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Foreword

The present literature review was prepared within the context of the work package WP1 ('Integrated knowledge reviews') of the FOOTPRINT project.

The preferred reference to the present document is as follows:

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1 INTRODUCTION

Early developments in pesticide fate modelling started in the early 1980s. Much progress has been made since in the numerical description and prediction of pesticide behaviour in the environment to the extent that a large number of models are now available to the risk assessor and pesticide fate modeller. Although much progress is being made by the various research teams in Europe and elsewhere, the scientific field has come to a certain *scientific maturity*. This can be exemplified through i) the significant number of literature reviews dealing with pesticide fate models (Parsons et al., 2001; Siimes & Kämäri, 2003; Simunek et al., 2003; Jantunen et al., 2005; Nolan et al., 2005), their calibration (Dubus et al., 2002) or the uncertainty associated with pesticide fate modelling (Dubus et al., 2003), ii) the availability of a dedicated helpline for models used in pesticide registration (FOCUS helpdesk, 2006), and, iii) the existence of initiatives aimed at sharing information regarding pesticide fate models and their use (PFMODELS, 2006). In contrast, the field of environmental indicators aimed at assessing the potential impact of pesticides on the environment and human health is relatively new and very much in development. Although reviews of environmental indicators are becoming increasingly available (Reus et al., 1999; Devillers et al., 2005), it is clear that much work remains to be done in terms of assessing the use, accuracy and usefulness of environmental indicators for pesticides.

The present paper aims at providing a balanced overview of the status of scientific knowledge in the field of pesticide fate modelling and environmental indicators for pesticides. Rather than presenting an extensive review of the various pesticide fate modellers and environmental indicators available to the risk assessor, the document provides an assessment of the scientific fields and discusses their status. The discussion leads to a call for a closer integration of pesticide fate modelling activities and the development of environmental indicators for pesticides.

2 CRITICAL REVIEW OF PESTICIDE FATE MODELS

2.1 Pesticide fate models: status, selection and data requirements

The present critical review focus on deterministic and empirical models which are commonly used in research-oriented applications and activities related to risk assessment, especially in the field of pesticide registration. Although a significant body of literature on stochastic and multimedia fate models exists, these models are considered to be outside the scope of the presented targeted work. Multimedia fate models were developed during the early 1980s (Mackay, 1979; Mackay 1991, Mackay & Paterson, 1991) and are mainly used to assess the environmental fate of persistent pesticides (e.g. lindane, DDT, dieldrin). The fact that these models represent the environment into a number of compartments and focuses on the evaluation of transfer between them makes these models particularly suited to the study of large-scale (global) transport of pesticides (Wania & Mackay, 1999). Their use for much smaller scale applications is however fairly limited. Stochastic pesticide fate models rely on a set of probability distribution functions to provide a statistically-based description of pesticide transfer. For instance, Jury (1982) in his Transfer Function Model used a probability distribution function to express the transfer time of a compound between the soil surface and a given depth. The model was later adapted to describe water and pesticide transfers in dualporosity systems (Grochulska & Kladivko, 1994). Mills & Leonard (1984) developed a stochastic model expressing the quantity of pesticides which is likely to be lost by run-off based on the observation that the frequencies of rainfall events which have the potential to generate run-off follow a Poisson law.

Deterministic and empirical pesticide fate models enabling the simulation of pesticide transfer through a soil column were initially developed in the mid-1980s (Carsel et al., 1985; Rao et al., 1985; Nofziger & Hornsby, 1986), a few years stochastic models based on transfer functions were released (Jury, 1982; Jury et al., 1983; Jury et al., 1986). The field of science has developed enormously over the last 20 years and a large number of environmental fate models have been developed, such as: Agriflux (Banton & Larocque, 1997), CALF (Nicholls, 1994), CMLS (Nofziger et Hornsby, 1986), CRACK-NP (Armstrong et al., 2000), EPIC (Williams et al., 1984), GLEAMS (Knisel et al., 1992), HSPF (Donigian et al., 1984), HYDRUS-1D (Simunek et al., 1998) and HYDRUS-2D, LEACHM/LEACHP (Hutson et Wagenet, 1992), MACRO (Jarvis et al., 1991; Larsbo & Jarvis, 2003), MACRO_DB (Jarvis et al., 1997), MOUSE (Steenhuis et al., 1987), MARTHE (Thiéry et al., 2004), MIKE SHE (DHI, 1998), OPUS (Smith, 1992), PEARL (Boesten & van der Linden, 1991; Tiktak et al., 2000), GEOPEARL (Tiktak et al., 2002), PELEP-DSS (PELEP-DSS, 2006), PELMO (Klein, 1991; Jene, 1998), PESTLA (van den Berg & Boesten, 1999), PESTRAS (Tiktak et al., 1991; Jene, 1998), PESTLA

1994), PESTRANS (Unlu et al., 1997), PLM (Nicholls et al., 2000), PRZM (Carsel et al., 1985), RZWQM (USDA-ARS, 1992), SIMULAT (Aden & Diekkrüger, 2000), SWAT (Arnold et al., 1992; Arnold & Fohrer, 2005), TurfPQ (Haith, 2001), VARLEACH (Walker, 1987) or WAVE (Vanclooster et al., 1995). A number of reviews regarding pesticide fate models have been published in the literature (e.g. Parsons et al., 2001; Simmes & Kämäri, 2003; Simunek et al., 2003; Jantunen et al., 2005; Nolan et al., 2005).

Data requirements vary greatly between the various models, but usually include data on: i) the climate (typically, rainfall, temperatures and potential evapotranspiration data or meteorological variables enabling the calculation of evapotranspiration), ii) soils (distribution of horizons with depth, organic matter and hydrological characteristics for each horizon), iii) crop cover (dates of sowing or emergence, harvest; indications with regard to the crop development); and, iv) pesticides (typically application rates, sorption and degradation characteristics of the compound under study). A significant amount of work in terms of literature searches, report examination and calculations is typically needed before values can be attributed to all model input parameters. Pre-modelling activities traditionally include the application of pedotransfer functions (van Genuchten et al., 1991; Tietje & Tapkenhinrichs, 1993; Wösten et al., 1999) as water retention and hydraulic conductivity curves are seldom available for the site under study. In an effort to improve the usability of their model, a number of scientists have constructed model shells which integrate pedotransfer functions. For instance, the MACRO_DB shell proposes to determine a set of parameters determining the extent of preferential flow in the simulation based on information on soil texture and structure (Jarvis et al., 1997). It should however be noted that the use of pedotransfer functions introduces uncertainty which is transferred through the modelling process to result in uncertainty in model predictions (Dubus et al., 2003).

The selection of a model for use in a modelling exercise is often given little attention although it will largely determine the capacity of the model to simulate and ultimately the trust to give to the modelling results. Criteria for selecting a particular pesticide fate model include: data and time requirements, computer systems, modelling expertise (Siimes & Kämäri, 2003) and the adequacy to the purpose and objectives of the modelling study (Herbst et al, 2006). Dubus et al. (2002) examined the various rationales for model selection and emphasised that a model which accounts for all processes affecting pesticide fate in the field in the field is beyond reach. In this context, concessions have to be made and the least imperfect of the models available should be selected.

2.2 The validation status of pesticide fate models

The extensive use of pesticide fate models within the context of the placement of crop protection products on the market (EEC, 1991) means that all actors involved, in particular the regulators, need to have confidence in the ability of these models to simulate and predict the fate of pesticides in the environment. This was recognised formally by the EU directive 95/36/EC which states that "models used for the estimation of predicted environmental concentrations must [...], where possible, be reliably validated with measurements carried out under circumstances relevant for the use of the model" (EEC, 1995).

Although a number of scientists stress that '(groundwater) models cannot be validated' or proven, but only tested and invalidated (Konikow & Bredehoeft, 1992; Oreskes et al., 1994), the phrasing in the EU Directive has led to a significant increase in the number of initiatives aimed at evaluating the validation status of models, mostly by considering a field or lysimeter dataset and by trying to get models to replicate water, tracer and pesticide fluxes and concentrations (Pennell et al., 1990; Bergström & Jarvis, 1994; Walker et al., 1995; Klein et al., 1997; Beulke et al., 1998; Vanclooster et al., 2000; Garratt et al., 2003). For instance, The COST Action 66 'Pesticide fate in the soil environment' in the late 1990s evaluated the capacity of 12 pesticide fate models to simulate 4 lysimeter and field leaching datasets and involved a total of 36 pesticide fate modellers and model users (Vanclooster et al., 2000). Given the large body of literature on the evaluation of pesticide fate models, some authors have published reviews of modelling studies for specific models (Jones & Mangels, 2002 for PRZM; Malone et al., 2004).

The numerous evaluation studies which have been carried out allow general conclusions to be drawn regarding the capability of pesticide fate models to replicate pesticide behaviour in the field:

- Except in rare instances where a decent description of field data was obtained using 'blind' or 'cold' simulations, all pesticide fate models need to go through a calibration phase to achieve an acceptable fit to the data (Dubus et al., 2002).
- ii) The level of fit which is obtained with pesticide fate models against lysimeter or field data is usually within one order of magnitude, i.e. a factor of 10, of the observed concentrations when site-specific sorption and degradation data are used (Trevisan et al., 2000) and where a calibration of the model is undertaken (Garratt et al., 2003).

- iii) Models can be used in a benchmarking context to compare their likely behaviour in the environment, provided the models implement a description of the main environmental processes at stake for the compounds under study. The potential (or lack of) for leaching is usually adequately derived by the models, as demonstrated by studies comparing model simulations to observed field leaching data (e.g. Tiktak, 2000) although the opposite has only been shown.
- iv) In cases where pesticide loss data are available for a number of years, model parameterisation generally only allows for good fit to the data to be obtained in a limited number of (usually one or two) years (Beulke et al., 1998; Francaviglia et al., 2000; Gottesbüren et al., 2000).
- v) In cases where data for measurements for water, bromide and pesticide fluxes are available, models tend to be unable to provide a good description to the three variables on the basis of a single input parameter set. A satisfactory simulation of soil moisture profiles in the soil may not be linked to a good description of drainage fluxes (Vanclooster & Boesten, 2000). Similarly, a good description of pesticide concentrations in soil and leachate can be obtained despite the transport of water through the soil profile is not adequately simulated

It is clear that further progress should be made towards the improvement of model predictions. Boesten (2000) considers that in general, the pesticide leaching models available are reliable enough to assess the leaching of the bulk of the dose (leaching levels above 1%), but the EU drinking water limit of 0.1 μ g/l implies leaching of less than 0.1% of a dose of 1 kg/ha. As noted by this author, the validation status of pesticide fate models at this level of leaching is still low, mainly because preferential flow processes in both structured and unstructured soils and the factors controlling the transformation rate in subsoil are not well enough understood (Boesten, 2000).

One of the difficulties associated with model evaluation is the exercise has generally more to do with a testing of the capability of the modeller himself/herself as opposed to the testing of the model. This is best exemplified in studies where different individuals have used the same model with the same supporting dataset and have come up with different predictions with regard to water fluxes and pesticide losses (e.g. Brown et al., 1996; Boesten, 2000; Jarvis et al., 2000; Vanclooster and Boesten, 2000; Gottesbüren et al., 2000). Some authors consider that the user subjectivity in model parameterisation is such that combined to the need for calibration, it questions the whole concept of model testing (Tiktak, 2000) and that familiarity with the dataset to be simulated is as important as the familiarity with the pesticide fate model used (Armstrong et al., 2000; Gottesbüren et al., 2000).

The influence of the knowledge, experience and know-how of the modeller undertaking the simulation work is only one source of uncertainty in the modelling. Dubus et al. (2003) reviewed the various sources of uncertainty in pesticide fate modelling as a prerequisite to deploying adequate approaches to deal with these uncertainties. Uncertainties which were identified included: i) the spatial and temporal variability of physical (Bosch and West, 1998), chemical (Wood et al., 1987) and biological (Parkin, 1993) variables in the field, including those which have a strong effect on the environmental fate of pesticides (Lennartz, 1999; Novak et al., 1997; Coquet and Barriuso, 2002); ii) sampling procedures (Walker and Brown, 1981) and measurement error; iii) the derivation of parameter values from primary data (Leake et al., 1995); iv) the use of laboratory data to simulate behaviour in the field (Beulke et al., 2000); v) the use of pedotransfer functions (Pachepsky et al., 1999); vi) the use and manipulation of GIS data (Loague et al., 1996); vii) the inability of the model to describe experimental or field data (Beck et al., 1997); viii) the selection of a given pesticide fate model (Pollock et al., 2002); ix) the modeller subjectivity (Brown et al., 1996); x) the inadequate use of concepts implemented in the models (Wauchope et al., 2002); and, xi) calibration procedures (Dubus et al., 2002). Some numerical and statistical techniques have been applied to pesticide fate models to deal with parameter uncertainty (Loague, 1991; Fontaine et al., 1992; Dubus & Brown, 2002; Freissinet et al., 1999), but as noted by Oreskes (1998), dealing with uncertainty is made difficult by the fact that only a few uncertainty are easily quantified, many or most are quantified with difficulty and several may not be quantifiable at all. Hence, parameter uncertainty that we are typically addressing could be the tip of the iceberg (Dubus et al., 2003).

Although it is clear that uncertainty should be accounted for in the decision-making process, dealing with information on uncertainty makes the work of decision-makers more difficult and they often express a reluctance to consider the uncertainty data. This was exemplified in FOOTPRINT during the kick-off meeting as members of the Advisory Committee expressed the view that the project partners should not be providing an uncertainty module in the FOOT tools. Dealing with uncertainty requires a different approach to risk assessment to be adopted, i.e. i) expressing the risk in terms of a probability of occurrence of a negative impact, and ii) recognising explicitly the potential for harm to the environment or to the human. In any case, the 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 (Dubus et al., 2003).

2.3 The issue of preferential flow in pesticide fate modelling

One recurring aspect in the field of pesticide fate modelling is the need (or not) to simulate preferential flow phenomena to simulate field data adequately and to estimate the risk of pesticides impacting on the quality of water resources. There is widespread evidence that preferential flow phenomena originating from cracks, fissures and biological activity have a strong influence on water and pesticide transport in the field (Flury, 1996; Jarvis & Dubus, 2006). This translates in the field as the appearance of inert tracers and pesticides at depth shortly after application (e.g. Kladivko et al., 1991; Jaynes et al., 2001; Brown et al., 2004). Preferential flow can also originate (Jarvis & Dubus, 2006) from unstable finger flow (Ritsema & Dekker, 1995) and funnel (or simply heterogeneous) flow (e.g. Kung, 1990; Roth, 1995). Although some consider preferential flow phenomena as processes restricted to highlystructured 'heavy clay' soils with clay contents exceeding 40-50% (such as those encountered at the Brimstone experimental farm in the UK; Harris et Catt, 1999), field evidence shows that macropore flow phenomena can show a very significant effect on pesticide transport for soils with as little as 15-20% of clay content (Beven and Germann, 1982; Brown et al., 1995; Flury et al., 1995). Preferential flow phenomena should therefore be considered the norm rather than the exception (Kordel & Klein, 2006) and models accounting for these phenomena. In this context, the use of models which cannot simulate the transport patterns which are characteristics of preferential flow (in particular, the appearance of compounds at depth shortly after application) are unlikely to be able to reflect results for leaching observed in the field. The non inclusion of preferential flow routines in models is indeed often identified as the main reason for failure to simulate field data (Vanclooster et al., 2000).

Early pesticide fate models which described preferential flow, such as CRACK-NP (Jarvis & Leeds-Harrison, 1987; Jarvis, 1989; Armstrong et al., 1995) or PLM (Hall, 1993; Hall, 1994; Hall & Webster, 1993), were specifically developed to simulate transport in heavy clay soils (clay content > 50%) where preferential flow in the form of bypass flow is the dominant hydrological pathway (Beulke et al., 1998). Developments of models went on to allow the simulation of preferential flow processes in soils of all textures, from sandy soils where bypass originating from fissures and cracks are unlikely and will have a negligible impact on water and pesticide transport, to heavy clays where fluxes will be heavily influenced by those phenomena. The three pesticide fate models which integrate a description of preferential flow and which are the most widely used at present are: MACRO (Jarvis et al., 1991; Larsbo & Jarvis, 2003; Larsbo et al., 2005), RZWQM (RZWQM team, 1992; Malone et al., 2004; Wauchope et al., 2004) and HYDRUS (Simunek et al., 1998). The macropore flow model MACRO is a physically based 1D model which considers two flow domains (i.e. 'micropores'

and 'macropores') to describe the transport of water and reactive solutes in soils. MACRO has benefited from numerous evaluation studies (Andreu et al., 1994; Jarvis et al., 1994; Larsson & Jarvis, 1999; Armstrong et al., 2000; Jarvis et al., 2000; Gottesbüren et al., 2000; Balderacchi et al., 2002; Strömqvist & Jarvis, 2005) over the last 15 years of its development and is the preferential flow model of choice for pesticide registration purposes in Europe. The Root Zone Water Quality Model RZWQM is a comprehensive agricultural systems model intended as a research tool to investigate the effects of agricultural management on crop production and environmental quality (Malone et al., 2004). The model was recently adapted to account for pesticide fate (Wauchope et al., 2004) and accounts for preferential flow processes in both macropores and the soil matrix where mesopores and micropores are conceptualised. HYDRUS-1D is a finite element model for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media (Simunek et al., 1998). HYDRUS implements a concept of physical non-equilibrium transport based on two regions with different porosities which was initially presented by van Genuchten and Wierenga (1976), known as the Mobile-Immobile Model. The two-region concept assumes that the liquid phase can be partitioned into mobile (flowing) and immobile (stagnant) regions. Preferential flow modelling components have been recently implemented in models which did not traditionally account for these phenomena, such as PEARL or PELMO (Jarvis et al., 2003; Vanclooster et al., 2003), but their use in environmental risk assessment for pesticide registration is not recommended at present given i) the lack of procedures and guidance to parameterise the preferential flow components, ii) the strong sensitivity of model predictions to the new preferential flow parameters; and, iii) the lack of evaluation of the models and their individual preferential flow routines. The reader is invited to consult the FOOTPRINT review on preferential flow processes and associated pesticide fate models for additional information (Jarvis & Dubus, 2006).

Differences in beliefs regarding the way preferential flow should be accounted for in a risk assessment context go beyond the activity of model selection as this underpins the whole concept of vulnerability to pesticide contamination. For some, a worst case situation with regard to leaching to depth is represented by a soil with a high sand and low organic matter contents. This principle has led to the definition of the so-called German (Resseler et al., 1997) and Dutch (Boesten & van der Linden, 1991; Brouwer et al., 1994) national scenarios which have been widely used in Germany and the Netherlands to assess the risk of groundwater contamination over the last 15 years. For others, a worst case situation with regard to the transport of pesticides through soil is represented by a soil where the topsoil where most of the degradation and sorption processes occur, is bypassed due to the preferential transport of water in macropores. These concepts have guided the development of

the Danish scenarios for groundwater (Heidi Barlebo Christiansen, personal communication) and the use of the Brimstone farm data to support surface water assessments in the UK (Mackay et al., 2004). Hence, pesticide transfer in a soil with a clay content of, say, 25% may be classified as likely or unlikely to result in a contamination of adjacent water resources depending on the belief regarding the relative importance of pesticide transfer mechanisms. Such discrepancies are undesirable in pesticide risk assessment activities. It is interesting to note that the importance attributed to preferential flow phenomena is somewhat related to the importance of clay soils and associated drainage systems in the Member States. For instance, it is estimated that ca. 50% of the winter cereal growing area in the UK is constituted by clay soils which are drained. The basic question of knowing what a worst case soil is should be debated among environmental fate specialists, pesticide risk assessor as differences in concepts lead to discrepancies in risk assessment results and subsequent risk management activities.

2.4 Current and future needs in pesticide fate modelling

As noted in the introduction of the present document, the science of pesticide fate modelling has reached a certain scientific maturity which can be exemplified by the availability of literature reviews dealing with pesticide fate models or their use and limitations, the availability of dedicated structures to support pesticide fate modelling activities for pesticide registration, the existence of initiatives aimed at sharing information regarding pesticide fate models and their use, and the fact that studies are specifically undertaken to elucidate differences in predictions made by different models (Vanderbor, 2005).

The science of pesticide fate modelling has made much progress over the last 20 years. Modelling activities have clearly strongly benefited from the fact that the importance of pesticide fate modelling in pesticide registration has increased dramatically over the last two decades. Improvements in the models and in the way they are used has clearly gained from the work of FOCUS (acronym for 'the FOrum for the Co-ordination of pesticide fate models and their Use'), 'an independent group of experts from regulatory authorities, registrants and government institutes/universities, which operates by consensus'. (FOCUS, 2001a). The FOCUS experts have produced a significant number of influential reports (FOCUS, 1995, 1997a, 1997b, 2000, 2001b, 2002, 2005a, 2005b, 2005c) and have stimulated the development of pesticide fate models, scenarios and risk assessment procedures for pesticide registration purposes. The main objective of FOCUS is 'the technical harmonisation of complex generic environmental issues in support of the 91/414/EEC process' (FOCUS,

2001a). Harmonisation aspects have been particularly reflected in the initiatives aimed at developing a number of scenarios to facilitate a common evaluation of pesticide risk to surface water and groundwater in Europe (FOCUS, 2000, 2001b). The importance of registration-related applications of pesticide fate models is such that this might have unwittingly negatively affected the development of research models used in the area. Developments in these models have closely mirrored the needs for registration requirements whereas other research models have had their development guided by the need to 'get closer to reality' and to accommodate the 'real environment', i.e. a multi-dimensional spatially- and temporally-variable interactions of multiple processes. As an example, two- and threedimensional models enabling the simulation of pesticide fate and transport in catchments of various sizes are now becoming increasingly available (Christiansen et al., 2004; Holvoet et al., 2005; Gärdenäs et al., 2006), enabling 2D simulations to be undertaken in contrast to applications involving the spatially-distributed running of 1-D models. Also, models allowing the simulation of the transfer of pesticides from the soil surface to and in groundwater, i.e. in the soil - unsaturated zone - saturated zone continuum, have been developed (e.g. Thiéry et al., 2004).

Limitations of current pesticide fate models are linked to the non-description to specific processes and their interaction, to difficulties in attributing values to all model input parameters and to the inherent variability of the environment. Despite that the models currently used are usually unable to provide a satisfactory description of field data when no calibration is undertaken, they remain useful in a decision-making context where the aim is to identify those compounds that are likely to pose significant threat to the aquatic and terrestrial ecosystems, and not to simulate behaviour in the field with a great accuracy. Current needs with regard to pesticide fate models have evolved significantly in the last few years, notably in response to the Water Framework Directive (EEC, 2000) which places the water body as the relevant scale to assess water quality and to deploy action plans to reduce contamination of water resources. Perhaps the greatest need at this scale is for catchment scale 2- or 3-D models which can adequately simulate the transport of pesticides originating from runoff and erosion. Future models should also attempt to integrate the various transport pathways for pesticides as they are closely linked in the agricultural landscape. For instance, groundwater levels will affect water levels in surface water bodies and exchanges between the two systems should be accounted for. One further aspect which should be increasingly considered is the use of pesticide fate models as tools for risk management as models are almost exclusively used for risk assessment activities at present. Very few models integrate routines enabling the study of the effect of modifications in agricultural practices on pesticide losses, with the exception of the USDA-ARS model RZWQM (Malone et al., 2004) which simulates the

effect of various tillage, irrigation, manure application and crop residue management options on pesticide transport.

One of the difficulties in pesticide fate modelling is that the model developer is often tempted to add descriptions of new processes in his/her model. Although this can in theory contribute to a better simulation of the observed pesticide behaviour in the field, the addition of extra parameters in the model means that the model becomes more difficult to parameterise and that the model becomes less suited to extrapolation and large-scale applications. The addition of extra-parameters also leads to parameter identifiability issues (Loague & Corwin, 1996; Dubus et al., 2002). Model developers should therefore pay attention to striking a balance between the complexity of their model and the need for parameterisation.

3 AN OVERVIEW OF ENVIRONMENTAL INDICATORS FOR PESTICIDES

An environmental indicator is a figure or a set of figures which are designed to inform easily and quickly about the conditions over time and space of a given system. According to the OECD (1994) and Dale & Beyeler (2001), an indicator should be: easily understandable, relevant to the system, theoretically well founded, sensitive to changes, technically measurable (reproducibility, costs involved) and appropriate to scale (in time as well as in space).

The aims of environmental indicators for pesticides may be to: i) provide an assessment of the risk of pesticides impacting on water quality or organisms, and/or, ii) provide an estimate of environmental performance with regard to pesticides, and/or iii) provide farmers with recommendations and suggestions to adapt their crop protection practices to minimise environmental impacts by pesticides; and/or, iv) compare various farming systems, and/or, v) advise policy-makers. The aims of environmental indicators are therefore fairly applied and mainly targeted towards the use of pesticides within a crop protection context at the farm level, which strongly contrast with pesticide fate models.

As for pesticide fate models, there is a breadth of environmental indicators available for pesticides, contrasting in their objectives, complexity and ease of use. Although most of them claim to be risk-based, environmental indicators for pesticides mostly estimate the exposure since impacts of pesticides in the field are particularly difficult to isolate and estimate. A particular approach in this context is the Toxicity Exposure Ratio or the Hazard Quotient, its equivalent. The risks which are most often assessed are the risks to humans resulting from

pesticide usage (operator exposure), the short- and/or long-term risks to aquatic (usually algae, daphnia and fish) and terrestrial organisms, and the risk of exceeding legal thresholds.

A literature review identified the following environmental indicators for pesticides: Environmental Yardstick (EYP) (Reus & Leendertse, 2000), Hasse Diagram (HD) (Sorensen et al., 1998), SYNOPS_2 (Gutsche & Rossberg, 1997), Environmental performance indicator of pesticides (p-EMA) (Lewis & Bardon, 1998; Brown et al., 2003), Pesticide environmental impact indicator (Ipest) (Van der Werf & Zimmer, 1998), Environmental Potential Risk Indicator for Pesticides (EPRIP) (Trevisan et al., 1999; Padovani et al., 2004), System for Predicting the Environmental Impact of Pesticides (SyPEP) (Beernaerts & Pussemier, 1997) and Pesticide Environmental Risk Indicator (PERI) (Nilsson, 1999). Table 1 provides a matrix allowing to identify the risks which are evaluated by the most common environmental indicators for pesticides while Table 2 provides a detailed description of the target user communities, remits and operational scale.

Indicator Name	Toxicity on water ecosystem	Toxicity on soil ecosystem	Toxicity on human being	Mobility in water	Mobility in air	Persistence
AARI	*					
ADSCOR	*			*		
CHEMS-1	*		*	*	*	*
DIAPHYT	*	*	*			
EcoRR	*	*		*	*	
EIQ	*	*	*	*		*
EPRIP	*	*		*	*	*
EYP	*	*		*		*
HD	*				*	*
l-phy	*			*	*	*
NRI	*	*		*		*
PAF	*	*		*		*
p-EMA	*	*	*	*		*
PERI	*	*		*	*	*
PESDECIDE	*	*	*			
PI		*				
POCER	*	*	*	*		*
Rating system	*	*		*		*
REXTOX	*			*		*
SIRIS	*			*		*
SRI	*		*	*		*
SYNOPS	*	*		*	(*)	*
SyPEP	*			*		*

(*) = optional

 Table 1: List of risks assessed in common environmental indicators for pesticides.

 The table was adapted from Devillers et al. (2005).

	۲ ۱	arget	Evaluation of		Scale of evaluation			
Indicator	Farmers /Land	Regulatory	an action	farming	environmental			
Name	owners	services	program	practices	risk	farm	regional	national
AARI		*			*			*
ADSCOR		*		*	*	*	*	*
CHEMS-1		*			*		*	*
DIAPHYT	*	*		*	*	*		
EcoRR	*	*		*	*	*		
EIQ	*	*		*	*	*		
EPRIP	*	*		*	*	*		
EYP	*	*	*	*	*	*	*	*
HD		*		*	*			*
I-phy	*	*		*	*	*		
NRI		*	*		*			*
PAF		*			*		*	*
p-EMA	*	*	*	*	*	*		
PERI	*			*	*	*		
PESDECIDE	*		*	*	*	*		
PI	*	*	*	*	*	*	*	
POCER	*	*	*	*	*	*		
Rating system		*		*	*	*	*	*
REXTOX		*	*	*	*	*	*	*
SIRIS		*			*		*	*
SRI		*	*		*			*
SYNOPS	*	*	*	*	*	*	*	*
SyPEP	*	*		*	*		*	
SEPTWA		*	*	*			*	

Table 2. Target end-user communities, remits and operational scaleof some common environmental indicators for pesticides.The table was adapted from Devillers et al. (2005).

The construction of an environmental indicator relies on the selection of i) the information to be integrated in the indicator; and, ii) the selection of an appropriate method to combine the information (Levitan et al., 1995). These two aspects will be briefly reviewed in the next two sections.

3.1 Information included in environmental indicators for pesticides

The information to be included in indicators varies widely among the different indicators and the selection process often reflects to a great extent the background of their developers, may they be pesticide fate specialists, ecotoxicologists or toxicologists. Some information such as pesticide fate properties may be obvious or easy to acquire while others may be difficult to obtain and may necessitate modelling activities by their own.

Almost all indicators take into account the basic environmental fate properties of pesticides, i.e. the persistence in soil and the retention of pesticides on soil components. The persistence is calculated in laboratory experiments and is usually expressed as a half life (DT50) while the retention is often expressed as a sorption coefficient normalised to organic carbon or organic matter contents. Sorption and degradation properties are used to evaluate the likely pesticide concentrations in a given environmental compartment. Some indicators rely on complex deterministic models to provide exposure assessment in environmental media. For instance, the Environmental Yardstick for Pesticides (Reus & Leendertse, 2000) uses the PESTLA model to estimate pesticide concentrations in groundwater.

Many of the environmental indicators account for the toxicity of pesticides to water organisms and/or to soil organisms. For flora and fauna, the assessment is usually undertaken for surface water organisms, soil organisms and above ground organisms. Each environmental compartment may be sub-divided in sub-compartments for taxa or specific organisms. LC50 (Lethal Concentration for which 50% of the population under study is dead) and NOEC (No effect Concentration) are used in most indicators. Since the estimation of impacts in the field is difficult, the focus so far has tended to be on hazard identification as opposed to risk.

Few of the indicators incorporate information on mitigation measures (e.g. pesticideexclusion strips along watercourses) although there is a clear need for tools which can evaluate and support the deployment of such measures. This is partly due to the local character of the information which needs to be fed into the indicators on an ad hoc basis. The information can be best fed into indicators using some sort of interactive interview or questionnaire filled in by the pest control manager, and delivered in the format of a workbook or computerized expert system based on a "decision-tree model". Unlike stand-alone rankings of pesticides by risk, this format permits "if-then-else" routines that can be extremely sensitive to situation-specific variability. For inputs that cannot be gleaned from the experienced insights of the property manager, the "decision-tree model" may need to be informed by an array of information drawn from the scientific literature. (Levitan, 2000). Some environmental indicators integrate economic or socio-economic features. For instances, PESTDECIDE considers production costs among the variables determining the pesticide ranking (PESTDECIDE). Although the consideration of socio-economic information to provide sound recommendations to farmers and water managers, it is important to assess such costs separately from environmental impacts (Levitan, 1997). In 2001, an OECD Workshop on the Economics of Pesticide Risk Reduction in Agriculture was held (OECD, 2001). The workshop agreed that despite their advantages, models for conducting economic assessment have limitations and must be selected and used with care. In particular, the workshop noted that economic assessment models, like all models, are based on a simulation and simplification of reality that is not always transparent; and may include a variety of assumptions and estimates.

3.2 The aggregation of information in environmental indicators for pesticides

The aggregation of the information contained in environmental indicators to result in one integrated index is a key stage in their development. Aggregation aims to represents a complex system in a few targeted figures, so that they can be used by decision-makers. Indicators use different methods of aggregation (Levitan et al, 1995; Devillers et al., 2005) and these are briefly presented below.

3.2.1 The mechanistic approach

In the mechanistic approach, indicators integrate the various variables using calculus. The integration can be realised by one or more models or through simple equations. This procedure leads to results which are more accurate, but this does not mean that the method is more reliable than their counterparts. The fact that the approach is mechanistic means that the aggregation is sometimes considered to be complex and not amenable to non experts, which may be an issue if the procedures leading to a given result are to be understood fully by decision makers.

3.2.2 The notational approach

In the notational method, indicators integrate notes in the calculus rather than direct values. This method requires an intermediate classification step where each variable values is assigned to a class defined by boundary values. One of the advantages of this procedure is that variables of very different kinds (quantitative or qualitative) can be aggregated. The difficulty usually lies in the assignment of boundary values, which can be made difficult in circumstances where little knowledge is available and expert judgement is required. The other disadvantage of the approach is the so called 'threshold effect'. For values closed to the thresholds, a short variation of the values may lead to changes in class, which may in turn result in significant changes in the overall risk assessment result. Conversely, large changes in values may not result in a change in class. These deficiencies can be addressed by using fuzzy logic procedures which explicitly considers the proximity to boundaries through membership functions (Figure 1). A widely used indicator implementing fuzzy logic rules is the indicator Ipest (van der Werf & Zimmer, 1998).

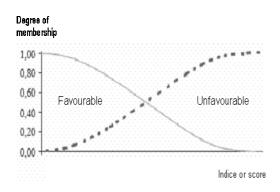


Figure 1: Classically the membership function only takes two values: 0 (nonmembership) and 1 (membership). In fuzzy sets the membership function can take any value from the interval [0,1]. The value 0 represents complete nonmembership, the value 1 represents complete membership, and values in between are used to represent partial membership. (from van der Werf & Zimmer, 1998)

Another issue associated with the notational method is the need to assign weights to each variable to be aggregated. Weighting is an algebraic way of expressing the relative importance of the variables considered in an assessment. Weights can reflect either the greater/lesser importance of certain variables to the system or to the evaluation of the system. For instance, the impact to aquatic organisms may be weighted heavily when farm fields are in close proximity to surface water bodies. Human life is traditionally valued highly compared to impacts on aquatic organisms. Although weighting is sometimes criticized on the basis that it involves human judgement, it should be noted that these judgments are not necessarily prejudicial or illogical (Levitan L., 1997).

3.2.3 The hybrid approach

Hybrid indicators are indicators which combine the two previous methods of aggregation. These indicators may be divided into two different sub-groups. For some indicators, only some of variable values are transformed into notes, the other values being integrated directly. For others, variables values are not transformed into notes, but the results of others equations or models are. For instance the output of the model PESTMOD (PESTicide MODel) which is based on response function method are used in a highly integrated index model called the Ecosystem Resilience Index (ERI) (Malkina-Pykh, 2002). The hybrid approach addresses

some of the concerns associated with the above-mentioned approaches, but the issue of class thresholds remains.

3.2.4 The expert judgement approach

The last of the aggregation procedure is based on expert judgement. The aim here is to reconstruct the expertise and reasoning capabilities of qualified specialists. The preliminary assumption is that experts construct their judgment from initial observations and pieces of knowledge applied in a suitable sequence. They have a set of solutions and a set of the knowledge for interweaving these solutions with a set of observations. Experts are able to express their knowledge in various ways. Consequently, there are various set of indicators of which expert systems can be built (Neumann, 2002). The procedure is based on the development of decision rules which mimic the decisions made by the experts. Since the decision rules are explicit, the construction of the indicator can be understood by all. Also, expert judgement allows the aggregation of variables of very different kinds. The major shortcoming of the approach is that expert judgement is subjective by essence and different decision rules are likely be obtained if different experts are consulted.

3.3 Overview of environmental indicators used in Europe

Member states in Europe use different environmental indicators depending on their needs and local conditions. For instance, the following indicators are used in different countries: AARI, EYP and PAF (The Netherlands), NRI (Norway), p-EMA (UK), SEPTWA (Belgium), SIRIS (France), SYNOPS (Germany) and SRI (Sweden).

An important landmark in the field of environmental indicators in Europe was the Concerted Action CAPER (Concerted Action of Pesticide Environmental Risk Indicators) which was funded by the European Union and finished in June 1999 (Reus et al., 1999; 2002). The objectives of the project were to: i) compare and discuss existing methods of scoring and ranking pesticides according to their environmental impact; and, ii) formulate recommendations for the improvement of existing methods in relation to the purposes for which they can be used. The consortium reviewed a total of eight indicators:

1. The Environmental Yardstick for Pesticides (EYP) (Reus & Leendertse, 2000). The EYP indicator was introduced in The Netherlands in 1994 and is currently used as i) a management tool for farmers and technical consultants, ii) a tool for monitoring the

environmental performance of farmers, iii) a tool for setting standards for ecolabels, and, iv) as a policy evaluation tool.

2. Hasse Diagram (HD) which was developed in Denmark (Sorensen et al., 1998)

3. SYNOPS_2 (Gutsche & Rossberg, 1997) which is used to calculate risk potential for pesticides in order to assess those which may be unacceptable at the national level in Germany

4. p-EMA (Lewis & Bardon, 1998). The EMA programme has been designed for farmers and their advisers to encourage more sustainable practices across the whole farm in the UK. This software uses auditing techniques to derive performance indices for a comprehensive range of farm practices, including pesticide use (p-EMA). The evaluation of pesticide practices is performed using a scoring system based on label warning phrases specified as a condition of use during the UK regulatory approvals process.

5. Pesticide environmental impact indicator (Ipest) (Van der Werf & Zimmer, 1998). IPEST was developed in France to estimate the potential environmental effect of pesticide applications. It is a fuzzy expert system which reflects the authors' perception of the potential environmental effects of pesticide use.

6. Environmental Potential Risk Indicator for Pesticides (EPRIP) (Trevisan et al., 1999; Padovani et al., 2004) which can assess short-term and long-term, direct and indirect, effects in relation to exposure.

7. The System for Predicting the Environmental Impact of Pesticides (SyPEP) (Beernaerts and Pussemier, 1997) developed for Belgian conditions

8. The Pesticide Environmental Risk Indicator (PERI) (Nilsson, 1999) developed and used in Sweden.

Only three of the indicators (EYP, SYNOPS and p-EMA) were in use at the time of the study during the evaluation, others being under development.

The work consisted in a comparison of the indicators with a view to identify the strengths and weaknesses of the various approaches. The comparative evaluation was based on the capabilities of the indicators as well as a case study for which environmental scores were calculated (Reus et al., 2002). Since the indicators yield results in different formats (e.g. a qualitative and quantitative estimate), results were analysed comparatively using a correlation study. The eight indicators differed with regard to the compartments, effects and methods used to calculate environmental impact scores. As a result, the scores obtained for the case study for the overall environmental assessment were found to be very variable. Still, the indicators provided similar rankings for the individual compartments of surface water, groundwater and soil. The project participants considered that it was not possible to recommend one indicator over the others because each has it own strengths and weaknesses.

It was concluded that although the indicators were believed to be important tools to reduce the contamination of water resources by pesticides and impacts, some changes to the existing indicators were needed to best meet this objective (Reus et al., 1999). The following recommendations were made: i) an ideal indicator should deal with real risks of a pesticide application, rather than hazard and include application rate, application factors and environmental conditions; ii) an indicator should give separate scores for different environmental effects (including human health), rather than producing only one overall score for environmental risk; iii) an indicator should provide guidance to users on how they can interpret the scores for different effects; iv) an indicator should be validated to ascertain its reliability; and, v) an indicator should be flexible in the output it delivers. The project also revealed lacks in supporting data, including the availability of pesticide properties and data for formulated products, formulations and metabolites. The project called for the construction of an EU-wide database on pesticide properties.

A significant number of indicators have emerged since the end of the CAPER. Roussel and coauthors (2000) have developed IPEST-B in France to compare the environmental effects of pesticide use in different crops. p-EMA has benefited from improvements (Brown et al., 2003) to support UK government policy of optimising agricultural pesticide use. The system estimates risks to a wide range of taxonomic groups and environmental compartments using methods consistent with current regulatory assessments, but also allows adjustments to reflect formulation, the local conditions and the environmental costs and benefits of varying management practices. The EPRIP indicator which was being developed at the time of CAPER has now been finalised (Padovani et al., 2004). EPRIP takes into account the requirements of multiple applications, provide separate scores for different environmental effects and is consistent with procedures used for registration purposes. In Belgium, Vercruysse & Steurbaut (2002) developed POCER (Pesticide Occupational and Environmental Risk indicator) which can be used to estimate the impact of pesticide treatments on the applicator, the worker, the bystander, groundwater, surface water, bees, earthworms, birds, useful arthropods and persistence in soil (Clayes et al., 2005). In addition, harmonised pesticide risk indicators are being developed as part of the EU-funded project HAIR (HAIR, 2006).

3.4 The issue of validation for environmental indicators

In contrast to pesticide fate models for which evaluation procedures have been discussed and are in place (e.g. Thorsen et al., 1998; Vanclooster et al., 2000; Dubus et al., 2002), approaches to evaluate environmental indicators for pesticides are still lacking. A scientific validation of indicators is however a necessity (Crabtree & Brouwer, 1999; Smith et al., 2000; Vos et al., 2000) and is required to establish the credibility of the indicator approach among scientists involved in modelling and to the future end-users (Bockstaller & Girardin, 2003). This is due to the fact that outputs of environmental indicators (traditionally a risk score) cannot be easily be compared to field observations and that indicator developers do not necessarily see the need to benefit from a robust validation of their tools and associated concepts. Bockstaller & Girardin (2003) stress that if many indicators cannot be validated in the same way as simulation models, validation based on expert judgement and expert consensus concerning the quality of the indicator design as well as the quality of the indicator outputs is always possible. These authors propose a validation framework based on three different components: i) the 'design validation' which evaluate if the indicator is scientifically founded, ii) the 'output' validation to assess the soundness of the indicator outputs, and, iii) the 'end use' validation to ascertain that the indicator is useful to the end-user and used as decision-aid tool. The benchmarking of indicators against other indicators should be undertaken with care as all indicators considered could be wrong for the same reason.

4 CONCLUSIONS AND PERSPECTIVES

4.1 Towards a closer integration between environmental indicators for pesticides and pesticide fate models

The approaches used to estimate pesticide exposure in environmental indicators are diverse and strongly contrast in their complexity. This is particularly obvious for the assessment of the likely magnitude of pesticide leaching within the context of the assessment of the risk of contamination of groundwater. Simple environmental indicators, such as PERI (Nilsson, 1999), tend to rely on the GUS index (Gustafson, 1989) which provides an estimation of the risk of leaching based on the sorption and degradation properties of the compound. Although the GUS index is interesting in terms of its low data requirements which are widely available in environmental fate databases, it benefits from a low validation status and ignores the contribution of the weather, soils and the subsoil to the risk of leaching. Some indicator developers rely on intermediate approaches to estimate the risk of leaching to groundwater. For instance, EPRIP considers a modified version of the Attenuation Factor / Retardation Factor approach (Rao et al., 1985), the 'leached quantity' (Trevisan et al., 1993), which integrates information on pesticide properties (sorption, degradation, potential for volatilisation), environmental conditions (soil properties, recharge, depth to groundwater) and pesticide application information (quantity applied, fraction intercepted by the canopy). Although the approach adopted in EPRIP is more advanced than the application of a simple GUS index, it is still based on the AF/RF approach which is an empirical approach to estimating the risk of leaching. The fact that the GUS index or the AF/RF factor are empirical approaches that have not benefited from extensive validation studies in the past means that the confidence in the estimates of the environmental indicators for the risk to groundwater is likely to remain low even if good quality data supporting the calculations of these estimates are available.

Table 3 provides a comparison between selected features of pesticide fate models and environmental risk indicators. Environmental indicators for pesticides are mainly devised to be used by farmers and extension advisers in a given set of agro-environmental conditions which are usually specific to one country. Indicators usually have low data requirements, are easy to use, can be run quickly, are amenable to the non-expert, but they suffer from a lack of scientific validation and the fact that the combination of the various processes is done on a subjective basis. In contrast, models are complex, data-hungry, difficult to understand and to use, but they benefit from a widely-recognised scientific validity. Given the very significant efforts which have been put into the evaluation and validation of pesticide fate models over the last 20 years and at the same time very opposite and complementary profiles of the two types of tools, **it would seem appropriate to use these deterministic models to support the estimation of the leaching risk in environmental indicators for pesticides.**

	Environmental indicators	Pesticide fate models
Main user communities	Farmers	Researchers
	Extension advisers	Risk assessors
Extent of use	National	International
Data requirements	Low	High
Combination of processes	Subjective	Objective (scientifically-based)
Running time	Short	Long
Validation status	Poor	Good
Ease of use	Easy	Difficult
Farm-level recommendations	Yes	No
Accessibility of the concepts to the non-expert	Good	Limited
Evaluation	Difficult	Possible

Table 3: Comparison between environmental indicators for pesticides and pesticide fate models

The two main obstacles towards a closer integration of complex models into simple environmental indicators have traditionally been: i) the lack of data supporting the parameterisation of the deterministic models; and, ii) the significant computing time required to run these models.

Data on the environmental fate properties of pesticides can be found in dedicated databases although it is known that sorption and degradation data are highly variable (Lennartz, 1999; Novak et al., 1997; Coquet and Barriuso, 2002) and a bias in the risk assessment is introduced when surrogate values such as means or medians are used in the modelling (Dubus et al., 2002b). The bottleneck with regard to data availability has traditionally been in soil data, but it can be alleviated by defining a range of 'representative' soil scenarios which covers a certain diversity in environmental conditions. In essence, the work consists in classifying soils in a number of classes and assigning a soil profile (and its associated characteristics) to each class. In practice, the deployment of the environmental indicator in the field will necessitate the classification of the soil on site into one of the representative classes previously defined. It is implicitly assumed that the risk for a given soil can be represented by the risk for the representative soil which is closest to the soil under study. The definition of the various representative soils is based on different assumptions depending on the risk being assessed. For instance, Dubus et al. (2002b) considered 4 soils on the basis of their likely potential to transfer pesticides to depth in an application looking at the risk of leaching of a maize herbicide in the UK. The main selection criteria for the four soils were their particle size distribution, organic matter contents and the depth of typical soil profiles. In another application dealing with the estimation of the risk of transfer of an acidic herbicide to surface water via drainage systems under wheat cultivation in the UK, Brown et al. (2004) selected six soils based on the relative mobility of the acidic herbicide (determined by soil pH) and the prevalence of rapid movement to drains via macropore flow (determined by clay content and structure).

The second hindrance to integrating deterministic pesticide fate models in environmental indicators is the time required to run these models. This is a particular important issue as the user of an environmental indicator system is unlikely to wish to wait more than a few minutes to get his risk estimates. The running time of pesticide fate models is significantly larger than a few minutes, especially for simulations involving several years of running and a number of soils. There are two possible solutions to alleviate the running time issue. The first option would be to resort to a dedicated high-performance IT architecture to decrease the running time of the models. The user would set up his risk assessment framework on site on a PC and the requests for simulations would then be sent via the internet or other suitable means to a

dedicated modelling platform which would constituted of a number of machines and/or supercomputers. Web-based applications are likely to become increasingly available in the future in the field of risk assessment. For instance, the cluster of projects WEBFRAM aims at developing a web-enabled model framework for the assessment of non-target risks, which incorporates variability and uncertainty into the assessment of risk to non-target species (WEBFRAM, 2006). The farm-scale system developed within FOOTPRINT to assess the risk of pesticide impacting on water resources at the local scale ('FOOT-FS') will also be available as a web portal (Dubus et al., 2006). Although desirable, the option of benefiting from high-performance computing resources through the internet for pesticide fate modelling applications is unlikely to be available in the near future. The second option to alleviate running time issues is to undertake all the modelling work beforehand and to have the modelling results ready for when they are needed, i.e. when the user wishes to evaluate an environmental risk. This option was first used in the field of pesticide risk assessment by the FIFRA Environmental Modelling Work Group who developed MUSCRAT (Multiple Scenario Risk Assessment Tool) which is used for Tier III risk assessments in the US. The system contains results of modelling undertaken for the whole of the US for 23 crops based on databases for soil and climate information (Mangels, 2001). The GLEAMS and PRZM modelling resulted in 1.7 million model runs which were executed on an Intel Paragon supercomputer. The MUSCRAT application allows the post-processed results to be consulted and displayed in the form of maps and probability distribution options. The pre-running of pesticide fate models was also used for the development (Holman et al., 2004) of the POPPIE system (Prediction of Pesticide Pollution in the Environment) which is used by the Environment Agency in England and Wales to optimise monitoring strategies with regard to the pollution of water resources by pesticides (Brown et al., 2002). The MACRO model was used to simulate the leaching of 49 combinations of sorption and degradation properties for 8 soils, 6 climates and 2 application scenarios, resulting in 4700 MACRO runs. The modelling effort was distributed across 4-8 machines over a three-month running period. Extrapolation routines were then derived to predict the likely leaching concentration of any pesticide registered in Europe from the results already obtained for the 49 theoretical pesticides. The resulting 'MACRO emulator' was then combined to information on subsoil characteristics and integrated in a GIS system to allow the identification of zones vulnerable to pesticide leaching (Holman et al., 2004).

The most advanced example of an environmental indicator for pesticides making use of results of a deterministic model is that of p-EMA (Brown et al., 2003; Lewis et al., 2003). p-EMA is the pesticide module of a wider computer software package (EMA, Environmental Management for Agriculture) which is used by the farming industry in the UK and other

countries to assess and improve environmental performance. The risk of transfer of pesticides to surface water via drainage and to groundwater was based on MACRO predictions for 5 climates, 4 soils, 2 application periods and 57 combinations of Koc and DT50. The approach is in essence similar to that used for development of the POPPIE system (see above) although different soil and climatic information were used. Given the body of work related to MACRO, the use of the model for leaching and drainage predictions enables the establishment of a certain degree of confidence in p-EMA assessments, in comparison to simpler systems which rely on non-validated equations or simple assumptions to estimate the risk of contamination of water resources. Another example of use of deterministic models for the derivation of environmental indicators is the development of DRIPS (Drainage Spraydrift and Runoff Input of Pesticides in Surface Waters indicator) in Germany (Ropke et al., 2004) where the models GLEAMS and PELMO are used to estimate pesticide loads and associated concentrations in surface water arising from diffuse sources.

2.5 Pesticide fate models, environmental indicators and the 3 FOOT tools

The three FOOT tools developed within the context of FOOTPRINT will allow estimates of the risk of the contamination of groundwater and surface water resources to be made at various scales. The tool to be used at the farm scale by farmers and extension advisers ('FOOT-FS') has a particular relevance to the field of environmental indicators as the information contained in the tool will allow simple assessments of the risk to be made. Within FOOTPRINT, exposure estimates for leaching, drainage and runoff will be based on deterministic models and these estimates are expected to provide a more robust assessment of the actual contamination in comparison to simpler approaches implemented in existing environmental indicators. The modelling effort will require the development of a specific IT architecture ('FOOTPRINT@work') allowing pesticide fate models to be run on a large number of networked PCs. Results of the modelling runs will be integrated in the FOOT tools in the form of look-up tables which will allow results to be accessed instantly and fed back to the user.

5 REFERENCES

- Aden K. & Diekkrüger B. (2000). Modeling pesticide dynamics of four different sites using the model system SIMULAT. Agricultural Water Management 44:337-355.
- Andreu L., Moreno F., Jarvis N.J. & Vachaud G. 1994. Application of the model MACRO to water movement and salt leaching in drained and irrigated marsh soils, Marismas, Spain. Agricultural Water Management, 25:71-88.
- Armstrong A.C., Aden K., Amraoui N., Diekkrüger B., Jarvis N., Mouvet C., Nicholls P. & Wittwer C. (2000). Comparison of the performance of pesticide-leaching models on a cracking clay soil: results using the Brimstone Farm data set. Agricultural Water Management, 44:85-104.
- Armstrong A.C., Matthews A.M., Portwood A.M. & Jarvis N.J. (1995). CRACK-NP. A model to predict the movement of water and solutes from cracking clay soils. Version 1.0. Technical description and user's guide. ADAS Land Research Centre, Gleadthorpe, Notts.
- Armstrong A.C., Matthews A.M., Portwood A.M., Leeds-Harrison P.B. & Jarvis N.J. (2000). CRACK-NP: a pesticide leaching model for cracking clay soils. Agricultural Water Management, 44:183-199.
- Arnold J.G. & Fohrer N. (2005). SWAT2000: Current capabilities and research opportunities in applied watershed modelling. Hydrological Processes, 19:563-572.
- Arnold, J.G. & Allen P.M. (1992). A comprehensive surface-groundwater flow model. Journal of Hydrology, 142:47-69.
- Balderacchi M., Alavi G., Capri E., Vicari A., Accinelli C. & Jarvis N.J. 2002. Losses of atrazine, metolachlor, prosulfuron, and trisulfuron in subsurface drainwater. II. Simulation results. Agronomie, 22:413-425.
- Banton O. & Larocque M. (1997). AGRIFLUX 2.0 User's manual. Software for the evaluation of environmental losses of nitrates and pesticides from agriculture. (In French.) INRS-Eau Rep. INRS-Eau, Quebec, Canada.
- Beck M.B., Ravetz J.R., Mulkey L.A. & Barnwell T.O. (1997). On the problem of model validation for predictive exposure assessments. Stoch Hydrol Hydraul, 11:229–254.
- Bergström L. & Jarvis N.J. (1994). Evaluation and comparison of pesticide leaching models for registration purposes. Journal of Environmental Science and Health, A29:1061-1072.
- Beulke S., Brown C.D. & Dubus I.G. (1998). Evaluation of the use of preferential flow models to predict the movement of pesticides to water sources under UK conditions. SSLRC contract report PL0516 for MAFF/PSD, 101p.

- 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.
- Beven K. & Germann P. (1982). Macropores and water flow in soils. Water Resources Research, 18: 1311-1325.
- Boesten J.J.T.I. & van der Linden A.M.A. (1991). Modeling the influence of sorption and transformation on pesticide leaching and persistence. Journal of Environmental Quality, 20:425-435.
- 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.
- Bosch D.D. & West L.T. (1998).Hydraulic conductivity variability for two sandy soils. Soil Sci Soc Am Journal, 62:90-98.
- Brouwer W.W.M., Boesten J.J.T.I., Linders J.B.H.J., van der Linden A.M.A., 1994. The behaviour of pesticides in soil: Dutch guidelines for laboratory studies and their evaluation. Pesticide Outlook 5, 23-28.
- Brown C.D., Baer U., Günther P., Trevisan M. & Walker A. (1996). Ring test with the models LEACHP, PRZM-2 and VARLEACH: variability between model users in prediction of pesticide leaching using a standard data set. Pesticide Science, 47:249-258.
- Brown C.D., Dubus I.G., Fogg P., Spirlet M. & Gustin C. (2004). Exposure to sulfosulfuron in agricultural drainage ditches: field monitoring and scenario-based modelling. Pest Management Science, 60:765-776.
- Brown C.D., Hart A., Lewis K.A. & Dubus I.G. (2003). p-EMA: simulating the environmental fate of pesticides for a farm-level risk assessment system. Agronomie, 23:67-74.
- Brown C.D., Hodgekinson R.A., Rose D.A., Syers J.K. & Wilcockson S.J. (1995). Movement of pesticides to surface waters from a heavy clay soil. Pesticide Science, 43:131-140.
- Carsel R.F., Mulkey L.A., Lorber M.N. & Baskin L.B. (1985). The Pesticide Root Zone Model (PRZM): a procedure for evaluating pesticide leaching threats to groundwater. Ecological Modelling, 30:49-69.
- Christiansen J.S., Thorsen M., Clausen T., Hansen S. & Refsgaard J.C. (2004). Modelling of macropore flow and transport processes at catchment scale. Journal of Hydrology, 299: 136-158.
- Coquet Y. & Barriuso E. (2002). Spatial variability of pesticide adsorption within the topsoil of a small agricultural catchment. Agronomie, 22:389-398.
- Danish Hydraulic Institute (DHI). (1998). MIKE 11 User Guide and Technical Reference Manual.

- Devillers J., Farret R., Girardin P., Rivière J.-L. & Soulas G. (2005). Indicateurs pour évaluer les risques liés à l'utilisation des pesticides. Tech & Doc editions, Lavoisier, Paris, 278p. ISBN: 2-7430-0747-8.
- Donigian, A. S., Imhoff J.C., Bicknell B.R. & Kittle J.L. (1984). Application Guide for the Hydrologic Simulation Program - FORTRAN. EPA 600/3-84-066, U.S. EPA, Athens, GA, 30605.
- Dubus I.G., Azimonti G., Bach M., Barriuso E., Bidoglio G., Bouraoui F., Fialkiewicz W., Fowler H., François O., Højberg A., Hollis J., Jarvis N., Kajewski I., Kjær J., Lewis K., Lobnik F., Lolos P., Réal B., Reichenberger S., Stenemo F., Suhadolc M., Surdyk N. & Vavoulidou–Theodorou E. (2006). Introducing FOOTPRINT: Functional Tools for Pesticide Risk Assessment and Management. Oral presentation at the Warwick conference on Pesticide Behaviour in Soils, Water and Air, Warwick, UK, 27-29 March 2006.
- Dubus I.G., Beulke S. & Brown C.D. (2002). Calibration of pesticide leaching models: critical review and guidance for reporting. Pest Management Science, 58:745-758.
- Dubus I.G., Brown C.D. & Beulke S. (2003). Sources of uncertainty in pesticide fate modelling. The Science of the Total Environment, 317:53-72.
- Dubus I.G., Brown C.D., Beulke S. & Turner N.L. (2002b). Uncertainty and probabilistic approaches to pesticide fate modelling. Cranfield Centre for EcoChemistry research report for DEFRA/PSD no. PL0548, 139p.
- EEC (1991). Council directive of 15/7/91 concerning the placing of plant protection products on the market. Official Journal of the EuropeanCommunities, 34, Brussels.
- EEC (1995). Commission Directive 95/36/EC of 14 July 1995 amending Council Directive 91/414/EEC concerning the placing of plant protection products on the market. Official Journal, L172:8-20.
- EEC (2000). Establishing a framework for community action in the field of water policy (2000/60/EC). Official Journal of the European Communities, No. L327. Commission of the European Communities, Brussels.
- Flury M., Leueneberger J., Studer B. & Flühler H. (1995). Transport of anions and herbicides in a loamy and a sandy field soil. Water Resources Research, 31:823-835.
- Flury, M. (1996). Experimental evidence of transport of pesticides through field soils a review. Journal of Environmental Quality, 25: 25-45.
- FOCUS (1995). Leaching models and EU registration. Doc 4952/VI/95, 124p.
- FOCUS (1997a). Soil persistence models and EU registration. 77p.
- FOCUS (1997b). Surface Water Models and EU Registration of Plant Protection Products. European Commission Document 6476/VI/96.
- FOCUS (2000). FOCUS groundwater scenarios in the EU plant protection product review

process. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000

- FOCUS (2001a). FOCUS constitution. Communication from the FOCUS Steering Committee, 30 April 2001, 2p.
- FOCUS (2001b). FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.1.
- FOCUS (2002). Generic guidance for FOCUS groundwater scenarios. Version 1.1, April 2002.
- FOCUS (2005a). "Landscape And Mitigation Factors In Aquatic Risk Assessment. Volume 1. Extended Summary and Recommendations". Report of the FOCUS Working Group on Landscape and Mitigation Factors in Ecological Risk Assessment, EC Document Reference SANCO/10422/2005. 133 pp.
- FOCUS (2005b). "Landscape And Mitigation Factors In Aquatic Risk Assessment. Volume
 2. Detailed Technical Reviews". Report of the FOCUS Working Group on Landscape
 and Mitigation Factors in Ecological Risk Assessment, EC Document Reference
 SANCO/10422/2005. 434 pp.
- FOCUS (2005c) "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration" Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 1.0, 431 pp.
- FOCUS helpdesk (2006). http://viso.ei.jrc.it/focus/
- Fontaine D.D., Havens P.L., Blau G.E. & Tillotson P.M. (1992). The role of sensitivity analysis in groundwater risk modelling for pesticides. Weed Technology, 6:716–724.
- Francaviglia R., Capri E., Klein M., Hosang J., Aden K., Trevisan M. & Errera G. (2000). Comparing and evaluating pesticide leaching models: results for the Tor Mancina dataset (Italy). Agricultural Water Management, 44:135-151.
- Freissinet C., Vauclin M. & Erlich M. (1999). Comparison of first-order analysis and fuzzy set approach for the evaluation of imprecision in a pesticide groundwater pollution screening model. J Contam Hydrol, 37:21-43.
- Gärdenäs A.I., Simunek J., Jarvis N., van Genuchten M.Th. (2006). Two-dimensional modelling of preferential water flow and pesticide transport from a tile-drained field. Journal of Hydrology, in press.
- Garratt J.A., Capri E., Trevisan M., Errera G. & Wilkins R.M. (2003). Parameterisation, evaluation and comparison of pesticide leaching models to data from a Bologna field site, Italy. Pest Management Science, 59:3-20.

- Gottesbüren B., Aden K., Bärlund I., Brown C., Dust M., Görlitz G., Jarvis N., Rekolainen S.
 & Schäfer H. (2000). Comparison of pesticide leaching models: results using the Weiherbach data set. Agricultural Water Management, 44:153-181.
- Grochulska J. & Kladivko E.J. (1994). A two-region model of preferential flow of chemicals using a transfer function approach. Journal of Environmental Quality, 23:498-507.
- Haith D.A. (2001). TurfPQ, A Pesticide Runoff Model for Turf. Journal of Environmental Quality 30:1033-1039.
- Hall D.G.M. & Webster C.P. (1993). An amended functional leaching model applicable to structured soils. II. Model application. Journal of Soil Science, 44, 589-599.
- Hall D.G.M. (1994). Simulation of dichlorprop leaching in three texturally distinct soils using the Pesticide Leaching Model. Journal of Environmental Science and Health Part A -Environmental Science and Engineering, 29:1211-1230.
- Harris G.L. & Catt J.A. (1999). Overview of the studies on the cracking clay soil at Brimstone Farm, UK. Soil Use and Management, 15:233–239.
- Herbst M., Diekkru B. & Vereecken (2006). Geostatistical co-regionalization of soil hydraulic properties in a micro-scale catchment using terrain attributes. Geoderma, 132:206-221.
- Holman I.P., Dubus I.G., Hollis J.M. & Brown C.D. (2004). Using a linked soil model emulator and unsaturated zone leaching model to account for preferential flow when assessing the spatially distributed risk of pesticide leaching to groundwater in England and Wales. The Science of the Total Environment, 318:73-88.
- Holvoet K., van Griensven A., Seuntjens P. & Vanrolleghem P.A. (2005). Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. Physics and Chemistry of the Earth, Parts A/B/C, 30:518-526.
- Hutson J.L. & Wagenet R.J. (1992). LEACHM: Leaching Estimation And Chemistry Model. A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Version 3, Department of Soil, Crop and Atmospheric Sciences. Research series no. 92-3, Cornell University, NY, USA.
- Jantunen A.P.K., Trevisan M. & Capri E. (2005). Computer models for characterizing the fate of chemicals in soil: Pesticide leaching models and their practical applications. In: Soil-Water-Solute Process Characterization: An Integrated Approach, Álvarez Benedí J and R Muñoz-Carpena (Eds.), CRC Press, USA, 715-756.
- Jarvis N., Boesten J.J.T.I., Hendriks R., Klein M., Larsbo M., Roulier S., Stenemo F., Tiktak A. (2003). Incorporating macropore flow into FOCUS PEC models. In: A.A.M. Del Re, E. Capri, L. Padovani, M. Trevisan (eds.). Pesticides in air, plant, soil and water system. Proceedings of the XII international symposium on Pesticide Chemistry, 4-6 June 2003, Piacenza, Italy, pp. 963-972.

- Jarvis N.J. & Dubus I.G (2006). State-of-the-art review on preferential flow. Report DL#6 of the FP6 EU-funded FOOTPRINT project [www.eu-footprint.org], 60p.
- Jarvis N.J. & Leeds-Harrisson P.B. (1987). Modelling water movement in a drained clay soil. I. Description of the model, sample output and sensitivity analysis. Journal of Soil Science, 38:487-498.
- Jarvis N.J. (1989). CRACK a model of water and solute movement in cracking soils. Department of Soil Sciences Report 159, Swedish University of Agricultural Sciences, Uppsala, Sweden, pp. 38.
- Jarvis N.J., Brown C.D. & Granitza E. (2000). Sources of error in model predictions of pesticide leaching: a case study using the MACRO model. Agricultural Water Management, 44:247-262.
- Jarvis N.J., Jansson P-E., Dik P.E. & Messing I. (1991). Modelling water and solute transport in macroporous soil. I. Model description and sensitivity analysis. Journal of Soil Science, 42:59-70.
- Jarvis N.J., Hollis J.M., Nicholls P.H., Mayr T. & Evans S.P. (1997). MACRO-DB: a decision-support tool for assessing pesticide fate and mobility in soils. Environmental Modelling and Software, 12(2-3):251-265.
- Jarvis, N.J., Brown, C.D. & Granitza, E. (2000). Sources of error in model predictions of pesticide leaching: a case study using the MACRO model. Agricultural Water Management, 44, 247-262.
- Jarvis, N.J., Stähli, M., Bergström, L. & Johnsson, H. 1994. Simulation of dichlorprop and bentazon leaching in soils of contrasting texture using the MACRO model. Journal of Environmental Science & Health, 29:1255-1277.
- Jaynes, D.B., Ahmed, S.I., Kung, K.-J.S. & Kanwar R.S. (2001). Temporal dynamics of preferential flow to a subsurface drain. Soil Science Society America Journal, 65: 1368-1376.
- Jene B. (1998). PELMO 3.00 Manual Extension. Staatliche Lehr-und Forschungsanstalt für Landwirstschaft, Weinbau und Gartenbau, Neustadt, Germany.
- Jones R.L. & Mangels G. (2002). Review of the validation of models used in federal insecticide, fungicide, and rodenticide act environmental exposure assessments. Environmental Toxicology & Chemistry, 21:1535-1544.
- Jury W.A., Spencer W.F., and Farmer W.J. (1983). Behaviour assessment model for trace organics in soil. I. Model description. Journal of Environmental Quality, 12:558-563.
- Jury W.A., Sposito G. & White R.E. (1986). A transfer function model of solute transport through soil. 1. Fundamental concepts. Water Resources Research, 22:243-247.
- Jury W.A. 1982. Simulation of solute transport using a transfer function model. Water Resources Research, 18:363-368.

- Kladivko E.J., van Scoyoc G.E., 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.
- Klein M. (1991). PELMO: Pesticide leaching model. Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, Schmallenberg, Germany.
- Klein M., Müller M., Dust M., Görlitz G., Gottesbüren B., Hassink J., Klowskowski R., Kubiak R., Resseler H., Schäfer H., Stein B. & Vereecken H. (1997). Validation of the pesticide leaching model PELMO using lysimeter studies performed for registration. Chemosphere, 35:2563-2587.
- Knisel W.G., Davis F.M. & Leonard R.A. (1992). GLEAMS Version 2.0, User Manual. USDA-ARS, Southeast Watershed Research Laboratories, Tifton, GA, USA.
- Konikow L.F. & Bredehoeft J.D. (1992). Groundwater models cannot be validated. Advances in Water Resources, 15:75-83.
- Kordel W. & Klein M. (2006). Prediction of leaching and groundwater contamination by pesticides. Pure and Applied Chemistry, 78:1081-1090.
- Kung, K-J.S. (1990). Preferential flow in a sandy vadose zone. I. Field observation. Geoderma, 46: 51-58.
- Larsbo M. & Jarvis N. (2003). MACRO 5.0. A model of water flow and solute transport in macroporous soil. Technical description. Emergo 2003:6. Swedish University of Agricultural Sciences, Department of Soil Sciences, Uppsala, Sweden.
- Larsbo M., Roulier S., Kasteel R., Stenemo F., Vanderborght J., & Jarvis N. (2005). An improved dual-permeability model of water flow and solute transport. Vadose Zone J. (in press).
- Larsson, M.H. & Jarvis, N.J. (1999). Evaluation of a dual-porosity model to predict fieldscale solute transport in a macroporous clay soil. Journal of Hydrology, 215, 153-171.
- Leake C.R., Humphreys S.P. & Austin D.J. (1995).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.62,195 –200.
- Lennartz B. (1999). Variation of herbicide transport parameters within a single field and its relation to water flux and soil properties. Geoderma, 91:327–345.
- Lewis K., Brown C.D., Hart A. & Tzilivakis J. (2003). p-EMA (III): overview and application of a software system designed to assess the environmental risk of agricultural pesticides. Agronomie, 23:85-96.
- Loague K. (1991). The impact of land use on estimates of pesticide leaching potential: assessements and uncertainties. J Contam Hydrol, 8:157–175.

- Loague K., Bernknopf R.L., Green R.E. & Giambelluca T.W. (1996). Uncertainty of groundwater vulnerability assessments for agricultural regions in Hawaii: Review. Journal of Environmental Quality, 25:475-490.
- Mackay D. (1979). Finding fugacity feasible. Environmental Science and Technology, 13 (10):1218-1223.
- Mackay D. (1991) Multimedia Environmental Models: The Fugacity Approach. Lewis, Boca Raton, FL, Florida, USA.
- Mackay D. & Paterson S. (1991). Evaluating the multimedia fate of organic chemicals. A level III fugacity model. Environmental Science and Technology 25:427-436.
- Mackay N., Terry A., Arnold D., Pepper T., Price O.& Mason P. (2004). Approaches and tools for higher tier assessment of environmental fate. CEA report for DEFRA PL0546 and PS2202, 275p.
- Malone R.W., Ahuja L.R., Ma L., Wauchope R.D., Ma Q. & Rojas K.W. (2004a). Application of the Root Zone Water Quality Model (RZWQM) to pesticide fate and transport: an overview. Pest Management Science, 60:205-221.
- Mangels G. (2001). The development of MUSCRAT (Multiple Scenario Risk Assessment Tool), a software tool for conducting surface water exposure assessments. http://www.waterborne-env.com/modeling/muscrat_documentation.pdf
- Mills W.C. & Leonard R.A. (1984). Pesticide pollution probabilities. Transactions of the ASAE, 27:1704-1710.
- Nicholls P.H. 1994. Simulation of the movement of bentazon in soils using the CALF and PRZM models. J. of Envir. Sci. and Health, A29(6):1157-1166.
- Nicholls, P.H., Harris, G.L., Brockie, D. (2000). Simulation of pesticide leaching at Vredepeel and Brimstone farm using the macropore model PLM. Agricultural Water Management, 44:307-315.
- Nofziger D.L. & Hornsby A.G. (1986). A micro-computer base management tool for chemical movement in soil. Applied Agricultural Research, 1:50-56.
- Nolan B.T., Bayless E.R., Green C.T., Garg S., Voss F.D., Lampe D.C., Barbash J.E., Capel P.D. & Bekins B.A. (2005). Evaluation of unsaturated-zone solute-transport models for studies of agrochemicals. USGS Open-file report 2005-1196, 16p.
- Novak J.M., Moorman T.B. & Cambardella C.A. (1997). Atrazine sorption at the field scale in relation to soils and landscape position. Journal of Environmental Quality, 26:1271-1277.
- Oreskes N. (1998). Evaluation (not validation) of quantitative models. Environ-mental Health Perspectives 106:1453-1460.
- Oreskes N., Shrader-Frechette K. & Belitz K. (1994). Verification, validation and confirmation of numerical models in the earth sciences. Science, 263:641-646.

- Pachepsky Ya.A., Rawls W.J., Timlin D.J. (1999). The current status of pedotransfer functions: their accuracy, reliability, and utility in field- and regional-scale modeling.p. 223-234. In D.L. Corwin et al. (ed.) Assessment of non-point source pollution in the vadose zone. Geophysical Monogr. 108. American Geophysical Union, Washington, DC.
- Parkin T.B. (1993). Spatial variability of microbial processes in soil –a review. Journal of Environmental Quality, 22:409-417.
- Parsons J.E., Thomas D.L. & Huffman R.L. (2001). Agricultural non-point source water quality models: their use and application. Southern Cooperative Series Bulletin #398, 195p. ISBN: 1-58161-398-9. Available from: http://www3.bae.ncsu.edu/Regional-Bulletins/Modeling-Bulletin/modeling-bulletin.pdf
- PELEP-DSS (2006). http://newwave.geru.ucl.ac.be/PELEP_DSS/
- Pennell K.D., Hornsby A.G., Jessup R.E. & Rao P.S.C. (1990). Evaluation of five simulation models for predicting aldicarb and bromide behavior under field conditions. Water Resources Research, 26:2679-2693.
- PFMODELS (2006). The Pesticide Fate MODELS discussion list. www.pfmodels.org
- Pollock D., Salama R. & Kookana R. (2002). A study of atrazine transport through a soil profile on the Gnangara Mound, Western Australia, using LEACHP and Monte Carlo techniques. Australian Journal of Soil Research, 40:455-464.
- Rao P.S.C., Hornsby A.G. & Jessup R.E. (1985). Indexes for ranking the potential for pesticide contamination of groundwater. Soil and Crop Science Society of Florida Proceedings, 44:1-8.
- Resseler H., Schäfer H., Görlitz G., Hermann M., Hosang J., Kloskowski, R. Marx R., Sarafin R., Stein B., Winkler B., 1997. Recommendations for conducting simulation calculations for the registration procedure. Nachrichtenblatt des Deutschen Pflanzenschutzdiensts 49, 305-309.
- Reus J., Leendertse P., Bockstaller C., Fomsgaard I., Gutsche V., Lewis K., Nilsson C.,
 Pussemier L., Trevisan M., van der Werf H., Alfarroba F., Blumel S., Isart J.,
 McGrath D. & Seppala T. (2002). Comparison and evaluation of eight pesticide
 environmental risk indicators developed in Europe and recommendations for future
 use. Agriculture ecosystems & Environment, 90:177-187.
- 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.
- Roth K. (1995). Steady-state flow in an unsaturated, two-dimensional, macroscopically homogeneous, Miller-similar medium. Water Resources Research, 31: 2127-2140.
- RZWQM Team (1992). Root Zone Water Quality Model, Version 1.0. Technical documentation. GPSR Technical Report no. 2., USDA-ARS-GSPR, Fort Collins, USA.

- Siimes K. & Kämäri J. (2003). A review of available pesticide leaching models: Selection of models for simulation of herbicide fate in Finnish sugar beet cultivation. Boreal Environment Research, 8:31-51.
- Simunek J., Huang K. & van Genuchten M.T. (1998). The HYDRUS code for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 6.0, Research Report No. 144, U.S. Salinity Laboratory, USDA, ARS, Riverside, California, 164pp.
- Simunek J., Jarvis N.J., van Genuchten M.T. & Gardenas A. (2003). Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. Journal of Hydrology, 272:14-35.
- Smith, R.E., 1992. Opus: An Integrated Simulation Model for Transport of Nonpoint-source pollutants and the Field Scale. Vol. 1, Documentation. USDA-ARS, ARS-98, 120 pp.
- Steenhuis T.S., Pacenka S., & Porter K.S. (1987). MOUSE: A management model for evaluating groundwater contamination from diffuse surface sources aided by computer graphics. Applied Agricultural Research, 2:277-289.
- Strömqvist J. & Jarvis N.J. (2005). Sorption, degradation and leaching of the fungicide Iprodione in a golf green under Scandinavian conditions: measurements, modelling and risk assessment. Pest Management Science, 61:1168-1178.
- Thiéry D., Golaz C., Gutierrez A., Fialkiewicz W., Darsy C., Mouvet C. & Dubus I.G. (2004). Refinements to the MARTHE model to enable the simulation of the fate of agricultural contaminants from the soil surface to and in groundwater. Proceedings of the COST international workshop, Saturated and unsaturated zone: integration of process knowledge into effective models, Rome, Italy, 5-7 May 2004. ISBN 88-7830-387-9, pp. 315-320.
- 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.
- Tietje O. & Tapkenhinrichs M. (1993). Evaluation of pedo-transfer functions. Soil Sci Soc Am Journal, 57:1088-1095.
- Tiktak A. (2000). Application of pesticide leaching models to the Vredepeel dataset. II. Pesticide fate. Agricultural Water Management, 44:119-134.
- Tiktak A., de Nie D., van der Linden T., Kruijne R. (2002). Modelling the leaching and drainage of pesticides in the Netherlands: the GeoPEARL model. Agronomie, 22:373-387.
- Tiktak A., van den Berg F., Boesten J.J.T.I., van Kraalingen D., Leistra M. & van der Linden A.M.A. (2000). Manual of FOCUS PEARL version 1.1.1. RIVM report 711401 008, Alterra report 28, Bilthoven, Wageningen, The Netherlands.

- Tiktak A., van der Linden A.M.A. & Swartjes F.A. (1994). PESTRAS: a one-dimensional model for assessing leaching and accumulation of pesticides in soil. National Institute of Public Health and the Environment. Report no. 715501003, Bilthoven, The Netherlands.
- Trevisan M., Errera G., Goerlitz B., Remy B. & Sweeney P. (2000). Modelling ethoprophos and bentazone fate in a sandy humic soil with primary pesticide fate model PRZM-2. Agricultural Water Management, 44:317-335.
- Unknown (2003). http://www.belspo.be/belspo/home/publ/pub_ostc/CP/CP33ann4_en.pdf
- Unlu K., Ozenirler G. & Sözudogru S. (1997). Classification of commonly used pesticides in Turkey based on pollution potentials. Turkish Journal of Engineering and Environmental Sciences, 21:189-202.
- USDA–ARS. (1992). Root zone water quality model. RZWQM V 1.0. Technical documentation. GPSR Tech. Rep. 2. USDA-ARS Great Plains Systems Res. Unit, Ft. Collins, CO.
- van den Berg F. & Boesten J.J.T.I. (1999). Pesticide leaching and accumulation model (PESTLA) version 3.4. Description and user's guide. Technical document 43, DLO Winand Staring Centre, Wageningen, The Netherlands.
- van Genuchten M.Th. & Wierenga P.J. (1976). Mass transfer studies in sorbing porous media: 1. analytical solutions. Soil Science Soc. of Am. Jour., 40:473-481.
- van Genuchten M.Th., Leij F.J. & Yates S.R. (1991). The RETC code for quantifying the hydraulic functions of unsaturated soils. USDA, US Salinity Laboratory, Riverside, CA.
- Vanclooster M., Boesten J.J.T.I., Trevisan M., Brown C.D., Capri E., Eklo O.M., Gottesbüren B., Gouy V. & van der Linden A.M.A. (2000). A European test of pesticide leaching models: methodology and major recommendations. Agricultural Water Management, 44:1-19.
- Vanclooster M., Piñeros Garcet J.D., Boesten J.J.T.I., Van den Berg F., Leistra M., Smelt J., Jarvis N., Roulier S., Burauel P., Vereecken H., Wolters A., Linnemann V., Fernandez E., Trevisan M., Capri E., Padovani L., Klein M., Tiktak A., Van der Linden A., De Nie D., Bidoglio G., Baouroui F., Jones A. and Armstrong A. (2003). Effective approaches for Assessing the Predicted Environmental Concentrations of Pesticides: A proposal supporting the harmonised registration of pesticides in Europe. Final report of the APECOP European project, 158 p.
- Vanclooster M., Viaene P., Diels J. & Christiaens K. (1995). WAVE: a mathematical model for simulating water and agrochemicals in the soil and vadose environment. Reference and user's manual (release 2.0), Institute for Land and Water Management, Katholieke Universiteit Leuven, Leuven, Belgium.

- Vanderborght J. (2005). Parameterization of dispersivity in pesticide fate models: why is it all but trivial? 4th European Modelling Workshop, Paris, France, 21-22 November 2005. http://www.pfmodels.org/emw4.html
- Walker A. & Brown P.A. (1983). Spatial variability in herbicide degradation rates and residues in soil. Crop Protection, 2:17-25.
- Walker A. (1987). Evaluation of a simulation model for prediction of herbicide movement and persistence in soil. Weed Research, 27:143-152.
- Walker A., Calvet R., Del Re A.A.M., Pestemer W. & Hollis J.M. (1995). Evaluation and improvement of mathematical models of pesticide mobility in soils and assessment of their potential to predict contamination of water systems. Mitteilungen aus der Biologischen Bundesanstalt f
 ür Land- und Forstwirtschaft, 307:1-115.
- Wania F. & Mackay D. (1999). The evolution of mass balance models of persistent organic pollutant fate in the environment. Environmental Pollution 100:223-240.
- Wauchope R.D., Rojas K.W., Ahuja L.R., Ma Q., Malone R.W. & Ma L. (2004). Documenting the pesticide processes module of the ARS RZWQM agroecosystem model. Pest Management Science, 60: 222-239.
- Wauchope R.D., Yeh S.; Linders B.H.J.J., Kloskowski R., Tanaka K., Rubin B., Katayama A., Kördel W/; Gerstl Z., Lane M. & Unsworth J.B. (2002). Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Management Science, 58:419-445.
- WEBFRAM (2006). WEB-integrated FRAMework. www.webfram.com.
- Williams J.R., Jones C.A. & Dyke P.T. (1984). A modeling approach to determining the relationship between erosion and soil productivity. Trans. ASAE, 27:129-144.
- Wood L.S., Scott H.D., Marx D.B. & Lavy T.L. (1987). Variability in sorption coefficients of metolachlor on a Captina silt loam. Journal of Environmental Quality, 16:251-256.
- Wösten, J., Lilly, A., Nemes, A., and Bas, C. L. (1999). Development and use of a database of hydraulic properties of European soils. Geoderma, 90:169-185.