Using geostatistics to evaluate spatial variation in pesticide/soil interactions

O R Price, A Walker
HRI, Wellesbourne, Warwick, CV35 9EF, UK
Email: Oliver.Price@hri.ac.uk

M Wood, M A Oliver
University of Reading, Soil Science, Whiteknights, Reading, RG6 6DW, UK

ABSTRACT

The scale and structure of the spatial variation in degradation of isoproturon, chlorpyrifos and chlorothalonil were quantified. Degradation rates of the three pesticides all showed similar structures in their spatial variation and their persistence was shown to be strongly correlated with both pH and microbial activity estimated by dehydrogenase activity.

INTRODUCTION

It is well known that soil properties vary in space and this variation appears to be random but spatially dependent. Flury (1996) commented that in terms of pesticide fate modelling, aspects of spatial variation in pesticide-soil interactions have generally been ignored, and that there is little information concerning the structure and scale of variation in pesticide fate. Recent work has shown that significant spatial variation occurs in isoproturon (IPU) degradation rates (Walker *et al.*, 2001; Wood *et al.*, 2001) and sorption (Lennartz, 1999) within a single field. There is a need to evaluate the significance of this spatial variation in degradation and sorption in terms of pesticide performance at the field scale and the assessment of environmental fate. Novak *et al.*, (1997) investigated the variation in sorption of atrazine within a field, and used geostatistical techniques to quantify the scale and structure of the variation observed. Richter *et al.*, (1996) reviewed the role of geostatistics in the modelling of pesticide fate.

The method of geostatistical estimation is known as kriging. The main aim of the present work was to use kriging to identify the spatial patterns in pesticide degradation rate and sorption across a specific study area. A secondary objective was to define an approach for soil sampling that would be suitable to estimate the behaviour of pesticides within a single field.

METHODS AND MATERIALS

Field site and sampling strategy

The study area was Deep Slade field at Horticulture Research International, Wellesbourne (grid ref: 426820,255600). The soil was classified as a sandy loam of the Wick Series.

In January 2000, a 240 m x 240 m grid was located in Deep Slade field with nine main grid nodes at 120 m intersections, which were located using an electronic distance measurement machine (Geodimeter 400). The grid covered most of the study site with a boundary of 30 m around the edge of the field. The sampling scheme was an unbalanced nested design, and a hierarchical analysis was used to estimate the components of variance associated with different scales and minimise the number of samples required (see Webster & Oliver, 2001). The scheme covered a range of distances in a single analysis with a minimal number of samples. A sampling interval of 1 m was chosen for the lowest stage as this was expected to encompass most of the small scale variation. The other intervals followed an approximate three-fold geometric progression with further samples at 3, 9 and 27 m, with two further stages at 60 and 120 m. Although the position of the nine main nodes was predetermined (120 m spacing), the positions of all other sampling points were located on random orientations. In total 108 soil samples were collected with 12 samples from each node (Figure 1).

In January 2001, a 180 m x 180 m grid was relocated in Deep Slade field to cover an area within that sampled in the previous year. A soil sample was taken every 20 m along the horizontal and vertical lines of the grid to give a total of 100 soil samples from the study area.

Soil analyses

Individual soil samples of about 1 kg were collected from each sampling position in both years. Precautions were taken to minimise cross contamination between samples (Walker *et al.*, 2001). The soil samples were left to air-dry overnight before being sieved to 2 mm. The sieves were cleaned with ethanol and dried in an oven at $110^{\circ}C$ between successive samples to further minimise microbial cross-contamination. Soil pH was measured using a glass electrode in a 1:2.5 suspension of soil/distilled water and organic matter content was estimated by loss on ignition at $450^{\circ}C$ (Rowell, 1994). Soil dehydrogenase activity was measured as outlined by Tabatabai (1994) and microbial biomass was estimated by the fumigation-extraction method (Mele & Carter, 1996).

Soil incubations and pesticide residue analysis

Soil samples taken in January 2000 from the nine main grid nodes were used to measure the average maximum water holding capacity (MWHC) and the average moisture content at 40% MWHC was then derived. Four sub-samples (25 g) from each of the 108 samples were weighed into glass jars (125 ml). All sub-samples were treated with an aqueous suspension of a commercial formulation of isoproturon (Arelon SC) to give an initial concentration of 15 mg IPU/kg soil. Soil moisture contents were adjusted to 40% of the average MWHC. A treatment check was carried out after every 50 samples dosed to ensure constant application rates. All soil samples were incubated at $15^{\circ}C$ and moisture contents were maintained by addition of sterile distilled water when required (usually once a week). Samples were extracted at 7, 14, 21 and 35 days after application, and four extractions immediately after application were made with soil from each of the nine main grid nodes. After the first day of incubation, all samples were shaken gently to thoroughly mix the IPU throughout the soil. Isoproturon residues were extracted by shaking the soil samples with 30 ml of acetonitrile/water (90/10 v/v) in the 125 ml glass jars on a wrist shaker for 60 minutes.

The average MWHC for the soil samples collected in January 2001 was determined as above. Three sub-samples (25 g) from each of the 100 soil samples were weighed into glass jars (125 ml). The soils were dosed individually to obtain 15 mg/kg of IPU, chlorpyrifos or chlorothalonil. They were incubated as before and the pesticide residues were extracted as above at 21, 35 and 69 d for chlorothalonil, IPU and chlorpyrifos, respectively.

Pesticide concentrations were measured by high performance liquid chromatography (hplc) using Kontron Series 300 equipment. The column used was a Lichrosorb RP-18 (25 cm x 4 mm i.d., Merck). The solvent system used for isoproturon and chlorothalonil was acetonitrile:water:orthophosphoric acid (75:25:0.25 by volume) at a flow rate of 1 ml/min. Detection of these two pesticides was by UV absorbance at 240 nm and 235 nm, respectively. Chlorpyrifos was analysed at 240 nm using a mobile phase of 85:15 acetonitrile:water.

RESULTS & DISCUSSION

The relationship between soil pH and IPU remaining after 21 days was non-linear (Figure 2). Soil samples with pH less than 6.7 generally contained high residues of IPU and those with pH greater than 7.0 had considerably lower IPU residues. Similar relationships were observed between IPU residues and total microbial biomass, with high IPU residues in soil samples with less than 100 mg microbial C/kg.
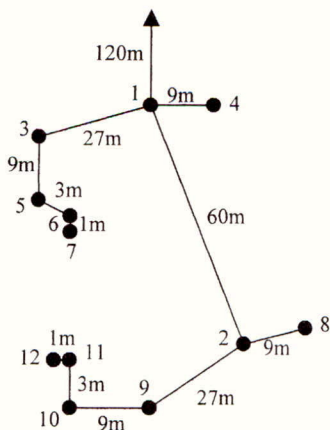
Figure 1. Spatial configuration of sampling points for one of nine main grid nodes
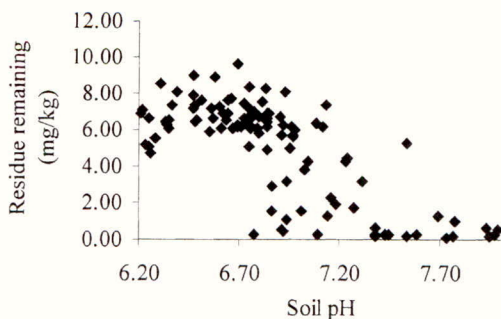
Figure 2. The relationship between IPU residues and soil pH (nested sampling)

The accumulated components of variance for the soil properties and IPU residues were plotted against distance on a logarithmic scale as a first approximation to the variograms. Generally the results indicated that the components of variance for the five lower stages accounted for at least 60% of the total variance i.e. a large proportion of the variation occurred at less than 60 m (e.g. IPU residues; Figure 3a). An exception was soil pH (Figure 3b) where stage 1 (120 m) accounted for 55% of the total variation. The sampling scheme generally accounted for much of the variation observed. A larger interval (>120m), however,

would begin to explain the unresolved variation observed above 60 m. Walker *et al.*, (2001) measured the variation of IPU degradation at sampling intervals of 50 m. The data in Figure 3a show that 50% of the variation observed in degradation occurred at less than 27 m, indicating that a smaller sampling interval would be optimal for the measurement of IPU degradation. However, sampling for soil pH at a spacing of less than 60 m would be a waste of resources and time as only 27.6% of the variation is accounted for at less than 27 m.
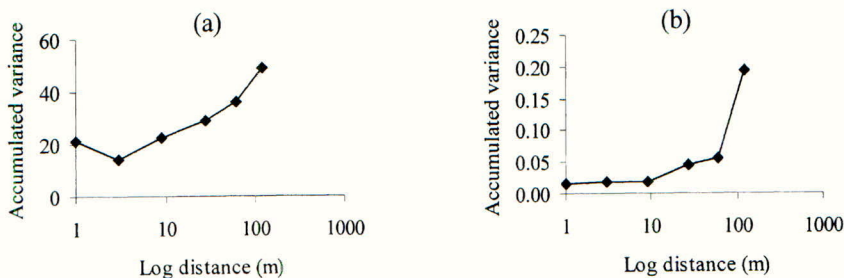

Figure 3. Accumulated components of variance plotted against distance on logarithmic scale: for: (a) IPU residues and (b) soil pH first approximation to variogram (nested sampling)

A 20 m interval was chosen for sampling in the second experiment to ensure that most of the variation in IPU persistence observed in the field would be accounted for. Most of the variates had near-normal distributions. Natural log-transformations were used to reduce skewness on data sets that were not normally distributed. Experimental variograms were computed from the data as described by Webster & Oliver (2001). Variogram models were fitted to the experimental values by weighted least squares approximation. The models that minimised the sums of squares were chosen. All the variables measured showed some evidence of spatial dependence. The nugget variances, i.e. the positive intercept on the ordinate were small suggesting that the sampling had resolved the variation well (with the exception of that for chlorothalonil). This embraces measurement error, but mainly variation associated to distances less than the sampling interval used. All of the variograms were bounded and had ranges varying between 60 m and 90 m, e.g. chlorpyrifos residues (Figure 4a) and dehydrogenase activity (Figure 4b). Using the appropriate variogram model and data for each variable, the kriging equations were solved to obtain estimates at 10 m intervals and the associated estimation errors for a block size of 10 m.
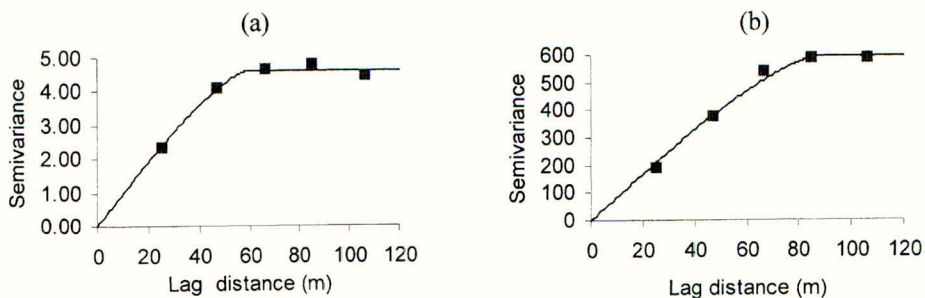

Figure 4. Variograms for: (a) chlorpyrifos residues and (b) dehydrogenase activity (grid sample)

The kriged estimates of the soil properties and pesticide persistence were contoured and mapped so that their patterns of variation could be examined (Figure 5a-5d). The maps of all of the variables show a distinctly patchy distribution in the values. The maps of dehydrogenase, soil pH (data not shown) and residues of the three pesticides all show similar distribution patterns. The variogram models for the pesticides and the soil properties were also similar with ranges of approximately 70 m. The northern part of Deep Slade field showed high values for dehydrogenase activity and soil pH and these correspond well with small values of pesticide residues. The extremes of this relationship are shown well in the contoured maps, Figure 5.
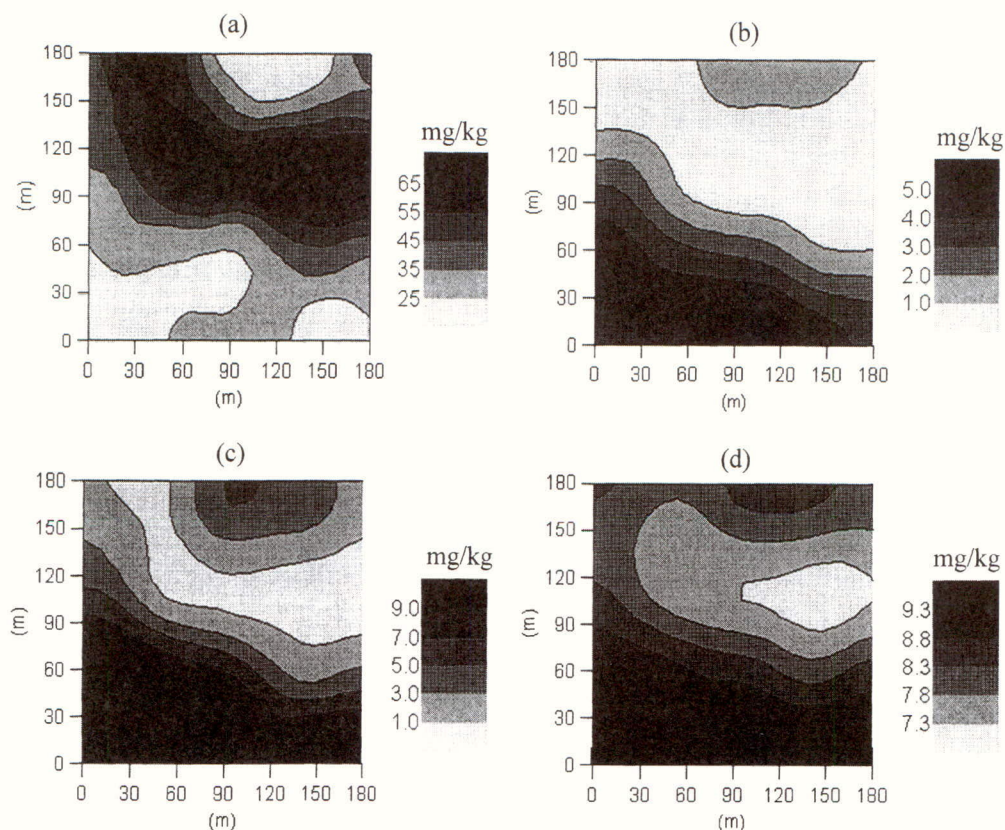

Figure 5   Map of kriged estimates for: (a) soil dehydrogenase activity, (b) IPU residues (35 days), (c) chlorpyrifos residues (69 days), (d) chlorothalonil residues (21 days). Based on laboratory measurements on samples from Deep Slade field (2001). The quantities of pesticide are expressed as residues remaining from an initial concentration of 15 mg/kg.

For the modelling of the environmental fate of pesticides, geostatistics has the potential to describe the variation accurately. It has been shown to provide an insight into the scale at which variation in pesticide degradation rate (and sorption) occurs within the study site. It

has enabled conclusions to be drawn concerning the effect of soil properties on pesticide degradation even when conventional correlation analysis does not suggest significant relationships. The data can be used to indicate areas at high risk with respect to pesticide leaching. After running the LEACHP model for 208 sub-sites within a single field Oliver *et al.,* (1999) concluded that significant leaching losses of atrazine would occur from only 10% of the 9 ha site, and the contribution through leaching to groundwater from the other 90% would be negligible. The data presented here indicate that small areas of Deep Slade field (where persistence is greater) would contribute more to possible leaching losses and that there is large within-field variation in the variables controlling pesticide availability.

ACKNOWLEDGEMENTS

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Sources of uncertainty in pesticide fate modelling

I G Dubus, C D Brown, S Beulke

Cranfield Centre for EcoChemistry, Cranfield University, Silsoe, Beds MK45 4DT, UK
E-mail: i.dubus@cranfield.ac.uk

ABSTRACT

Current risk assessment procedures for estimating the possible environmental impact of crop protection products do not explicitly account for uncertainty in exposure estimates and ecotoxicological endpoints. The level of protection provided by the use of safety factors in the risk quotient approach is unknown. Probabilistic risk assessment is considered as a possible refinement to procedures in place and Monte Carlo approaches have been proposed to obtain more realistic assessments of exposure. A number of scientific challenges need to be met for the approach to be robust and useful with regard to risk assessment. These include: i) attributing probability density functions to input parameters and choosing how much uncertainty to include in the analysis; ii) addressing correlation between parameters; iii) dealing with sources of uncertainty which are not covered by Monte Carlo simulations; and, iv) making decisions on the basis of probabilistic information. Effective risk communication is essential for probabilistic risk assessment to be accepted by all stakeholders.

INTRODUCTION

Current environmental risk assessment procedures for pesticide registration in the EU rely on the comparison between exposure and ecotoxicological endpoints (surface waters) or a legal threshold concentration (groundwater). A tiered approach is implemented to focus on those compounds which might be harmful to the environment and not penalise those which pose little threat. Relevant ecotoxicological endpoints are typically derived by laboratory tests using a range of representative organisms although a range of relationships between ecotoxicity and compound properties may also be used in the early stages of the risk assessment. In contrast to the derivation of effect concentrations, the estimation of predicted environmental concentrations for exposure (PEC's) relies heavily on the use of predictive models, especially at higher tiers.

For surface waters, the ratio between PEC's and ecotoxicological endpoints is calculated (termed TER for Toxicity:Exposure Ratio) and compared to threshold values which are dependent on the target organism considered (typically 10 or 100). A compound is considered to pose little threat to surface water organisms if TERs exceed the relevant threshold. For groundwater, PEC's for the parent are compared to a limit concentration of 0.1 µg a.i./l, irrespective of the toxicity and ecotoxicity of the compound.

Current risk assessment procedures are likely to be subject to significant uncertainty originating from both the exposure and the effects side. Uncertainty is indirectly taken into account in the process through the use of TER threshold values which act as safety factors. The level of protection provided by these safety factors is unknown and a number of

initiatives are currently underway to try to quantify associated safety margins. Uncertainty in the derivation of ecotoxicological endpoints may arise, for instance, from not knowing the most sensitive species or from the use of constant concentration in laboratory tests. A range of initiatives have been proposed to make ecotoxicological endpoints more realistic, including the establishment of species sensitivity distribution, the refinement of experimental conditions and the use of microcosm/mesocosm studies. Uncertainty on the exposure side may be addressed using probabilistic modelling.

The present paper presents the different sources of uncertainty in the assessment of PEC's and discusses the appropriateness of methods proposed to deal with uncertainty in exposure.

SOURCES OF UNCERTAINTY IN PESTICIDE FATE MODELLING

"Uncertainty" is a capacious term used to encompass a multiplicity of concepts (Morgan and Henrion, 1990). According to these authors, uncertainty in empirical quantities may be classified according to the different sources from which it can arise: random error and statistical variation, systematic error and subjective judgement, linguistic imprecision, variability, randomness and unpredictability, disagreement, and approximations. Uncertainty may also originate for other reasons, for instance from the fact that environmental models only provide an incomplete description of reality. For the purpose of clarity, we use a classification of sources of uncertainty based on their occurrence in relation to the modelling.

Uncertainty arising prior to any modelling activity

Although a number of input parameters in pesticide leaching models have no physical basis and cannot be determined experimentally, values for most inputs can be estimated on the basis of field or laboratory measurements. Examples include model input related to soil and that related to pesticide sorption and degradation properties. The field environment is inherently variable in space and time and this variability will introduce uncertainty into the modelling. Wood *et al.,* (1987) reported Koc values varying from 66 to 1445 l/kg in a 4-ha field (coefficients of variations 17-47%) while Elabd *et al.,* (1986) reported a CV of 38% for the Koc of napropamide in a 0.6-ha plot. Walker *et al.,*(2001) found large variation of isoproturon degradation in 30 samples taken from a 5-ha field (DT50 6.5 to 30 days). Apart from natural variations at the field scale, variability arising prior to modelling may originate from the use of different sampling techniques in the field, differences in sample storage and preparation (e.g. frozen vs. refrigerated soil samples; air dried vs. moist soil samples), the use of different procedures for analytical measurements or different environmental conditions in the laboratory.

Uncertainty arising from model parameterisation

One of the most important stages in modelling is the attribution of a value to each input parameter of the model. Although experimental data can be directly fed into the model in some instances (e.g. rainfall and temperature data, molecular weight of the compound), model parameterisation traditionally requires manipulation of field or laboratory measurements. Uncertainty may arise because of the variety of procedures in deriving an input value from experimental data. The derivation of a DT50 value from a set of laboratory degradation data is a typical example. Leake *et al.,* (1995) used a degradation dataset (decrease in pesticide

concentrations over time) and calculated DT50 values using a range of equations and fitting packages. Resulting DT50 values ranged between 4 and 93 days (mean 27.9 days; median 21.0 days). Uncertainty in the selection of a DT50 value may then arise from the selection of a representative value (typically mean or median) from a range of values derived for different soils or different environmental conditions. Where data are missing or cannot fully support the selection of input values, the model is parameterised using established numerical relationships (e.g. pedotransfer functions) or expert judgement. These estimation methods which are likely to introduce uncertainty into the modelling are also used for attributing values to parameters which do not have a physical basis and cannot be determined experimentally.

Other types of uncertainty

Other significant sources of uncertainty which are less well documented are: i) the influence of model selection on risk assessment results; ii) the influence of the modeller on modelling results (user subjectivity); iii) the fact that models only provide an inaccurate description of field behaviour (model inaccuracy); and, iv) the individual subjectivity in decision making on the basis of probabilistic results. All these sources of uncertainty related to non-empirical quantities are typically ignored in probabilistic modelling.

METHODS TO INCORPORATE UNCERTAINTY INTO THE MODELLING

Methods available

A number of methods are available for taking into account the uncertainty associated with empirical quantities. These include *stochastic modelling* where model input and output are expressed probabilistically, *interval analysis* which is applicable where few assumptions on the form of the parameter variation can be made, *Monte Carlo simulations* where a number of input parameterS are attributed a statistical distribution reflecting their uncertainty and a large number of model runs are carried out, *first-order uncertainty analysis* where Taylor series expansion for key model equations is used, and *fuzzy logic* which describes imprecision in a non-probabilistic framework.

The Monte Carlo approach to integrating uncertainty into the modelling

The Monte Carlo approach to dealing with uncertainty has been used for numerous years in different fields of science and has been proposed as an adequate method for a probabilistic framework for pesticide exposure (ECOFRAM, 1999). This versatile approach is based on numerous runs of a model. Once parameters to be included in the analysis have been selected, a probability density function is attributed to each of them. This reflects the fact that these parameters are considered uncertain and can take a range of values. Correlations between input variables may be introduced into the analysis. A large number of input values for each parameter (say, 1000 values) are sampled randomly from the probability density functions using an adequate sampling procedures and these are used to generate 1000 model input files. The model is run for all these input files and model outputs are aggregated to enable a presentation of the results in probabilistic terms. An example of output of a probabilistic assessment of PEC's for groundwater is provided in Figure 1. The chart can be used to estimate the probability of simulating a concentration above or below a particular threshold.

In Figure 1, concentrations below 0.07 µg/l are predicted in 75% of the cases and the probability of the pesticide concentration exceeding the threshold of 0.1 µg/l is *ca.* 12%.
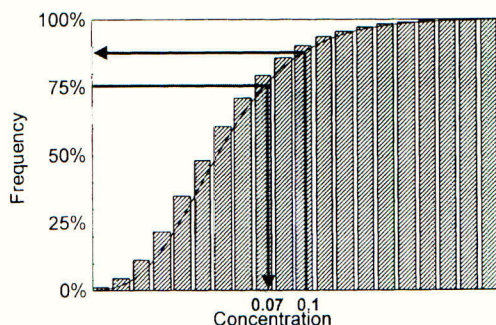

Figure 1.   Example of probabilistic modelling results.

DISCUSSION

The transfer of knowledge from fields of science where uncertainty has historically played an important role (nuclear safety in particular) to environmental risk assessment for chemicals has been extremely fast. Monte Carlo simulations are particularly used since they are easy to implement and understand by all stakeholders. Monte Carlo simulations have thus been considered the panacea for dealing with uncertainty and the challenges associated with the technique are frequently overlooked. These include i) attributing probability density functions to input parameters and choosing how much uncertainty to include in the analysis; ii) dealing with correlations; iii) integrating uncertainty other than that associated with empirical quantities (i.e. that not covered by Monte Carlo simulations); iv) making decisions on the basis of probabilistic information; and, v) communicating risk.

Attribution of probabilistic distributions to input parameters

The determining step in a Monte Carlo exercise is the description of the variation of selected input parameters using probability density functions. The attribution of these probability distributions should ideally be based on the examination of a large amount of data (say >100 datapoints). Generating so many data on the variation of input parameters of pesticide fate models for a particular situation is impractical and alternative methods have to be considered. These include the use of literature information on the likely pattern and magnitude of variations of model inputs and the use of expert judgement. These methods are likely to introduce subjectivity and uncertainty into the probabilistic approach and research is needed to estimate the influence of using different estimation methods and data sources on probabilistic results. Also, it is not clear how much uncertainty should be reflected by these probabilistic distributions. In the case of DT50 values or degradation rates, should probability density functions reflect the variation in values between different soils? the spatial variability in the field? the uncertainty introduced by differences in experimental and analytical conditions in the laboratory? that associated with the treatment of outliers? that arising with the derivation of values from a set of degradation data? that introduced by the choice of representative statistics to be used in the modelling? It is essential that the extent to which

uncertainty has been considered in the analysis is specified so that regulators can assess the confidence that should be assigned to risk estimations.

Correlations

If a positive correlation exists between variables, then ignoring these correlations in a probabilistic risk assessment will result in an underestimate of the extremes in environmental impact. Conversely, if correlations between variables are negative, the result will be overly conservative (Millstein, 1995). Although correlations can be handled through Monte Carlo simulations, specifying adequate correlations between parameters remains a challenge because of the lack of associated experimental data. For instance, one would expect some sort of correlation between sorption and degradation in the modelling of the fate of pesticides since increased sorption leads to a decrease of the compound in the liquid phase and hence smaller degradation (it is assumed that degradation mainly occurs in the liquid phase). Translating this intuitive relationship into correlation coefficients is not straightforward although it is felt that this might need integrating into the modelling in some way.

Uncertainty not covered by the Monte Carlo approach

The Monte Carlo approach, in common with most other methods for probabilistic modelling, concentrates on accounting for uncertainty in the values attributed to input parameters. Sources of uncertainty other than that related to empirical quantities are numerous and are likely to be significant (a few examples of these uncertainties are provided earlier in the text). These will be ignored in Monte Carlo analyses and will affect the confidence that should be assigned to results from probabilistic assessments.

Decision making on the basis of probabilistic information

Regulators currently make decisions with regard to the placement of crop protection products on the basis of a large amount of data which are brought together in a deterministic risk assessment. Although the approach is considered to be conservative, the lack of knowledge on the level of protection involved has prompted the application of probabilistic methods to environmental risk assessment for pesticides and a number of research projects on the subject have been initiated. Probabilistic outputs will quantify the likelihood of an adverse impact occurring. As such, there will need to be a revised definition of the regulatory endpoints as absolute protection is *de facto* impossible within a probabilistic framework.

Risk communication

It is likely that the scientific community will address remaining issues in probabilistic risk assessment in the years to come. Still, the scientific challenge in this instance is surpassed by the critical importance of risk communication. With regard to uncertainty, no matter how scientifically robust the answer, it is of limited use unless it can be explained clearly to a lay audience (Hoffman *et al.*, 1999). Recent health scares demonstrate that the lay person can depict strong emotional responses to risk information. The current TER approach carries the message that there is no risk of impact even though this cannot be truly established. In contrast, the acknowledgement and quantification of risk (however small) is inherent in the probabilistic approach. The challenge is hence to communicate effectively the benefits of understanding uncertainty and the rationale for considering low levels of risk acceptable.

CONCLUSIONS

Taking uncertainty into account is being seen as a natural 'next step' for environmental risk assessment. However, a number of key issues need to be addressed before probabilistic techniques can be used with confidence in risk assessment for pesticides.

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