

# **SESSION 1**

## **INTRODUCTION**

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## **Role of modelling in environmental risk assessment**

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### **ABSTRACT**

Environmental models are currently used for screening purposes as well as deterministic and probabilistic exposure assessments. Recently, a number of modelling scenarios have been developed in the EU and USA to standardize regulatory assessments of pesticides. Current issues associated with exposure modelling include selection of input parameters, selection of models with appropriate transport mechanisms and use of appropriate modelling endpoints to support regulatory risk assessments.

### **INTRODUCTION**

Environmental fate models are increasingly being used to provide estimates of the concentrations of agricultural chemicals to support environmental and ecological risk assessments. This trend has led to the development of a number of standardized models and modelling scenarios which have been officially endorsed for use in regulatory risk assessments. This paper provides an overview of the various types of models currently being used for regulatory assessments and discusses some of the current issues associated with regulatory modelling.

### **CURRENT ENVIRONMENTAL MODELS**

There are many ways to classify the various types of environmental models. For regulatory purposes, there are three basic types of models, distinguished primarily by the degree of sophistication, level of data required and type of result produced:

- 1) Screening or regression models – relatively simple models based either on experimental data or the results of more sophisticated models.
- 2) Deterministic models – moderately to highly complex models with individual algorithms for the various transport and degradative processes in the environment; deterministic models are generally run with a fixed set on input values and provide a single, fixed set of output values.
- 3) Probabilistic models – moderately to highly complex models which utilize distributions of input values and provide distributions or probabilities of various output values.

## Examples of current models

There are currently a wide range of models that have been developed or adapted for regulatory use. Examples of some of the current model are provided in Table 1.

Screening models are generally relatively simple, require minimal input data and provide conservative (i.e. high) estimates of likely environmental concentrations. Environmental concentrations obtained using screening models are useful for initial assessments of the relative importance of various dissipative/degradative pathways, e.g., leaching or fate in aquatic systems. Unfavorable risk assessments based on the result of screening models indicate the need for more refined exposure estimates.

Table 1. Examples of current regulatory environmental models

Model	Type (1)	Purpose (2)	Developer
SCI-GROW	s	gw	USEPA
GENEEC	s	sw	USEPA
EU Step 1-2*	s	sw	EU-FOCUS
EU Drift Calculator*	d	sw	EU-FOCUS
TOXSWA	d	sw	ALTERRA
EXAMS	d, p	sw	USEPA
PELMO*	d, p	gw, ro	Fraunhofer Institut
PRZM*	d, p	gw, ro	USEPA, EU-FOCUS
PEARL*	d, p	gw	RIVM, ALTERRA
MACRO*	d, p	gw, dr	SLU

(1) s = screening, d = deterministic, p = probabilistic

(2) sw = surface water, gw = groundwater, ro = runoff, dr = drainage

\* FOCUS versions of these models available at ISPRA (2001).

Deterministic models typically have more extensive requirements for input data but can also provide more realistic estimates of environmental concentrations than screening models. Most deterministic models allow the user to provide detailed information on the various transport and degradation mechanisms and provide a time series of output values which can be compared to the duration of various ecotoxicological studies.



A common approach to obtaining probabilistic exposure estimates is to perform a series of deterministic calculations, varying in time (temporal variation) or both time and location (temporal and spatial variation). A probabilistic assessment based on climatic variations can be obtained by running the deterministic model for an extended period of time (typically, 20-30 years) and summarizing the probability of obtaining various exposure concentrations.

A more detailed approach involves varying additional parameters, some of which may be spatially correlated (e.g. chemical properties, soil type, and climatic data). The results of probabilistic modelling provide insights into the range and frequency of temporal and spatial variation in environmental concentrations. Probabilistic results are typically expressed in terms of exceedence probabilities, reflecting the frequency with which specific concentrations are observed throughout the range of scenarios being considered

### **Development of regulatory modelling scenarios**

Deterministic and probabilistic environmental modelling requires the use of large numbers of parameters to appropriately characterize chemical properties and use patterns, characteristics of the soil profiles, climatic variations, and agronomic practices. In order to standardize the modelling approaches used for risk assessment, a number of regulatory modelling scenarios for groundwater and surface water have been developed in the EU and the USA (ISPRA 2001; FOCUS Surface Water 2001; MUSCRAT 2001).

A single modelling scenario typically consists of a selected soil profile, a fixed set of agronomic and cropping factors and a fixed meteorological file. To use the scenario, the user selects an appropriate set of chemical input values and application rates and runs the model for a specific scenario (combination of crop, soil, agronomic practices and climatic conditions). The modelling results can be expressed either deterministically or probabilistically.

Of necessity, modelling scenarios incorporate a large number of assumptions and include consideration of various spatial data layers as well as expert judgment. As a result, environmental concentrations predicted using these scenarios are intended to provide estimates of environmental concentrations in a range of locations that correspond to the assumptions made in the scenario. In some cases, the transport mechanisms in the scenarios studies (e.g. runoff rates and drainage rates) have been calibrated to data from appropriate field to help ensure the establishment of appropriate driving forces.

One of the major challenges with the creation of fixed scenarios is the determination of the likelihood of experimentally observing the calculated result. The mean environmental concentration can be estimated through use of a "typical" scenario and selection of typical (e.g. mean or median) input values. Less likely environmental concentrations (e.g. "worst case") can be created through using a series of worst-case assumptions for creating scenarios and selecting input values, resulting in the creation of an exposure concentration that is thought to be relatively high but with an unknown probability of occurrence. The problem with both of these approaches is that the final calculated results have an unknown probability of occurrence.



Increasingly, probabilistic modelling is being used to help provide more information on the range of environmental concentrations that can result from normal variations in chemical properties and use patterns, soil types and climatic data. The use of multiple modelling scenarios can also provide valuable insights into the variability expected due to location and time. Probabilistic modelling results can help determine specific environmental settings or specific use practices that result in concentrations of concern.

## **CURRENT ISSUES ASSOCIATED WITH MODELLING**

With the widespread adoption of modelling as a tool to provide exposure values for risk assessment, it is appropriate to identify some of the key issues associated with modelling that can influence the simulated results and impact the resulting risk assessment.

### **Selection of empirical or non-measured input parameters**

Almost all models include input parameters which are either empirical or are not readily measurable in laboratory or field studies. These parameters can influence the hydrologic balance in the model (e.g. maximum root depth, maximum plant canopy, pan evaporation correction factor) as well as the chemical balance (e.g. dispersion length, relative rate of degradation with depth).

As a result, it is important that models be parameterized using the best available estimates of these non-measured parameters to ensure appropriate mass fluxes of water and chemical in the modelling scenarios. This problem is commonly addressed through the developed of tables of recommended values and/or the creation of regulatory modelling scenarios in which the empirical and non-measured parameters are fixed.

### **Selection of chemical input properties**

Detailed mechanistic models require a wide range of chemical input data in order to provide acceptably accurate estimates of concentrations in various environmental compartments. The chemical data used for regulatory modelling is obtained entirely from required regulatory laboratory and field environmental fate studies. Most of these studies were not originally designed to provide modelling inputs and may require some judgment and/or reinterpretation prior to being used for modelling. In some cases, it may be necessary to obtain more data than the core regulatory data set to perform environmental fate modelling.

Examples of chemical environmental fate issues that arise in modelling include:

- First-order kinetics are generally required in current models. More complex kinetics may require reinterpretation using standard first-order equations for use in modelling.
- Modelling of foliarly applied chemicals may require measurement of chemical degradation and washoff studies which are not routinely conducted for regulatory submissions.

- More realistic degradation rates in aquatic systems may be obtained from studies in microcosms involving a water column, sediment and aquatic plants in an outdoor setting.
- For some chemicals, it may be necessary to consider sorption kinetics and/or sorption to matrices other than soil (e.g. macrophytes).
- For mobile, slowly degrading chemicals, it may be necessary to measure the variation of degradation rate with soil depth to obtain reasonable estimates of potential concentrations in shallow groundwater.
- To permit simulation of metabolites, the pathway and kinetics for degradation must be defined, including the formation of bound residues.
- To support probabilistic modelling, it may be necessary to perform additional laboratory and/or field studies in order to determine an appropriate distribution of environmental fate values.

### **Simulation of transport mechanisms**

Current models use varying degrees of sophistication to represent the major transport mechanisms responsible for moving applied agricultural chemicals from one compartment to another. Key transport mechanisms associated with surface water and groundwater modelling include spray drift, runoff, drainage and infiltration rates.

#### **Spray drift**

Single values of spray drift are commonly obtained from either regression equations or tables of experimental values. These single values include the effects of crop type as well as wind speed and direction. The FOCUS drift calculator is based on drift data published by the BBA (BBA 2000) and adjusts the probability of individual drift events to obtain an overall 90th percentile probability. In addition, it integrates the drift deposition across the width of the receiving water body.

#### **Infiltration, runoff and tile drainage rates**

The rate of leaching simulated by groundwater models can vary widely depending upon the assumptions made concerning dispersion coefficients and extent of preferential flow or macropore flow permitted by the model. Similarly, the rate of runoff simulated by a model can vary depending upon the soil type, soil moisture, rainfall intensity and the selection of curve numbers. The rate of tile drainage is a highly site-specific value and is best modeled by calibrating the rate to actual experimental data. For regulatory modelling, it is appropriate to create scenarios in which the infiltration, runoff and/or drainage have been calibrated to representative field studies to ensure appropriate hydrologic responses from the models.

#### **Scale issues**

Current regulatory models focus almost exclusively on simulating in-field and/or edge-of-field concentrations. However, there are many natural geographic features which can



attenuate offsite movement from agricultural fields. Vegetated filter strips (also called buffer zones) can reduce both runoff and erosion loadings into adjacent surface water while catchment-scale processes integrate individual edge-of-field loadings with runoff and drainage from non-agricultural land. Currently, larger-scale evaluations of pesticide impacts on a catchment scale are based primarily on monitoring studies and efforts are underway to develop appropriate modelling approaches to represent the observed data.

#### Surface water issues

Most current models represent the hydrology of surface water bodies in a simplistic manner, using a constant volume together with a constant flow rate in and out of the control volume. The newest version of TOXSWA being developed by FOCUS will incorporate consideration of the hydrology of catchments and dynamic water flow rates and depths in calculating concentrations of chemicals entering ditches, ponds and streams (Adriaanse 2001). For more slowly flowing water bodies (ditches and ponds), complete sets of PEC<sub>sw</sub> (predicted environmental concentration in surface water) and PEC<sub>sed</sub> (predicted environmental concentration in sediment) values can be obtained within minutes. For more dynamic settings (e.g. streams), the computational times may require several hours.

#### Issues in using modelling results in risk assessments

Most current environmental models provide a output series of hourly or daily concentrations in the compartments of interest. This concentration time series can be highly variable with dramatic changes from hour to hour or day to day. In contrast, most ecotoxicological studies are performed either using a constant exposure concentration (e.g. a flow-through aquatic study) or a single dose which declines over time due to degradation or dissipation/dilution (e.g. a static aquatic study).

In order to appropriately compare modelling results to ecotoxicological studies, it is necessary to consider the both the mode-of-action and environmental properties of the chemical as well as the duration of the effects study. For rapidly-acting chemicals which are acutely toxic, it is appropriate to compare the initial predicted concentration with the endpoints from effects studies. For more slowly acting, chronically toxic chemicals, it is more appropriate to use time-weighted-average concentrations from modelling that match the durations used in the effects studies.

When the simulated exposure concentrations are highly transient, it may be appropriate to consider conducting higher-tier effects studies that evaluate the toxicological response of organisms to transient concentrations rather than constant concentrations. In addition, it may be useful to analyze the simulated exposure profile to determine the frequency with which organisms are exposed to concentrations that are know to have a biological effect. Higher-tiered evaluations such as pulsed-dose studies and time-to-event analyses combine elements of exposure modelling with the the conduct of effects studies to provide a more realistic assessment of the toxicological impact of chemicals in the environment.



## CONCLUSION

Exposure modelling, supporting field studies and ecotoxicological testing should be performed in a logical sequence of progressive refinement. The degree of sophistication of the modelling should match the ecotoxicological data.

It is reasonable to compare the results of screening and deterministic modelling with standard ecotoxicological endpoints using the concept of a toxicity to exposure ratio (TER). However, when more refined probabilistic modelling assessments are performed, it is appropriate to consider developing probabilistic ecotoxicological endpoints for comparison with these endpoints. Numerous workshops and projects have addressed this probabilistic risk assessment and regulatory guidance is currently being developed both in the EU and the USA (EUPRA 2001; ECOFRAM 2001; PELLSTON 2001).

## REFERENCES

- Adriaanse P (2001). TOXSWA, Version for FOCUS Surface Water Working Group, Release scheduled for early 2002 on ISPRA website.
- Adriaanse P; Russell M H; Yon D (2001). EU drift calculator, Version for FOCUS Surface Water Working Group, Release scheduled for early 2002 on ISPRA website.
- Barrett Michael R (1998). The Screening Concentration in Ground Water (SCI-GROW). Documentation provided to Exposure Modelling Work Group in USA.
- BBA (2000). Bekanntmachung des Verzeichnisses risikomindernder Anwendungsbedingungen für Nichtzielorganismen. Bundesanzeiger Nr. 100, 9879-9880, Germany.
- Burns LA (1997). Exposure Analysis Modelling System (EXAMS II), User's Guide for Version 2.97.5. EPA/600/R-97/047.
- ECOFRAM (1999). URL: [www.epa.gov/oppefed1/ecorisk/index.htm](http://www.epa.gov/oppefed1/ecorisk/index.htm)
- EUPRA Workshop (2001). European Workshop on Probabilistic Risk Assessment for the Environmental Impacts of Plant Protection Products. Leeuwenhorst, The Netherlands, 5-8 June 2001.
- FOCUS Surface Water (2001). Regulatory scenarios using MACRO, PRZM and TOXSWA, Release scheduled for early 2002 on ISPRA website.
- ISPRA (2001). ISPRA website for FOCUS models: [arno.ei.jrc.it/focus/](http://arno.ei.jrc.it/focus/)
- Jarvis N (2001). MACRO, Version for FOCUS Surface Water Working Group, Release scheduled for early 2002 on ISPRA website.
- Klein M; Allen R, Russell M H (2001). EU Step 1-2 Calculator, Version for FOCUS Surface Water Working Group, Release scheduled for early 2002 on ISPRA website.
- Mangels G; Havens P; Parker R D (1997). Multiple scenario risk assessment tool (MUSCRAT). Version 1.0, beta. Provided to ACPA Exposure Assessment Modelling Working Group and currently under development by USEPA.
- Parker R D; Nelson H P, Jones R D (1995). GENEEC: A Screening Model for Pesticide Environmental Exposure Assessment. In *Water Quality Modelling, Proceedings of the International Symposium*, ASAE.



SETAC Pellston Workshop (2001). Application of Uncertainty Analysis to Ecological Risks of Pesticides. Pellston, Michigan, USA, 15-20 September 2001.

Tiktak A; van den Berg F; Boesten J J T I; Leistra M; van der Linden A M A; van Kraalingen D (2000). Manual of PEARL, Version 1.1-sr3. Report 711401008, RIVM, Bilthoven, 142 pp.

## **Modelling pesticide environmental fate : process understanding and knowledge gaps**

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### **ABSTRACT**

This paper reviews the state-of-the-art of pesticide environmental fate modelling, emphasizing interactive effects of non-linear and non-equilibrium processes affecting leaching to groundwater, and the incorporation and application of this knowledge in simulation models. The paper also highlights significant gaps in our current understanding of specific environmental compartments where more research is clearly needed.

### **INTRODUCTION**

Since the early 1970's, beginning with the pioneering work of Walker (1974) and Leistra & Dekkers (1976), simulation models have been developed to describe the complex interactions of physical, chemical and biological processes that determine the environmental fate of pesticides. Many of these models are now used in the regulatory process by public authorities, industry and consultants. Models are cost-effective tools, being both cheap and powerful. At best, they can lead to valuable insights and improved understanding, and also allow the user to evaluate the likely impacts of alternative mitigation strategies, while minimizing the need for expensive long-term field experiments. For reasons of cost, field experiments on pesticide environmental fate can only be carried out at a few research sites, and usually only for a limited number of years. Without the theoretical framework and context provided by a model, conclusions that are drawn from the results of such short-term experiments can often be misleading. The results of field experiments are also strongly influenced by the prevailing weather and are only applicable to soils of similar properties. Validated models enable extrapolation of the results of field experiments to strongly contrasting environmental conditions.

It is impossible to discuss process descriptions in models without defining what the model is to be used for. Therefore, this paper largely focuses on the prediction of pesticide leaching to groundwater. However, many of the considerations discussed in this paper will also be relevant to pesticide movement to surface waters via sub-surface flow and drainage. Loss by surface runoff and erosion is also mostly outside the scope of the paper, but some of the discussion relating to generation of macropore flow may also be relevant for surface losses, since macropore flow can, in some respects, be considered as a kind of 'subsurface runoff'. Volatilization is another loss process which is only briefly mentioned, but this is not intended as a general reflection of its importance.

This paper reviews the state of the modelling art, attempting to answer the following questions: which processes are important? What do we know about these processes? Why don't we always make use of this process knowledge? Where do we need to improve our understanding?



## OVERVIEW OF KEY PROCESSES

The fate of a pesticide applied to soil depends on the nature and strength of the sources and sinks, the partitioning between phases in the soil (water, air and solid), and the transport process itself. The ultimate source of the pesticide is the dose multiplied by the fraction of the application reaching the soil, which in turn is affected by crop interception, and loss processes such as volatilization and photolysis. Since leaching responds approximately linearly to dose, even in the presence of preferential flow, these loss processes at the surface may not be so critical for leaching predictions. The major sink term for most pesticides is usually degradation. Small errors in the prediction of degradation, either due to inappropriate process descriptions, or incorrect parameter values, result in disproportionately large errors in the leaching prediction. This is not only because the leaching loss is usually very small compared to degradation, but also because leaching is an exponential function of the half-life, assuming first-order kinetics (Jury *et al.*, 1987). An accurate description of sorption is also necessary, because partitioning determines the availability of pesticide for both leaching and degradation. Model sensitivity analyses, both using the simple 'one-at-a-time' method, and also Monte Carlo approaches, show that leaching is highly sensitive to parameters describing sorption and degradation (Boesten, 1991; Soutter & Musy, 1999). Preferential flow is also a critical process, since from a regulatory point of view, we are usually interested in leaching losses of much less than 1% of the applied amount. In many soils, this is likely to be the result of rapid transport in preferential flow pathways quite unconnected to the much slower movement of the bulk of the compound (Flury *et al.*, 1994).

## PROCESS UNDERSTANDING

In recent years, improved understanding of the complex interaction of processes that govern pesticide fate has led to linear/equilibrium model concepts being replaced by non-linear, non-equilibrium approaches. Some examples of this general trend are the use of Freundlich sorption instead of a linear isotherm, kinetic sorption models instead of equilibrium sorption, non-equilibrium preferential flow rather than the physical equilibrium implied by Richards equation, and non-linear degradation models derived by accounting for sorption-degradation interactions or microbial growth processes, rather than simple first-order kinetics. These more advanced process descriptions can predict many phenomena commonly observed in field and laboratory experiments (Richter *et al.*, 1996). For example, 'two-site' (kinetic/equilibrium) sorption models predict increases in the apparent sorption constant with time (Walker *et al.*, 1995). Linear kinetic sorption combined with linear degradation in the liquid phase only (assuming that sorbed pesticide is not available for biodegradation) leads to a biphasic degradation pattern (e.g. McCall *et al.*, 1981). A non-linear equilibrium sorption isotherm combined with first-order degradation in the liquid phase only, leads to a quasi-linear degradation process which may be experimentally indistinguishable from first-order, but where the (apparent) rate constant is strongly dependent on the initial concentration (e.g. Walker, 1976). Models which account for microbial population growth can predict the rapid disappearance of pesticide due to microbial adaptation to repeated applications (e.g. Walker & Welch, 1990). The most important underlying physical reason for the non-equilibrium sorption, degradation and transport processes observed is the heterogeneous nature of the pore space in field soils (Bergström & Stenström, 1998). Much of the soil pore volume (microporosity less than c. 2  $\mu\text{m}$  in size) is physically inaccessible to microorganisms. Pesticide diffusing into such small pores is unavailable for degradation, and this slow diffusion into a sorbing matrix is also largely responsible for the time-dependence observed in sorption, and 'biphasic' departures from first-order degradation kinetics (Scow & Hutson, 1992). Pesticide



residing in micropores is also effectively protected against leaching, since diffusion is slow compared to the rapid vertical convective transport occurring in the larger pores. Dual- and even multi-region models have been developed to account for this physical non-equilibrium (Jarvis, 1998), which often results in the accelerated or 'preferential' transport of a small but significant fraction of the pesticide through the unsaturated zone (e.g. Flury, 1996).

This improved process understanding has been incorporated into simulation models designed to predict the environmental fate of pesticides, including some of those used for registration. For example, the PEARL model (<http://www.alterra.nl/models/pearl>) includes two-site sorption with a Freundlich isotherm, in which the kinetic sites are protected from degradation. The MACRO model (<http://www.mv.slu.se/bgf/macrohtm/macro.htm>) includes treatment of non-equilibrium water flow in macropores, Freundlich sorption, and also allows the user to specify separate degradation rate coefficients for four different 'pools' in the soil (solid and liquid phases in macropores and micropores). Nevertheless, there are few examples of the application of these more advanced modelling concepts to predict pesticide fate in field soils, even though they clearly can have a large impact on the outcome. Indeed, the failure to account for non-linear, non-equilibrium processes is certainly the cause of significant discrepancies between predictions and measurements in many model applications (Walker, 1976; Thorsen *et al.*, 1998; Beulke *et al.*, 2000). With respect to regulatory modelling, none of these newer modelling concepts have really gained a firm foothold, except for non-linear Freundlich sorption. There are perhaps several reasons for this, but one of the most important is the lack of data and perceived lack of appropriate tools to parameterize these more advanced process descriptions. In principle, the tools for parameter estimation do exist, in the form of inverse modelling techniques (Vink *et al.*, 1994; Dienes *et al.*, 1999; Kätterer *et al.*, 2001). The main problem is that more complex model descriptions require more detailed experiments and more comprehensive data in order to unequivocally distinguish between the many different process descriptions and parameterisations that are possible. Two examples of the potential pitfalls in distinguishing different process descriptions should suffice: Richter *et al.* (1996) demonstrated that biphasic degradation curves can be equally well explained by a deterministic model based on linear kinetic sorption and linear degradation restricted to the liquid phase, and by a model based on first-order degradation kinetics, but assuming spatial variability of the rate coefficient described by a gamma function (Gustafson & Holden, 1990). They pointed out that only additional data on the time-course of bound residues would allow discrimination between the two models. Gaber *et al.* (1995) demonstrated that both physical non-equilibrium and kinetic sorption influenced the leaching of atrazine in undisturbed soil columns, and that without the application of a tracer, it would have been impossible to distinguish between parameters controlling diffusion exchange between pore regions and parameters controlling kinetic sorption. Indeed, it is well known that the 'mobile-immobile' model of physical non-equilibrium is mathematically identical to a one region flow model assuming two-site (equilibrium-kinetic) sorption (Nkeddi-Kizza *et al.*, 1984).

## KNOWLEDGE GAPS

### Soil surface conditions

Tillage affects the 'roughness' or microrelief of the soil surface, the number, size distribution and continuity of large pores, and thus the extent of macropore flow (e.g. Trojan & Linden, 1992; Brown *et al.*, 1999). Therefore, it may be possible to control preferential flow through soil surface preparation, but little research has been performed on this topic, even though conceptual



models of these processes were developed as early as the 1970's (Dixon & Petersen, 1971). Microtopography of the soil surface may also play an important role in sandy soils without macropores. Hydrophobicity of the thin air-dry surface layer will cause small-scale surface runoff and flow concentration in depressions. Ritsema & Dekker (1995) demonstrated a significant lateral re-distribution of bromide tracer into preferential regions of the near-surface soil following just 1 mm of rain soon after application. A related problem is the microtopography deliberately created by ridge till systems, commonly used, for example, in potato cultivation (Boesten, 2000), so that infiltration is concentrated to the furrow regions.

Following tillage, the soil surface is exposed to rainfall for several weeks before crop growth provides effective surface cover. This leads to a consolidation of the cultivated layer and on susceptible soils, destruction of macroporosity and sealing of the surface. These surface crusts have significantly smaller hydraulic conductivities, but they are not continuous. Local surface runoff will occur during rain, leading to concentration of infiltration through non-crust patches and desiccation cracks. Nothing is known about the influence of this kind of preferential flow on pesticide leaching, but some preliminary simulations based on measured seasonal variations in soil surface hydraulic conductivity due to crusting suggest that it may lead to order of magnitude differences in pesticide leaching from the topsoil (Messing, 1993).

During dry weather, the surface few millimetres of soil quickly becomes air-dry. Sorption is known to dramatically increase as the soil gets very dry (Hance & Embling, 1979) and this, in turn, strongly affects pesticide availability for volatilization and perhaps also for leaching by preferential flow. However, it is difficult to measure moisture effects on sorption of concentrated pesticide solutions in thin surface layers (Boesten, 2000). Furthermore, numerical limitations in models, together with a lack of knowledge of near-surface hydraulic properties, mean that the occurrence of very dry conditions in the surface few millimetres of soil is not easy to simulate. For these reasons, Boesten (2000) concluded that accurate modelling of volatilization from the soil surface is impossible with current knowledge and techniques.

Processes occurring at and very close to the soil surface cannot be investigated satisfactorily with current models. One-dimensional models implicitly assume a flat soil surface, and often employ a rather coarse spatial discretisation, with computational layers several centimetres thick close to the soil surface. Two-dimensional models applicable to pesticide fate in the soil unsaturated zone do exist (e.g. HYDRUS-2D, <http://www.ussl.ars.usda.gov/models/hydrus2d.htm>), but they do not account for preferential flow processes. Application of improved two-dimensional models, including physical non-equilibrium concepts, should lead to a better understanding of the importance of soil surface conditions for pesticide leaching.

### **Preferential flow pathways through the root zone**

It is important to understand better the properties and functioning of preferential flow pathways. In recent years, it has become increasingly clear that the location of the pesticide in relation to the location of the water flow pathways is critical for leaching (Bergström *et al.*, 2001). If a mobile pesticide diffuses into the soil matrix, and is no longer in contact with water flowing in macropores, then preferential flow may reduce leaching compared to chromatographic transport (Larsson & Jarvis, 1999). On the other hand, macropore flow soon after application will dramatically increase leaching of otherwise non-mobile compounds, because the pesticide mostly resides either at the soil surface or adsorbed to aggregate surfaces within the topsoil, and is therefore exposed to interaction with the rapidly flowing



water. In one preliminary study, Larsson & Jarvis (2000) showed in scenario simulations using MACRO pre-calibrated to a field experiment on a structured clay soil, that the effects of macropore flow should depend strongly on the overall leachability of the pesticide. However, much more work is clearly needed to understand the complex interactions of preferential flow and the sorption and degradation characteristics of pesticides.

The properties of macropore linings and aggregate surfaces are different to those of the bulk soil, with larger clay and organic carbon contents, better nutrient supply and oxygen status, and larger microbiological activity, which results in a larger sorption and degradation capacity per unit mass of soil (Stehouwer *et al.*, 1993; Mallawatanri *et al.*, 1996). The extent to which this is important for pesticide leaching is not known. Much should depend on the characteristic time scales of the processes: macropore flow is fast and degradation is relatively slow, so enhanced microbial activity in macropores may not be important, although some preliminary studies suggest otherwise (Pivetz *et al.*, 1996). The significance of sorption retardation in macropores is still not clear, but it does not seem too important, probably because flow rates are fast in relation to sorption kinetics, and the adsorptive surface area in macropores is small. Field experiments where leaching in the presence of preferential flow has been monitored for several compounds applied simultaneously (Kladivko *et al.*, 1991; Traub-Eberhard *et al.*, 1994) seem to show an equally fast breakthrough regardless of sorption characteristics, but that concentrations are clearly dependent on sorption. It is still unclear whether this sorption effect occurs within macropores during transport, or whether it is a result of the source strength, that is, the solution pesticide concentration in the surface soil layers where macropore flow is most likely generated.

### **Subsoil and the deep vadose zone**

In contrast to topsoil, very little seems to be known about long-term pesticide degradation and transport in the deeper vadose zone. Even though sensitivity analysis suggests that different assumptions concerning subsoil degradation rates may not greatly influence predictions of total leaching (Boesten, 1991), the long-term persistence of small amounts of pesticide in subsoil may act as a diffuse source of pesticide for groundwater contamination. This may have implications for the time required for self-remediation of polluted aquifers. Few studies have investigated the extent of non-equilibrium preferential flow in the deep vadose zone. In many cases, this may diminish with depth (e.g. Li *et al.*, 1997), since soil structure generally becomes weaker in the absence of faunal activity and physical processes like wetting/drying and freeze/thaw. However, preferential flow can occur to significant depths in some hydrogeological conditions, such as in fractured glacial till or chalk (e.g. Jørgensen *et al.*, 1998; Wellings & Cooper, 1983). Preferential flow in the soil root zone may still be critical even when matrix flow dominates transport at depth. This is because the attenuation of pesticides by sorption and degradation will generally be much weaker in the vadose zone (Pothuluri *et al.*, 1990; Moreau & Mouvet, 1997).

### **Upscaling to the field**

One unresolved problem is the extrapolation of results from small-scale experiments to the field-scale relevant for management caused by the spatial variability of soil properties and pesticide sorption and degradation characteristics (e.g. Walker *et al.*, 2001). Stochastic approaches have been applied to this upscaling problem that demonstrate the potentially large effects of field-scale heterogeneity on leaching (e.g. van der Zee & Boesten, 1991). However, the results of such analyses depend on both the assumptions underlying the process descriptions used in the model and on how the model is parameterised. In particular, a lack of information on

parameter distributions, and especially correlations, has severely limited progress. For example, many studies have treated the sorption constant and degradation rate coefficient as independent parameter distributions (Di & Aylmore, 1997), which will almost certainly tend to overestimate variability in leaching, since sorption and degradation are often inversely related (Cantwell *et al.*, 1989). Other studies focus on variability in transport characteristics, but ignore variability in sorption and degradation because of lack of data (e.g. Wu & Workman, 1999). One dilemma is that data may exist to characterize parameter distributions in simple screening models (e.g. Jury *et al.*, 1987), but the process descriptions in these models are in some respects too simple (i.e. steady flow, no dispersion). In contrast, process descriptions in complex models are much more realistic, but knowledge of parameter distributions and their correlations is incomplete.

## CONCLUDING REMARKS

Great progress has been made in recent years in improving our understanding of the interplay of non-linear and non-equilibrium processes governing pesticide fate in soils. This improved knowledge is also recognized in the process descriptions now included in many models, even though it is not often fully exploited due to lack of data. The challenge now is to design and carry out the necessary experiments to meet the requirements of more complex models. Poor predictions of pesticide fate in field soils are often blamed on inadequate process descriptions in models (models are always simplifications of reality), but are just as likely to result either from a lack of experimental data leading to errors in model identification and parameterisation, or from errors due to extrapolation from limited data to the field-scale in the face of soil heterogeneity.

## REFERENCES

- Bergström L; Stenström J (1998). Environmental fate of chemicals in soil. *Ambio*, **27**:16-23.
- Bergström L; Jarvis N ; Larsson M ; Djodjic F; Shirmohammadi A (2001). Factors affecting the significance of macropore flow for leaching of agrochemicals. In: *Preferential flow. Water movement and chemical transport in the environment*, pp 25-28, ASAE, MI, U.S.A.
- Boesten J J T I (1991). Sensitivity analyses of a mathematical model for pesticide leaching to groundwater. *Pesticide Science*, **31**: 375-388.
- Boesten J J T I (2000). From laboratory to field: uses and limitations of pesticide behaviour models for the soil/plant system. *Weed Research*, **40**: 123-138.
- Brown C D; Marshall V L; Carter A D; Walker A; Arnold D; Jones R L (1999). Investigation into the effect of tillage on solute movement to drains through a heavy clay soil. I. Lysimeter experiment. *Soil Use and Management*, **15**: 84-93.
- Beulke S; Dubus I G; Brown C D; Gottesbüren B (2000). Simulation of pesticide persistence in the field on the basis of laboratory data – A review. *Journal of Environmental Quality*, **29**: 1371-1379.
- Cantwell J R; Liebl R A; Slife F W (1989). Biodegradation characteristics of imazaquin and imazethapyr. *Weed Science*, **37**: 815-819.
- Di H J; Aylmore L A G (1997). Modeling the probabilities of groundwater contamination by pesticides. *Soil Science Society of America Journal*, **61**: 17-23.
- Dieses A E; Schlöder J P; Bock H G; Richter O; Aden K; Gottesbüren B (1999). A parameter estimation tool for nonlinear transport and degradation processes of xenobiotics in soil. In: *Human and environmental exposure to Xenobiotics*, eds. A A M Del Re; C Brown; E Capri; G Errera; S P Evans; M Trevisan, pp. 171-180, Cremona, Italy.



- Dixon R M; Petersen A E (1971). Water infiltration control: a channel system concept. *Soil Science Society of America Proceedings*, **35**: 968-973.
- Flury M; Flühler H; Jury, W A; Leuenberger J (1994). Susceptibility of soils to preferential flow of water. *Water Resources Research*, **30**: 1945-1954.
- Flury M (1996). Experimental evidence of transport of pesticides through field soils – a review. *Journal of Environmental Quality*, **25**, 25-45.
- Gaber H M; Inskip W P; Comford S ; Wraith J (1995). Nonequilibrium transport of atrazine through large intact soil cores. *Soil Science Society of America Journal*, **59**: 60-67.
- Gustafson D I; Holden L R (1990). Non-linear pesticide dissipation in soil: a new model based on spatial variability. *Environmental Science & Technology*, **24**: 1032-1038.
- Hance R J; Embling S J (1979). Effect of soil water content at the time of application on herbicide content in soil solution extracted in a pressure membrane apparatus. *Weed Research*, **19**: 201-205.
- Jarvis N J (1998). Modelling the impact of preferential flow on non-point source pollution. In: *Physical non-equilibrium in soils: modeling and application*, ed. H H Selim; L Ma, pp. 195-221, Ann Arbor Press, Chelsea, MI, U.S.A.
- Jørgensen P R; McKay L D; Spliid N H (1998). Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed columns and numerical modeling. *Water Resources Research*, **34**: 539-553.
- Jury W A; Focht D D; Farmer W J (1987). Evaluation of pesticide ground water pollution potential from standard indices of soil-chemical adsorption and biodegradation. *Journal of Environmental Quality*, **16**: 422-428.
- Kätterer T; Schmied B; Abbaspour K C; Schulin R (2001). Single- and dual-porosity modelling of multiple tracer transport through soil columns: effects of initial moisture and mode of application. *European Journal of Soil Science*, **52**: 1-12
- Kladivko E J; van Scoyoc E G; Monke E J; Oates K M; Pask W (1991). Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *Journal of Environmental Quality*, **20**: 264-270.
- Larsson M H; Jarvis N J (1999). Evaluation of a dual-porosity model to predict field-scale solute transport in a macroporous soil. *Journal of Hydrology*, **215**: 153-171.
- Larsson M H; Jarvis N J (2000). Quantifying interactions between compound properties and macropore flow effects on pesticide leaching. *Pest Management Science*, **56**: 133-141.
- Leistra M; Dekkers W A (1976). Computed leaching of pesticides from soil under field conditions. *Water, Air and Soil Pollution*, **5**: 491-500.
- Li K; Amoozegar A; Robarge W P; Buol S (1997). Water movement and solute transport through saprolite. *Soil Science Society of America Journal*, **61**: 1738-1745.
- Mallawatanri A P; McConkey B G; Mulla D (1996). Characterization of pesticide sorption and degradation in macropore linings and soil horizons of Thatuna silt loam. *Journal of Environmental Quality*, **25**: 227-235.
- McCall P J; Vrona S A; Kelley S S (1981). Fate of uniformly carbon-14 ring labeled 2,4,5,-Trichlorophenoxyacetic acid and 2,4-Dichlorophenoxyacetic acid. *Journal of Agricultural and Food Chemistry*, **29**: 100-107.
- Messing I (1993). Saturated and near-saturated hydraulic conductivity in clay soils. *Reports and Dissertations, 12, Department of Soil Sciences, Swedish University of Agricultural Sciences*, Uppsala, Sweden, 66 pp.
- Moreau C; Mouvet C (1997). Sorption and desorption of atrazine, deethylatrazine, and hydroxyatrazine by soil and aquifer solids. *Journal of Environmental Quality*, **26**: 416-424.



- Nkeddi-Kizza P; Biggar J W; Selim H M; van Genuchten M T; Wierenga P J; Davidson J M; Nielsen D R (1984). On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resources Research*, **20**: 1123-1130.
- Pivetz B E; Kelsey J W; Steenhuis T S; Alexander M (1996). A procedure to calculate biodegradation during preferential flow through heterogeneous soil columns. *Soil Science Society of America Journal*, **60**: 381-388.
- Pothuluri J V; Moorman T B; Obenhuber D C; Wauchope R D (1990). Aerobic and anaerobic degradation of alachlor in samples from a surface-to-groundwater profile. *Journal of Environmental Quality*, **19**: 525-530.
- Richter O; Diekkrüger B; Nörtershauser P (1996). *Environmental fate modelling of pesticides*. VCH Verlag: Weinheim, Germany.
- Ritsema C J; Dekker L W (1995). Distribution flow: a general process in the top layer of water repellent soils. *Water Resources Research*, **31**: 1187-1200.
- Scow K M; Hutson J (1992). Effect of diffusion and sorption on the kinetics of biodegradation: theoretical considerations. *Soil Science Society of America Journal*, **56**: 119-127.
- Soutter M; Musy A (1999). Global sensitivity analyses of three pesticide leaching models using a Monte Carlo approach. *Journal of Environmental Quality*, **28**: 1290-1297.
- Stehouwer R C; Dick W A; Traina S J (1993). Characteristics of earthworm burrow lining affecting atrazine sorption. *Journal of Environmental Quality*, **22**: 181-185.
- Thorsen M; Jørgensen P R; Felding G; Jacobsen O H; Spliid N H; Refsgaard J C (1998). Evaluation of a stepwise procedure for comparative validation of pesticide leaching models. *Journal of Environmental Quality*, **27**: 1183-1193.
- Traub-Eberhard U; Kördel W; Klein W (1994). Pesticide movement into subsurface drains on a loamy silt soil. *Chemosphere*, **28**: 273-284.
- Trojan M D; Linden D R (1992). Microrelief and rainfall effects on water and solute movement in earthworm burrows. *Soil Science Society of America Journal*, **56**: 727-733.
- van der Zee, S E A T M; Boesten J J T I (1991). Effects of soil heterogeneity on pesticide leaching to groundwater. *Water Resources Research*, **27**: 3051-3063.
- Vink J P M; Nörtershauser P; Richter O; Diekkrüger B; Groen K P (1994). Modeling the microbial breakdown of pesticides in soil using a parameter estimation technique. *Pesticide Science*, **40**: 285-292.
- Walker A (1974). A simulation model for prediction of herbicide persistence. *Journal of Environmental Quality*, **3**: 396-401.
- Walker A (1976). Simulation of herbicide persistence in soil. I. Simazine and prometryne. *Pesticide Science*, **7**: 41-49.
- Walker A; Welch S J (1990). Enhanced biodegradation of dicarboximide fungicides in soil. In: *Enhanced biodegradation of pesticides in the environment*, eds. K D Racke; J R Coats, ACS Symposium Series, **426**: 53-67.
- Walker A; Welch S J; Turner I J (1995). Studies of time-dependent sorption processes in soils. In: *Pesticide movement to water*, eds. A Walker, R Allen, S W Bailey, A M Blair, C D Brown, P Günther, C R Leake, P H Nicholls, pp 13-18, BCPC Farnham, U.K.
- Walker A; Jurado-Exposito M; Bending G D; Smith V J R (2001). Spatial variability in the degradation rate of isoproturon in soil. *Environmental Pollution*, **111**: 407-415.
- Wellings S R; Cooper J D (1983). The variability of recharge of the English chalk aquifer. *Agricultural Water Management*, **6**: 243-253.
- Wu Q J; Workman S R (1999). Stochastic simulation of pesticide transport in heterogeneous unsaturated fields. *Journal of Environmental Quality*, **28**: 498-512.