875.

Heber V, Siebers J, Nolting HG, Vetten HJ, Kreuzig R, Bahadir M. Investigations on the applicability of two ELISA types for the determination of chlorpyrifos in soil samples com-pared with a gas chromatographic method. Fresen J Anal Chem 1998;360:739–741.

Heuvelink GBM. Error propagation in environmental model-ling with GIS. London: Taylor and Francis, 1998. p. 127

Heuvelink GBM, Pebesma EJ. Spatial aggregation and soil process modelling. Geoderma 1999;89:47–65.

Hoffman FO, Hammonds JS. Propagation of uncertainty in risk assessments: the need to distinguish between uncertainty due to lack of knowledge and uncertainty due to variability. Risk Anal 1994;14:707–712.

Hollis JM, Hallett SH, Keay CA. The development and application of an integrated database for modelling the environmental fate of pesticides. In: Proceedings Brighton Crop Protection Conference–Weeds, 1993, pp. 1355–1364.

IAEA. Evaluating the reliability of predictions made using environmental transfer models. Safety series No. 100, Vienna, Austria, 1989, 106.

Iman RL, Conover WJ. A distribution-free approach to inducing rank correlation among input variables. Commun Stat B-Simul 1982;11:311–334.

Inskeep WP, Wraith JM, Wilson JP, Snyder RD, Macur RE, Gaber HM. Input parameter and model resolution effects on predictions of solute transport. J Environ Qual 1996;25:453–462.

Jacques D, Mouvet C, Mohanty B, Vereecken H, Feyen J. Spatial variability of atrazine sorption parameters and other soil properties in a podzoluvisol. J Contam Hydrol 1999;36:31–52.

Jager T, Vermeire TG, Rikken MGJ, van der Poel P. Opportunities for a probabilistic risk assessment of chemicals in the European Union. Chemosphere 2001;43:257–264.

Jansen MJW. Prediction error through modelling concepts and uncertainty from basic data. Nutr Cycl Agroecosys 1998;50:247–253.

Jarvis NJ, Brown CD, Granitza E. Sources of error in model predictions of pesticide leaching: a case study using the MACRO model. Agr Water Manage 2000;44:247–262.

Jaynes DB, Novak JM, Moorman TB, Cambardella CA. Estimating herbicide partition coefficients from electromagnetic induction measurements. J Environ Qual 1995;24:36–41.

Johnson JA, Farmer WJ. Batch vs. column method for determining distribution of organics between soil and water phases. Soil Sci 1993;155:92–99.

Johnson DH, Shaner DL, Deane J, Mackersie LA, Tuxhorn G. Time-dependent adsorption of imazethapyr to soil. Weed Sci 2000;48:769–775.

Jury WA, Gruber J. A stochastic analysis of the influence of soil and climatic variability on the estimate of pesticide groundwater pollution potential. Water Resour Res 1989;25:2465–2474.

Jury WA, Focht DD, Farmer WJ. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. J Environ Qual 1987;16:422–428.

Kelly EJ, Campbell K. Separating variability and uncertainty in environmental risk assessment–making choices. Hum Ecol Risk Assess 2000;6:1–13.

Koskinen WC, Cecchi AM, Dowdy RH, Norberg KA. Adsorption of selected pesticides on a rigid PVC lysimeter. J Environ Qual 1999;28:732–734.

Krajewski WF, Kruger A, Nespor V. Experimental and numerical studies of small-scale rainfall measurements and variability. Water Sci Technol 1998;37:131–138.

Lafrance P, Banton O. Implication of spatial variability of organic carbon on predicting pesticide mobility in soil. Geoderma 1995;65:331–338.

Leake CR, Humphreys SP, Austin DJ. Factors influencing the modelling of pesticide degradation in soil and the estimation of half-life (DT50) and DT90 values. In: Pesticide movement to water, BCPC monograph No. 62, 1995, 195–200.

Lennartz B. Variation of herbicide transport parameters within a single field and its relation to water flux and soil properties. Geoderma 1999;91:327–345.

Li ZC, Yost RS, Green RE. Incorporating uncertainty in a chemical leaching assessment. J Contam Hydrol 1998;29:285–299.

Loague K. The impact of land use on estimates of pesticide leaching potential: assessements and uncertainties. J Contam Hydrol 1991;8:157–175.

Loague K. Regional scale groundwater vulnerability estimates: impact of reducing data uncertainties for assessments in Hawaii. Ground Water 1994;32:605–616.

Loague K, Bernknopf RL, Green RE, Giambelluca TW. Uncertainty of groundwater vulnerability assessments for agricultural regions in Hawaii: review. J Environ Qual 1996;25:475–490.

Ma L, Ascough JC, Ahuja LR, Shaffer MJ, Hanson JD, Rojas KW. Root zone water quality model sensitivity analysis using Monte Carlo simulation. T ASAE 2000;43:883–895.

Maund SJ, Travis KZ, Hendley P, Giddings JM, Solomon K. Probabilistic risk assessment of cooton pyrethroids: V Combining landscape-level exposures and ecotoxicological effects data to characterize risks. Environ Toxicol Chem 2001;20:687–692.

Melching CS. Reliability estimation. In: Singh VP, editor. Computer models of watershed hydrology. CO: Water Resources Publication, 1995. p. 69–118.

Millstein JA. Propagation of measurement errors in pesticide application computations. Int J Pest Manage 1994;40:159–165.

Morgan MG, Henrion M. Uncertainty: a guide to dealing with uncertainty in quantitative risk and policy analysis. New York: Cambridge University Press, 1990. p. 353

Mosleh A. Hidden sources of uncertainty: judgement in the collection and analysis of data. Nucl Eng Des 1986;93:187–198.

Mouvet C, Jücker C. Influence of various filters on the concentration of pesticides dissolved in water. Environ Sci Technol 1997;31:2434–2437.

Mowrer HT. Uncertainty in natural resource decision support systems: sources, interpretation and importance. Comput Electron Agr 2000;27:139–154.

Nemes A, Wösten JHM, Lilly A, Oude Voshaar JH. Evaluation of different procedures to interpolate particle-size distributions to achieve compatibility within soil databases. Geoderma 1999;90:187–202.

Nofziger DL, Chen JS, Haan CT. Evaluating the chemical movement in layered soil model as a tool for assessing risk of pesticide leaching to groundwater. J Environ Sci Heal A 1994;29:1133–1155.

Northcott GL, Jones KC. Spiking hydrophobic organic compounds into soil and sediment: a review and critique of adopted procedures. Environ Toxicol Chem 2000;19:2418–2430.

Novak JM, Moorman TB, Cambardella CA. Atrazine sorption at the field scale in relation to soils and landscape position. J Environ Qual 1997;26:1271–1277.

Oliveira RS, Koskinen WC, Ferreira FA, Khakural BR, Mulla DJ, Robert P. Spatial variability of imazethapyr sorption in soil. Weed Sci 1999;47:243–248.

Oreskes N. Evaluation not validation; of quantitative models. Environ Health Persp 1998;106:1453–1460.

Ott WR. A physical explanation of the log–normality of pollutant concentrations. JAPCA J Air Waste Mater 1990;40:1378–1383.

Pachepsky YA, Rawls WJ, Timlin DJ. The current status of pedotransfer functions: their accuracy, reliability, and utility in field- and regional-scale modelling. In: Corwin DL, Loague K, Ellsworth T, (Eds.) Assessment of non-point source pollution in the vadose zone. AGU Geophysical Monograph 108, 1999, pp. 223–234.

Parkin TB. Spatial variability of microbial processes in soil–a review. J Environ Qual 1993;22:409–417.

Pollock D, Salama R, Kookana R. A study of atrazine transport through a soil profile on the Gnangara Mound, Western Australia, using LEACHP and Monte Carlo techniques. Aust J Soil Res 2002;40:455–464.

Price OR, Walker A, Wood M, Oliver MA. Using geostatistics to evaluate spatial variation in pesticide/soil interactions. In: Walker A., (Ed.), Pesticide behaviour in soils and water, BCPC Symposium Proceedings No. 78, Farnham, UK, 2001, pp. 233–238.

Ramsey MH. Sampling as a source of measurement uncertainty: techniques for quantification and comparison with analytical sources. J Anal Atom Spectrom 1998;13:97–104.

Rao PSC, Davidson JM. Retention and transformation of selected pesticides and phosphorus in soil–water systems: a critical review. EPA 600/3-82-060, 1982.

Rao PSC, Wagenet RJ. Spatial variability of pesticides in field soils: methods for data analysis and consequences. Weed Sci 1985;33:18–24.

Russell MH, Layton RJ, Tillotson PM. The use of pesticide leaching models in a regulatory setting–an industrial perspective. J Environ Sci Heal A 1994;29:1105–1116.

Saltelli A, Chan K, Scott EM. Sensitivity analysis. Chichester, UK: John Wiley and Sons, 2000. p. 475

Shaw LJ, Burns RG. Biodegradation-transport interactions of pulse applied 2,4-D in repacked soil column microcosms. J Environ Qual 1998;27:1472–1478.

Shimizu Y, Yamazaki S, Tersahima Y. Sorption of anionic pentachlorophenol in aquatic environments: the effect of pH. Water Sci Technol 1992;25:41–48.

Shukla S, Mostaghimi S, Shanholt VO, Collins MC, Ross BB. A county-level assessment of ground water contamination by pesticides. Ground Water Monit R 2000;20:104–119.

Simmonds LP, Nortcliff S. Small scale variability in the flow of water and solutes, and implications for lysimeter studies of solute leaching. Nutr Cycl Agroecosys 1998;50:65–75.

Singh G, van Genuchten MT, Spencer WF, Cliath MM, Yates SR. Measured and predicted transport of two *s*-triazine herbicides through soil columns. Water Air Soil Poll 1996;86:137–149.

Smith CN, Parrish RS. A field study to evaluate leaching of aldicarb, metolachlor and bromide in a sandy loam soil. J Environ Qual 1993;22:562–577.

Smith AE, Ryan PB, Evans JS. The effect of neglecting correlations when propagating uncertainty and estimating the population distribution of risk. Risk Anal 1992;12:467–474.

Solomon K, Giesy J, Jones P. Probabilistic risk assessment of agrochemicals in the environment. Crop Prot 2000;19:649–655.

Soulas G, Lagacherie B. Modelling of microbial degradation of pesticides in soils. Biol Fert Soils 2001;33:551–557.

Soutter M, Pannatier Y. Groundwater vulnerability to pesticide contamination on a regional scale. J Environ Qual 1996;25:439–444.

Soutter M, Musy A. Coupling 1D Monte-Carlo simulations and geostatistics to assess groundwater vulnerability to pesticide contamination on a regional scale. J Contam Hydrol 1998;32:25–39.

Soutter M, Musy A. Global sensitivity analyses of three pesticide leaching models using a Monte Carlo approach. J Environ Qual 1999;28:1290–1297.

Stine PA, Hunsaker CT. An introduction to uncertainty issues for spatial data used in ecological applications. In: Hunsaker CT, Goodchild MF, Friedl MA, Case TJ, editors. Spatial uncertainty in ecology. New York: Springer, 2001. p. 91–107.

Tarantola S, Giglioli N, Jesinghaus J, Saltelli A. Can global sensitivity analysis steer the implementation of models for environmental assessments and decision-making? Stoch Environ Res Risk A 2002;16:63–76.

Tietje O, Hennings V. Bewertung von Pedotransferfunktionen zur Schätzung der Wasserspannungskurve. Z Pflantzenernähr Bodenk 1993;156:447–455.

Tietje O, Tapkenhinrichs M. Evaluation of pedo-transfer functions. Soil Sci Soc Am J 1993;57:1088–1095.

Tiktak A, Leijnse A, Viddenberg H. Uncertainty in a regional-scale assessment of cadmium accumulation in the Netherlands. J Environ Qual 1999;28:461–470.

Tiktak A. Application of pesticide leaching models to the vredepeel dataset. II Pesticide fate. Agr Water Manage 2000;44:119–134.

Topp E, Smith W. Sorption of herbicides atrazine and metolachlor to selected plastics and silicone rubber. J Environ Qual 1992;21:316–317.

Travis KZ. Pesticide leaching models–past, present and future. In: Proceedings of the Brighton Crop Protection Conference–Pests and Diseases, BCPC, Farnham, Surrey, UK, 2000, pp. 69–76.

Trevisan M, Calandra R, Vischetti C, Esposito A, Padovani L. Pesticide leaching potential in the Trasimeno Lake area. Assessment of uncertainty associated with the simulation process. In: Walker A, (Ed.) Pesticide behaviour in soils and water, BCPC Symposium Proceedings No. 78, Farnham, UK, 2001, pp. 245–250.

Ukrainczyk L, Ajwa HA. Primisulfuron sorption on minerals and soils. Soil Sci Soc Am J 1996;60:460–467.

US EPA. Summary report for the workshop on Monte Carlo analysis, EPA/630/R-96/010, Risk assessment forum, Washington, DC, 1996.

van der Zee SEATM, Boesten JJTI. Effects of soil heterogeneity on pesticide leaching to groundwater. Water Resour Res 1991;27:3051–3063.

van der Zee SEATM, Boesten JJTI. Pesticide leaching in heterogeneous soils with oscillating flow: approximations. Sci Total Environ 1993;132:167–179.

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

Vereecken H. Derivation and validation of pedotransfer functions for soil hydraulic properties. In: van Genuchten MT, Leij FJ, editors. Indirect methods for estimating the hydraulic properties of unsaturated soils. Riverside: University of California, 1992. p. 473–488.

Verschoor AJ, Boesten JJTI, Leistra M, van der Linden AMA, Linders JBHJ, Pol JWW. Evaluation of pesticide leaching in lysimeter and field studies. Parent substances. RIVM report 601506 007/2001, 2001, 44.

Verro R, Calliera M, Maffioli G, Auteri D, Sala S, Finizio A, Vighi M. GIS-based system for surface water risk assessment of agricultural chemicals. 1. Methodological approach. Environ Sci Technol 2002;36:1532–1538.

Vink JPM, Gottesbüren B, Diekkrüger B, van der Zee SEATM. Simulation and model comparison of unsaturated movement of pesticides from a large clay lysimeter. Ecol Model 1997;105:113–127.

Vischetti C, Businelli M, Marini M, Capri E, Trevisan M, DelRe AAM, Donnaruma L, Conte E, Imbroglini G. Characterisation of spatial variability structure in three separate field trials on pesticide dissipation. Pestic Sci 1997;50:175–182.

Vischetti C, Perniola M, Scarponi L, Tarantino E. Field and lysimeter study on the leaching of bromide ion and the herbicides imazethapyr and bentazone in a clay loam soil in southern Italy. Fresen Environ Bull 1998;7:641–648.

Vischetti C, Scarponi L, Esposito A, Vianello M, Zanin G. Characterisation of the structure of spatial variability for initial pesticide concentration in a field trial. In: Walker A (Ed.), Pesticide behaviour in soils and water. BCPC Symposium Proceedings No. 78, Farnham, UK, 2001, pp. 295–300.

Viton P. Pluviomètres et pluviographes utilises par la Météorologie Nationale. Techniques d'étude des facteurs physiques de la biosphère. Paris: INRA, 1970. p. 245–253.

Vose D. Risk analysis, a quantitative guide. Chichester, UK: John Wiley and Sons Ltd, 2000. p. 418

Walker A, Brown PA. Effects of soil storage on degradation rates of metamitron, atrazine and propyzamide. Proceedings of the EWRS Symposium: Theory and practice of the use of soil applied herbicides, 1981, pp. 63–71.

Walker A, Brown PA. Spatial variability in herbicide degradation rates and residues in soil. Crop Prot 1983;2:17–25.

Walker A, Jurado-Exposito M, Bending GD, Smith VJR. Spatial variability in the degradation rate of isoproturon in soil. Environ Pollut 2001;111:407–415.

Walker A, Bromilow RH, Nicholls PH, Evans AA, Smith VJR. Spatial variability in the degradation rates of isoproturon and chlorotoluron in a clay soil. Weed Res 2002;42:39–44.

Warren-Hicks WJ, Moore DRJ. Uncertainty analysis in ecological risk assessment. Proceedings from the Pellston workshop on uncertainty analysis in ecological risk assessment, August 23–28, 1995, Society of Environ Toxicol Chem, 1998, pp. 341.

Warren-Hicks W, Carbone JP, Havens PL. Using Monte Carlo techniques to judge model prediction accuracy: validation of the pesticide root zone model 3.12. Environ Toxicol Chem 2002;21:1570–1577.

Wauchope RD, Yeh S, Linders JBHJ, Kloskowski R, Tanaka K, Rubin B, Katayama A, Kordel W, Gerstl Z, Lane M, Unsworth JB. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag Sci 2002;58:419–445.

Webster R, Oliver MA. Geostatistics for environmental scientistsJohn Wiley and Sons Ltd, 2001. p. 286

Wolt JD, Nelson HP, Cleveland CB, van Wesenbeeck IJ. Biodegradation kinetics for pesticide exposure assessment. Rev Environ Contam T 2001;169:123–164.

Wolt J, Singh P, Cryer S, Lin J. Sensitivity analysis for validating expert opinion as to ideal data set criteria for transport modelling. Environ Toxicol Chem 2002;21:1558–1565.

Wood LS, Scott HD, Marx DB, Lavy TL. Variability in sorption coefficients of metolachlor on a Captina silt loam. J Environ Qual 1987;16:251–256.

Wösten JHM, Veerman GJ, Stolte J. Water retention and hydraulic conductivity characteristics of topsoils and subsoils in the Netherlands: the Staring series. Technical document 18, DLO-Winand Staring Centre, Wageningen, The Netherlands, 1994, 66.

Wösten JHM, Lilly A, Nemes A, Le Bas C. Development and use of a database of hydraulic properties of European soils. Geoderma 1999;90:169–185.

Wu QJ, Ward AD, Workman SR, Salchow EM. Applying stochastic simulation techniques to a deterministic vadose zone solute transport model. J Hydrol 1997;197:88–110.

Yapo PO, Gupta HV, Sorooshian S. Multi-objective global optimization for hydrologic models. J Hydrol 1998;204:83–97.

Yost R, Loague K, Green RE. Reducing variance in soil organic carbon estimates: soil classification and geostatistical approaches. Geoderma 1993;57:247–262.

Zacharias S, Heatwole CD, Persaud N, Bruggeman AC, Kumar D, Smith CN. Stochastic simulation of field-scale pesticide transport using opus and GLEAMS. J Environ Qual 1999;28:411–423.

Zhang J, Goodchild MF. Uncertainty in geographical information. London: Taylor and Francis, 2002. p. 266

Zhang H, Haan CT, Nofziger DL. An approach to estimating uncertainties in modeling transport of solutes through soils. J Contam Hydrol 1993;12:35–50.