Vulnerability Assessments of Pesticide Leaching to Groundwater

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Abstract

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Pesticides may have adverse environmental effects if they are transported to groundwater and surface waters. The vulnerability of water resources to contamination of pesticides must therefore be evaluated. Different stakeholders, with different objectives and requirements, are interested in such vulnerability assessments. Various assessment methods have been developed in the past. For example, the vulnerability of groundwater to pesticide leaching may be evaluated by indices and overlay-based methods, by statistical analyses of monitoring data, or by using process-based models of pesticide fate. No single tool or methodology is likely to be appropriate for all end-users and stakeholders, since their suitability depends on the available data and the specific goals of the assessment.

The overall purpose of this thesis was to develop tools, based on different process-based models of pesticide leaching that may be used in groundwater vulnerability assessments. Four different tools have been developed for end-users with varying goals and interests: (i) a tool based on the attenuation factor implemented in a GIS, where vulnerability maps are generated for the islands of Hawaii (U.S.A.), (ii) a simulation tool based on the MACRO model developed to support decision-makers at local authorities to assess potential risks of leaching of pesticides to groundwater following normal usage in drinking water abstraction districts, (iii) linked models of the soil root zone and groundwater to investigate leaching of the pesticide mecoprop to shallow and deep groundwater in fractured till, and (iv) a meta-model of the pesticide fate model MACRO developed for 'worst-case' groundwater vulnerability assessments in southern Sweden. The strengths and weaknesses of the different approaches are discussed.

Keywords: groundwater, vulnerability, pesticide, leaching, modelling

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Cover illustration: Pineapple field on the island of O’ahu, Hawaii

Contents

Appendix

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I. Stenemo, F., Ray, C., Yost, R. and Matsuda, S., 2007. A screening tool for vulnerability assessment of pesticide leaching to groundwater for the islands of Hawaii, U.S.A. *Pest Management Science*, 63: 404-411.

II. Stenemo, F. and Jarvis, N. 2007. Accounting for uncertainty in pedotransfer functions in vulnerability assessments of pesticide leaching to groundwater. *Pest Management Science*. In press.

III. Stenemo, F., Jørgensen, P.R. and Jarvis, N., 2005. Linking a one-dimensional pesticide fate model to a three-dimensional groundwater model to simulate pollution risks of shallow and deep groundwater underlying fractured till. *Journal of Contaminant Hydrology*, 79: 89-106.

IV. Stenemo, F., Lindahl, A.M.L., Gärdenäs, A. and Jarvis, N., 2007. Meta-modeling of the pesticide fate model MACRO for groundwater exposure assessments using artificial neural networks. *Journal of Contaminant Hydrology*. In press.

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In Paper I, I had the main responsibility for the updating of the software tool and writing the paper. In Paper II, the work was planned jointly by the authors, but I was responsible for all the analyses and the writing. The study reported in Paper III was planned jointly by the authors. I carried out the linkage of the models, all the simulations and analyses and was also responsible for the writing. I initiated the work described in Paper IV, developed and tested the meta-model and I was also responsible for the writing. The second author performed the sensitivity analyses and the case-study using field data collected by the third author.

Introduction

Pesticides play an important role in modern agriculture. However, both accidental spills and routine usage may have adverse environmental effects, if pesticides are transported to groundwater or surface waters. There is therefore a need to evaluate the potential risks of pesticide usage that may lead to contamination of water resources, both for regulatory authorities, extension services and water managers. A risk assessment methodology consists of risk determination, risk evaluation and risk management (Shukla et al., 1996). One part of this process is to evaluate the vulnerability of a water body, for example a groundwater resource, to contamination. Once the vulnerability has been established, more detailed studies concerning exposure levels and effects on target organisms might be pursued. The terms vulnerability and exposure assessment are often used interchangeably. However, in this thesis, which is concerned with pesticide leaching to groundwater, vulnerability is broadly defined as "the tendency or likelihood for contaminants to reach a specified position in the groundwater system after introduction above the uppermost aquifer" (NRC, 1993). Exposure assessment is used to describe the process of estimating actual loads to, or concentrations in, a water body. Of course, estimated loadings and concentrations may be used as a measure of the "tendency or likelihood" of a contaminant to reach a specific location.

The purpose of assessing the vulnerability of groundwater to pesticide leaching might be to either identify active ingredients that pose a potential threat, for example in a regulatory setting (FOCUS, 2000) or to identify soils and regions where pesticide usage is more likely to have negative environmental effects on groundwater. Identification of vulnerable soils might, for example, help local water managers to direct monitoring and mitigation strategies within a catchment. The most suitable approach to assess the vulnerability of groundwater to pesticide leaching will ultimately depend on the goal of the application and the end-users, as well as the available data. A relatively simple approach might be suitable if the aim is to rank different contaminants, whereas a more complex approach is needed to perform scenario analyses to evaluate mitigation measures (Loague et al., 1998). In general, it is considered important that the method uses easily obtainable information and that the uncertainty of data and predictions is quantified (Stewart and Loague, 1999).

Groundwater vulnerability assessment is a data-driven process, with soil data, the hydrological situation and the pesticide properties forming the foundation on which the assessment rests. In addition to basic data, knowledge of the processes that govern the environmental fate of the pesticide and its transport to the environmental compartment for which the vulnerability assessment is performed is equally necessary. Groundwater vulnerability assessments may be based on relatively simple index and overlay-based methods (Aller et al., 1985; NRC, 1993). In these approaches, different attributes that are considered important for groundwater vulnerability are combined with weights to arrive at a vulnerability index. Overlay methods usually only account for soil properties and hydrogeological conditions (so-called intrinsic vulnerability assessments). Given the importance of pesticide properties for the potential leaching, these methods may be of limited value by themselves, but might be useful in combination with methods based on process-oriented models (Gogu and Dassargues, 2000).

Groundwater vulnerability assessments can also be based on statistical analyses of monitoring data (Burkart et al., 1999; Worrall and Kolpin, 2003; Mishra et al., 2004). These methods aim to relate observable characteristics in the environment to the vulnerability of groundwater to pesticide contamination. Troiano et al. (1999) developed a method to describe the groundwater vulnerability as a function of soil attributes, whereas Worrall and Kolpin (2004) predicted the presence or absence of a compound in the groundwater from soil factors, the depth to groundwater and the molecular characteristics of the pesticide.

Process-based models of pesticide fate are commonly used to assess the vulnerability of pesticide leaching to groundwater (Khan and Liang, 1989; Petach et al., 1991; Bleecker et al., 1995; Soutter and Pannatier, 1996; Diaz-Diaz et al., 1999). The range of models used includes, for example, simple indices or analytical solutions to transport equations (Rao et al., 1985; Jury et al., 1987), detailed numerical simulation models (Mullins et al., 1993; Larsbo et al., 2005) and meta-models (Bouzaher, 1993; Padovani et al., 2001; Holman et al., 2004; Tiktak et al., 2006). The term 'meta-model' is used in this thesis to refer to a simplified representation of a simulation model, designed to approximate selected input-output mappings of the simulation model (Bouzaher et al., 1993; Kleijnen and Sargent, 2000). The input-output mapping for a pesticide fate model might, for example, predict the fraction of the applied pesticide leaching to a specific depth (output) as a function of pesticide properties (input) for specific site and weather conditions.

Process-based models provide an environmental fate measure, for example the simulated annual average concentration at a specific depth. This measure is not necessarily used as the final estimate of vulnerability. A vulnerability assessment methodology, or a decision rule, in combination with additional data, is needed to arrive at the final vulnerability measure. Various decision rules are conceivable, for example simply stating that if the simulated concentration exceeds a specific value then the groundwater is judged to be vulnerable (FOCUS, 2000), or it may include a ranking and comparison with the results for other pesticides, with more or less known leaching behaviour (Li et al., 1998). The predicted environmental fate measure may also be combined with additional data, for example data on the depth to groundwater or the subsoil geology, and more complex decision rules to arrive at a judgment on vulnerability.

Different stakeholders, both organizations and individuals, are interested in groundwater vulnerability assessments. Each of these groups has different objectives, perspectives and requirements. Therefore, no single tool or methodology is likely to be useful for all of these groups. Groundwater vulnerability assessments are used, for example by registration authorities in approval schemes for pesticide registration. Within the European Union (EU), simulation models are used to evaluate pesticide transport to surface and groundwater in a tiered approach (FOCUS, 1995, 2000), before active ingredients are registered for use. Pre-defined 'reasonable worst-case' scenarios have been developed to support this procedure, which are considered to represent major agricultural regions within Europe. Following the same approach, several EU member states have developed their own national scenarios (Jarvis et al., 2003). Extension services may also have an interest in tools that assess the potential transport of pesticides to various environmental compartments (groundwater, surface waters, air). They may use the tools in discussions with farmers on how to minimize potential negative environmental impacts of pesticide usage at the farm level, and to evaluate different mitigation strategies. In Sweden, local authorities must assess the potential risk of leaching of pesticides in a groundwater protection area, before deciding on pesticide application permits. Another potentially important group of users are water managers working under the recent EU Water framework Directive, charged with the task of maintaining and improving water quality across larger catchments. Groundwater vulnerability assessments could be used to identify hot-spots within catchments or regions, where monitoring programs and mitigation measures should be focused, and also to estimate likely time-scales for self-remediation of contaminated groundwater.

Although straightforward in principle, there are several important practical problems associated with assessing the vulnerability of groundwater to pesticide leaching using methods based on simulation models. Soil data, pesticide properties, and climate data are needed to parameterize and run transient simulation models. Data might be available in soil survey databases, but they may be uncertain and incomplete. Thus, although some model parameters can be determined directly from measured data, others must be estimated from model parameter estimation routines, so-called pedotransfer functions (Wösten et al., 2001). However, these pedotransfer functions introduce a considerable degree of uncertainty in the model predictions (Wösten et al., 1990; Vereecken et al., 1992). In addition to uncertainties in the model parameter estimation and the primary data, there is also considerable uncertainty in predictions arising from 'model errors' due to the fact that processes are not well described or even considered.

Aims and objectives

The overall purpose of this thesis was to develop groundwater vulnerability assessment tools based on process-based models of pesticide leaching. Different tools were developed for potential end-users with different goals and interests. The requirements concerning data availability and level of process detail vary with the purpose of the groundwater vulnerability assessment. Paper I presents a groundwater vulnerability assessment methodology used by the Hawaii Department of Agriculture based on the attenuation factor (Rao et al., 1985). Paper II describes a tool designed for leaching risk assessments in drinking water abstraction districts, where only standard soil survey data are available. The tool, which is based on a detailed numerical model, incorporates a safety factor to account for prediction uncertainty due to parameter errors. Paper III discusses the possibilities and limitations of an approach in which two numerical models are linked to simulate coupled unsaturated-saturated pesticide transport from the soil surface to deep and shallow groundwater in fractured till. This model tool was designed for water managers wishing to evaluate the consequences of contamination of groundwater resources. A meta-model based on the pesticide fate model MACRO (Larsbo et al., 2005) is developed in Paper IV. This tool was designed for spatial applications at larger scales, combining the speed of execution and simplicity of leaching indices whilst retaining some of the process complexity in the original model.

In the following, the processes that affect pesticide leaching are first described. A brief overview of the sources of error in predicting pesticide leaching is then presented. This is followed by a description of the simulation model based groundwater vulnerability assessment methods explored in this thesis. Their various strengths and weaknesses are discussed. The thesis concludes with some general remarks and suggestions for future research.

Processes affecting pesticide leaching to groundwater

After a pesticide has been applied to a field, and entered the soil, several interacting processes determine the fate of the pesticide (Sawhney and Brown, 1989; Walker, 2001). The properties of the pesticide influencing sorption and degradation determine, to a great extent, pesticide behaviour in the soil. Sorption to soil minerals (clay minerals, iron oxides, etc.) and organic material retards pesticide movement in the soil, and increases the time available for degradation by micro-organisms. However, sorption can also limit the rate of degradation (Guo et al., 2000). Sorption of non-polar compounds has been shown to depend mainly on soil organic carbon content (Chiou, 1989), except when the content is low, for example in deeper subsoil layers. The partition of the pesticide between the dissolved and sorbed phases in the soil is often described using the non-linear Freundlich isotherm, where the sorption strength is expressed by a partition constant, or the partition constant normalized to the soil organic carbon content, the K_{oc} value (Wauchope et al., 2002). The degree of non-linearity of the isotherm is described by the Freundlich exponent.

Biodegradation is usually the main loss path of pesticides in the soil. This process depends on many factors, such as micro-organism activity, water content, pH, temperature, and the availability of the compound to the degraders, which in turn depends on both sorption strength and physical accessibility (Bergström and Stenström, 1998). These interacting processes can lead to complex or 'non-ideal' degradation kinetics (Richter et al., 1996; Jarvis, 2007). However, in the simplest case, which assumes first-order kinetics, pesticide degradation can be expressed in terms of a ‘half-life’ under ‘reference’ conditions with respect to temperature and water. In general, degradation rates are highest in the topsoil and decrease with increasing depth, mainly due to less favourable conditions for the microbial community. Volatilization is another loss pathway from the soil for some pesticides (Glotfelty and Schomburg, 1989).

Pesticide transport in the soil may be described by the advection-dispersion equation if the soil meets the underlying assumption of a homogeneous porous medium which is in equilibrium within a representative elementary volume. However, non-equilibrium preferential flow and transport processes are important in many soils (Kladivko et al., 1991; Traub-Eberhard et al., 1994; Brown et al., 1995; Flury, 1996; Jarvis, 2002) and the advection-dispersion equation will then fail to describe solute movement. The term preferential flow encompasses several processes with the similar consequence of rapid flow and/or transport through a small portion of the soil. Preferential flow may occur as macropore flow through cracks and wormholes (Beven and Germann, 1982), as finger flow in layered (Hill and Parlange, 1972; Hillel, 1987) or homogeneous water repellent sandy soils (Ritsema et al., 1993), or as heterogeneous flow in soils with materials of differing texture. The textural composition of the soil mainly determines the hydraulic properties in the matrix (e.g. the unsaturated hydraulic conductivity and water retention characteristics), while soil structural development and surface boundary conditions will determine the extent of rapid flow in soil macropores. Texture and organic carbon content have been shown to exert a strong control on the structure-forming processes in the soil, and therefore indirectly influence the extent of macropore flow (Jarvis et al., 2007; Jarvis, 2007).

Preferential flow normally leads to increases in pesticide leaching, since a large portion of the topsoil, where the sorption and degradation processes are in general most effective, is by-passed, (Harris et al., 1994; Brown et al., 1995; Zehe and Flühler, 2001). The effect of macropore flow on predicted leaching has been shown to be the largest for less leachable (i.e. strongly sorbing and quickly degrading) pesticides (Larsson and Jarvis, 2000). It is important to develop methods that account for the effects of preferential flow on groundwater vulnerability, since it is a significant process influencing pesticide leaching in a wide range of soils.

Total pesticide leaching may be related to the total amount of precipitation or recharge, although these relationships are not likely to be simple, except for unstructured sandy soils (Beulke et al. 1999). The application timing in relation to the seasonal climate patterns may also affect pesticide leaching risks. Pesticides applied during the autumn, when the soil is becoming wetter and colder, are more likely to leach deeper in the soil. The timing of application in relation to rainfall or irrigation events affects leaching. This is especially so for structured soils that exhibit macropore flow, where intensive rainfall or irrigation events following soon after the application might lead to increased leaching due to induced macropore flow (Gish et al., 1991; Jarvis, 2007). In contrast, dry weather or low-intensity rainfall following application can reduce the potential leaching risk since the pesticide is then incorporated into the matrix, and becomes, to some extent, "protected" from macropore flow induced by subsequent rainfall (Shipitalo et al., 1990; Edwards et al., 1993). Reduced-tillage practices generally increase the mass of the applied pesticide leached to groundwater, because they preserve the soil structure (Barbash and Resek, 1996; Jarvis, 2007).

Sources of prediction uncertainty

The processes and factors that affect pesticide transport in the soil interact in various ways, which makes it a complex system to describe. Therefore, models which capture the major processes are potentially useful tools to support groundwater vulnerability assessments. However, modelling of pesticide transport is associated with several sources of uncertainty. Dubus et al. (2003) provides an overview of these sources, and in the following only a brief summary is given. Fig. 1 provides an overview of the various sources of error.

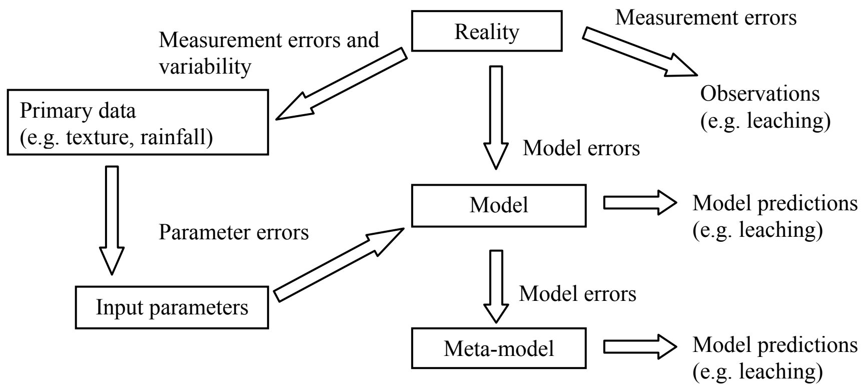

Fig. 1 Schematic overview of the sources of error in model predictions

A model is a simplified description of reality aiming to describe one or several specific aspects. Models are, by definition, always more or less 'wrong': not all processes are correctly described in a model and some are ignored. The failure of a model to correctly simulate experimental data, given accurate input parameters, may be termed model error (Beck et al., 1997).

Parameter error arises from incomplete knowledge of the appropriate values for model parameters. Direct measurements are subject to error and variation. In addition, not all parameters in complex models can be directly measured and so they must be estimated from primary data (i.e. physical and chemical properties), which are also subject to measurement and sampling errors and the inherent spatial and temporal variability of environmental properties. Prediction of model input from primary data is also associated with uncertainty. Pedotransfer functions

(Wösten et al., 2001) used to estimate model parameters are often associated with large uncertainties due to unexplained variation (Espino et al., 1995; Wösten et al., 2001). This is discussed further in the section 'Simulation models'. Parameter errors (e.g. in the parameters of the van Genuchten water retention function or the pesticide degradation rate) can also be introduced by poor fits of model functions to measured data (Dubus et al., 2003). Furthermore, assumed values for parameters that are difficult or impossible to measure may be wrong. In general, the subjectivity inherent in model parameterisation means that the influence of the modeller is important and has to be taken into consideration (Brown et al., 1996; Boesten, 2000; Boesten and Gottesbüren, 2000; Vanclooster et al., 2000).

Methods of groundwater vulnerability assessment

This chapter discusses different methods used in groundwater vulnerability assessments to predict pesticide leaching, introducing the methods developed in this thesis, which are also described in detail in Papers I-IV. The description of the various methods is not meant to be exhaustive, but aims to provide a background to the methods developed in this thesis. Three types of methods are discussed: (i) index-based, or screening, approaches, (ii) simulation models, and (iii) meta-models.

Index-based approaches

Index-based approaches, or screening models, are developed mainly to provide a relative ranking of pesticides. Mobility index models (Laskowski et al., 1982; Gustafson, 1989), which only account for pesticide properties, have been developed to screen pesticides with respect to their mobility in soil. Another group of index-based models is based on physical and chemical principles governing pesticide transport in soil (Rao et al., 1985; Meeks and Dean, 1990; Bacci and Gaggi, 1993; Hantush and Marino, 2000, Connell and van Daele, 2003) and considers both pesticide properties (e.g. pesticide half-life, sorption and volatilization), soil properties (e.g. bulk density, organic carbon content) and hydrological factors (e.g. recharge). Hantush et al. (2002) developed a screening model to predict leached mass fraction in dual porosity soils based on an analytical solution of the two-region advection-dispersion equation.

The attenuation factor (AF) used in Paper I is based on assumptions of convective transport, first-order kinetics for degradation and constant soil properties with depth (Rao et al., 1985) and reflects the fraction of the pesticide that leaches to a specific depth, d (m):

$$AF = \exp\left(\frac{-\ln 2 \cdot d \cdot RF \cdot \theta_{FC}}{q \cdot t_{1/2}}\right) \quad [1]$$

where θ_{FC} is the volumetric water content at field capacity (-), q is the average recharge rate (m/d), $t_{1/2}$ is the pesticide half-life (d) and RF is a retardation factor (-) defined as:

$$RF = 1 + \frac{\rho_b \cdot f_{oc} \cdot K_{oc}}{\theta_{FC}} \quad [2]$$

where ρ_b is the dry soil bulk density (kg/m^3), f_{oc} is the organic carbon content (-) and K_{oc} is the partition coefficient for soil organic carbon (m^3/kg).

Index based approaches are easy to implement in a geographical information system and have been widely used to evaluate pesticide leaching potential (e.g. Khan and Liang, 1989; Loague et al., 1989; Meeks and Dean, 1990; Diaz-Diaz et al., 1999). Khan and Liang (1982) and Loague et al. (1989) classified the relative leaching risk based on arbitrary classes of the attenuation factor. Access to monitoring data on pesticide occurrence in groundwater can be used as a calibration or 'reality check' for vulnerability assessments based on attenuation factors. If no measured data are available, a relative ranking of pesticides can be made, but it is difficult to make predictions of pesticide leaching risk with any confidence. It may be misleading to assign class names, such as 'low risk' or 'high risk', to ranges of the attenuation factor values without relating these to observed or assumed behaviour of actual pesticides.

Index and screening methods require relatively few input parameters. Often, data available from standard surveys should be sufficient to define the soil properties. However, an estimate of the recharge rate is also required to calculate the attenuation factor. The input requirements are even lower if the purpose is to rank pesticides for a specific soil on the basis of the attenuation factor, since the actual values of the compliance depth, water content at field capacity, and the recharge rate in equation 1 do not matter. However, if the purpose is to rank different soils, in different locations, with respect to leaching risk for a specific pesticide, these parameters need to be determined for each location.

The index based approaches are associated with uncertainties related to the spatial and temporal variability of model parameters, as well as measurement errors and model errors. The effect of model parameter uncertainties for the attenuation factor has been quantified analytically (Loague et al., 1990; Diaz-Diaz ret al., 1999) using first-order uncertainty analysis (Cornell, 1972).

Groundwater vulnerability assessment for the islands of Hawaii

Paper I describes an updated version of a GIS-based tool that is used by the Hawaii Department of Agriculture for first assessments of the potential risk of pesticide leaching to groundwater. Maps are generated for the islands depicting the estimated groundwater vulnerability. The tool is based on the attenuation factor and parameter uncertainty is accounted for by first-order uncertainty analysis. A soil properties database is included in the tool (Yost et al., 1994; SCS-USDA, 1976), as well as a pesticide database (Oshiro et al., 1994), together with spatially-distributed estimates of recharge rates for the islands of Hawaii. Individual pesticides are classified as being 'likely', 'unlikely' or 'uncertain' to pose a threat to groundwater. This is done by comparing revised attenuation factor (AFR) values (Li et al., 1998) with values calculated for two reference chemicals, that are considered to represent a ‘leacher’ and a ‘non-leacher’ under Hawaii conditions (Fig. 2).

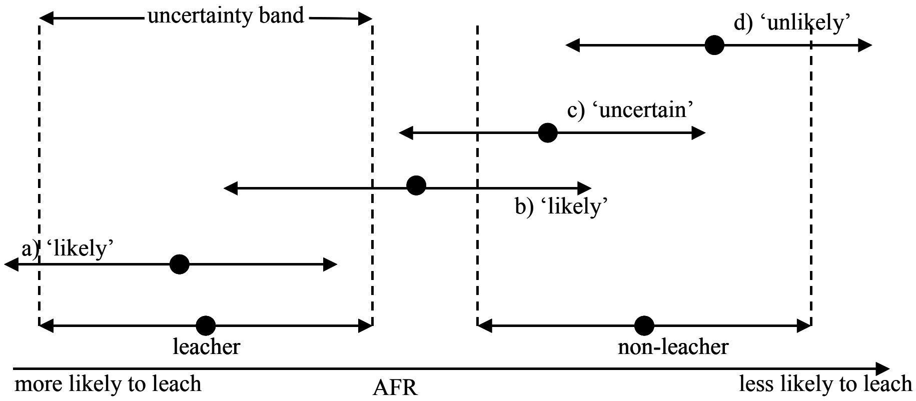

Fig. 2 Classification scheme used in the vulnerability assessment tool for the islands of Hawaii

The use of reference chemicals (Li et al., 1998) provides a means to account for observed behaviour of pesticides in the assessment. The uncertainty is combined with the value of the revised attenuation factor to provide an uncertainty band (defined as the value of the revised attenuation factor ± the error), both for the pesticide being evaluated and the reference chemicals. The uncertainty bands are then used in the classification scheme (Fig. 2). The classification scheme is somewhat subjective, and different definitions are conceivable for case b, which could also be classified as 'uncertain', and case c, which could be classified as 'unlikely', depending on the decision-maker's view on risk and precaution.

The output from the tool consists of maps of the main islands of Hawaii where the risk classification of the pesticide is identified for different soil mapping units (Fig. 3). In the present version of the tool, no account is taken of where different crops are grown, and therefore where pesticides are likely to be applied. In future improvements of the tool, this aspect could be included in additional GIS layers to the extent that such data are available.

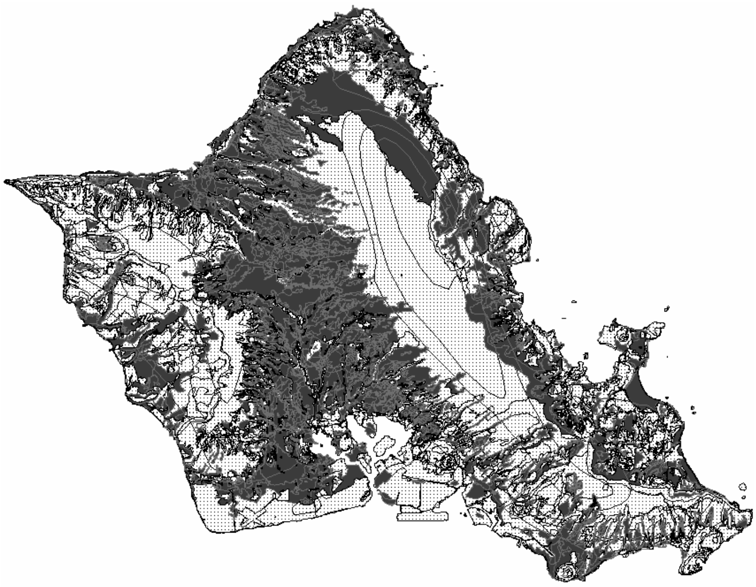

Fig. 3 Vulnerability classification map for chlorpyrifos for the island of O'ahu (black = 'unlikely', dotted = 'no data')

Strengths and weaknesses

The main advantage of index-based approaches is that they require relatively few input parameters but are still based on theory of solute transport in soil. This makes them suitable for relative vulnerability assessments for situations where only limited data are available, for example for larger-scale regional assessments. They are also easy to implement in a geographical information system or a wider decision-support system, since they are simple and fast to execute.

The main disadvantage is that several processes and factors that affect groundwater vulnerability are not accounted for in index-based approaches. For example, the attenuation factor does not account for macropore flow, which is a widespread phenomenon that strongly affects pesticide leaching. Additional factors that affect the leaching potential of a pesticide that are not accounted for include the timing of application during the year in relation to the main recharge period (although it may be possible to consider this by varying the recharge rate) and the application method.

Index based methods are useful for providing a relative ranking of pesticide leaching potential. Relative rankings of pesticides and soils with respect to leaching potential can for example be useful in agricultural advisory work. However, the vulnerability assessments should be calibrated against groundwater monitoring data in order to determine limit values of the index that can define the boundary between potential leachers and non-leachers. Using reference chemicals, as in Paper I, the ranking of pesticides can to some extent be related to observed, or assumed, behaviour of the pesticides in the environment. This is a useful and practical way to enable management decisions to be based on current knowledge of pesticide leaching, since absolute values are not needed to define class boundaries (Li et al., 1998). One problem with the definition of the reference chemicals is that it is assumed that their leaching behaviour is fixed for all locations. However, for sites with a shallow groundwater table, occurrence of preferential flow, or under intensive irrigation regimes, the leaching behaviour may be different.

Simulation models

Several simulation models have been developed to predict pesticide leaching (Carsel et al., 1985; Boesten and van der Linden, 1991; Klein, 1995; Larsbo et al., 2005). They vary in their degree of complexity, model assumptions and process descriptions. Vanclooster et al. (2000) reported the conclusions of a comprehensive test of several widely-used pesticide leaching models, using four different datasets. With respect to the validation exercise itself, it was concluded that reliable information on boundary conditions, soil hydrology, soil heat and tracer behaviour is necessary. It was further concluded that deterministic models can simulate the observed experimental data reasonably well, given a proper parameterization. Vanclooster et al. (2000) further stressed the importance of dealing with the uncertainty associated with predicted pesticide fluxes. Another major conclusion was that the modeller has a large influence on the results of a validation exercise, due to the subjectivity inherent in model parameter estimation methods (Francaviglia et al., 2000; Gottesbüren et al., 2000).

Simulation models are in general data-intensive and require detailed information about the soil physical and hydraulic properties. These data are not usually available in, or easily derived from, standard soil survey databases. Simulation models that account for macropore flow require additional parameters, some of which are difficult or impossible to measure directly. Model parameters can be derived by calibration against the results of field or laboratory experiments. However, this requires a detailed data set to avoid problems due to non-uniqueness (Larsbo and Jarvis, 2005). Such data are expensive and time-consuming to obtain, so this is not a viable approach to parameterize simulation models for vulnerability assessments. Instead, pedotransfer functions may be used to estimate model parameters that cannot be directly inferred from available measured soil data (Wösten et al., 2001). A pedotransfer function is a statistical relationship between one or more easily measured properties of the soil and a model parameter. Most effort has been put into the development of pedotransfer functions for soil water retention parameters (e.g. Vereecken et al., 1989), less so for hydraulic conductivity. The development of pedotransfer functions for parameters in models that account for macropore flow is in its infancy. Simulation models have been used to assess the leaching of pesticides to groundwater on a regional scale (e.g. Carsel et al., 1988; Soutter and Pannatier, 1996) and pedotransfer functions have been used to parameterize simulation models in several studies (e.g. Petach et al., 1991; Bleecker et al., 1995).

The use of pedotransfer functions to parameterize simulation models introduces additional uncertainty (Espino et al., 1995; Wösten et al., 2001). These uncertainties stem from both the prediction errors of the pedotransfer functions and the spatial variability of input parameters to the pedotransfer functions (Minasny and McBratney, 2002). The performance of various pedotransfer functions has been evaluated in several studies (Tietje and Tapkenhinrichs, 1993; Cornelis et al., 2001; Wagner et al., 2002). Soet and Stricker (2003) compared three sets of pedotransfer functions to predict soil hydraulic properties. Poor agreement was found, both between measured and predicted soil hydraulic properties and between the results of the different pedotransfer functions. An evaluation of the use of pedotransfer functions to predict hydraulic parameters in soil water modelling prompted Mermoud and Xu (2006) to question their value. They further stressed that the validity of pedotransfer functions should be assessed on a case-by-case basis. A somewhat different conclusion was drawn by Wösten et al. (1990) after a functional evaluation of different methods to derive soil hydraulic properties. They found no significant differences in simulated water storage, although model parameterization with direct measurements did lead to a better agreement with the measurements than pedotransfer functions. Considering the trade-off between cost and accuracy, they further concluded that the use of pedotransfer functions might be a viable alternative to directly measured data for certain applications. Given the above, it is clear that the uncertainties in pedotransfer functions need to be considered if they are used to parameterize models used in groundwater vulnerability assessments. Paper II describes such an uncertainty analysis, the results of which were used to define a safety factor in a decision-support tool based on the macropore flow model MACRO (Larsbo et al., 2005).

Simulation tool for pesticide leaching to groundwater

Paper II describes a simulation tool based on the MACRO model (Larsbo et al., 2005), developed to support decision-makers at Swedish local authorities who have the responsibility to assess potential risks of leaching of pesticides to groundwater following normal usage in drinking water abstraction zones. The tool consists of a simplified user interface to the MACRO model, which guides the user through the model set-up. One requirement when developing the tool was that it should only require easily available data for model parameterization, such as texture and soil organic carbon content. Furthermore, the user of the tool should not need to have in-depth knowledge of simulation modelling.

The simulation set-up and output from the tool is similar to that of the FOCUS (2000) groundwater scenarios. Output from the tool consists of simulated average yearly leaching concentrations for a 20-year simulation at one metre depth, as well as the long-term average concentration, including an uncertainty factor. Thus, the tool may be considered to provide site-specific simulation scenarios that can be used to provide a measure of the risk of pesticide leaching for locations where little input data are available. It follows the same philosophy as the older MACRO_DB simulation system (Jarvis et al., 1997), but differs in some important aspects. First, the simulation tool includes weather data for Swedish conditions only. Second, most of the parameterization routines have been changed. In addition, the tool is easier to use, but less flexible than MACRO_DB, which can be seen as an advantage, since it makes it easier to compare and communicate simulation results between various end-users.

The MACRO model

In Papers II-IV the one-dimensional dual-permeability pesticide fate model MACRO (Larsbo et al., 2005) is used. Flow and solute transport are simulated in two pore regions, micro- and macropores, and diffusive water and solute exchange between the two domains is simulated using a first-order approximation. The exchange between pore regions is governed by an 'effective' diffusion pathlength, a key parameter in MACRO that to a large extent regulates the strength of macropore flow, together with the matrix hydraulic conductivity. The diffusion pathlength can be considered as a surrogate parameter for soil structure. Water flow in the micropore region is calculated using Richards' equation and solute transport is described by the advection-dispersion equation. In the macropore region only advective solute transport is simulated and water flow is assumed to be governed by gravity alone. Water retention is described using a modified form of the van Genuchten equation (van Genuchten, 1980) and the unsaturated hydraulic conductivity is described using the Mualem model (Mualem, 1976).

Pesticide degradation is assumed to follow first-order kinetics and different rate coefficients can be set for micro- and macropores and sorbed and dissolved phases. The degradation rate is temperature and water content dependent. Pesticide sorption is given by the Freundlich isotherm and can either be simulated as instantaneous or kinetic using a two-site model (Altfelder et al., 2000). Applications of a pesticide are simulated as irrigation events, and the fraction intercepted by the crop can be specified. Volatilization of pesticide is not simulated and can only be accounted for, in an approximate way, by reducing the dose. Driving data to the model consist of daily or hourly rainfall, daily minimum and maximum air temperatures, and either pre-calculated potential evapotranspiration (PE), or meteorological data needed to calculate PE with the Penman-Monteith equation.

The MACRO model has been used to model solute transport to field drains (e.g. Larsson and Jarvis, 1999; Larsbo and Jarvis, 2005), solute leaching in soil columns (e.g. Roulier and Jarvis, 2003; Jarvis et al., 2007) and deep leaching in fractured soils and rocks (Roulier et al., 2006). Furthermore, MACRO is used in the FOCUS surface water scenarios (FOCUS, 1995) and in one of the FOCUS groundwater scenarios (FOCUS, 2000) to assess leaching risks for registration purposes within the EU. The model is also used in national groundwater scenarios used for product registration purposes in Sweden (Jarvis et al., 2003), Denmark and Norway.

Model parameterization

In the simulation tool, the MACRO model is parameterized using a combination of pedotransfer functions (e.g. Wösten et al., 1998; Jarvis et al., 2002; Bergkvist and

Jarvis, 2004), default model parameter values and reasonable worst-case parameter values. The pedotransfer functions of Wösten et al. (1998), developed from a large database of European soils, are used to calculate the parameters in the van Genuchten water retention equation from the clay and sand contents, the organic carbon content and the dry bulk density. In turn, dry bulk density is calculated from the organic carbon content assuming a simple 'S'-shaped function (Bergkvist and Jarvis, 2004). Bulk density and organic carbon content are used to calculate the total porosity (Jarvis et al., 1997). The effective porosity concept is used to estimate the saturated hydraulic conductivity (including macropores) according to a function developed from a database of Swedish soils (Messing, 1993). The saturated hydraulic conductivity of the micropores (i.e. the hydraulic conductivity at -10 cm) is estimated from the geometric mean particle size (Jarvis et al., 2002). The effective diffusion pathlength, *d* (mm), reflecting soil structural development, is estimated from soil texture and organic carbon content as:

$$d = 10^{2.41 - 1.86 * d_g - 9.3 * f_{oc}} \quad [4]$$

where d_g is the geometric mean particle size (Shirazi and Boersma, 1984). Equation 4 is based on a limited amount of experimental data collected at one site in southern Sweden (Roulier and Jarvis, 2003). Nevertheless, the functional control of soil texture and organic matter on macropore flow is well established in the literature (Brown et al., 2000; Shaw et al. 2000; Jarvis et al., 2007).

A pesticide database is included in the tool, based on the latest review of active ingredients within the EU, with data on pesticide half-life under reference conditions, K_{oc} and the Freundlich exponent.

Functional evaluation of pedotransfer function errors

A functional evaluation of the pedotransfer function errors was performed. The input parameters to the pedotransfer functions were assumed to be known without uncertainty, and only the error of the functions themselves was evaluated. This may underestimate the uncertainty, since the input parameters to the pedotransfer functions are also to some extent uncertain, due to measurement errors and spatial variation. Vereecken et al. (1992) found that uncertainty in the pedotransfer functions overshadowed the influence of spatial variability of the input parameters. In contrast, Minasny and McBratney (2002) found that the uncertainty in input variables was important, since small errors in the pedotransfer function input resulted in large uncertainties in model predictions. Thus, further study of the combined effect of pedotransfer function error and input uncertainty would be desirable. The pedotransfer function errors were propagated through the simulation tool in a Monte Carlo approach, in which pedotransfer function errors were sampled using Latin hypercube sampling (McKay et al., 1973) for different scenarios of soil properties, pesticide properties and application timings (autumn or spring). It was concluded that large uncertainties are introduced in the model predictions due to the errors in the pedotransfer functions. Simulation results for any given scenario often varied across several orders of magnitude (Fig. 4). The uncertainty was largest for scenarios that resulted in small simulated concentrations.

Sensitivity analysis

The sensitivity of model predictions to the various pedotransfer function errors was investigated. Such information can be useful to direct future research efforts to decrease the uncertainty in the simulation results. Parameter errors related to the generation and maintenance of macropore flow in the model (the saturated hydraulic conductivity of the micropores and the effective diffusion pathlength) were found to strongly influence the results for fine-textured soils. The predictions were also sensitive to two parameters in the van Genuchten water retention function (N and α), for both coarse and fine-textured soils. Uncertainty in pesticide properties is also important (Dubus et al., 2003), but this was not included in the analysis, since the vulnerability assessment tool makes use of fixed pesticide properties based on the outcome of EU registration procedures.

Uncertainty factor

An uncertainty factor was defined as the ratio of the simulated 80^{th} percentile leachate concentration to that simulated in the absence of pedotransfer function error. Linear regression was used to investigate relationships between the uncertainty factor, input parameters and the simulated concentration (Fig. 5). The uncertainty factor was strongly related to the simulated concentration in the absence of pedotransfer error, but other variables, such as the clay and sand content, were not significant. Thus, the concentration predicted by the simulation tool is multiplied by the uncertainty factor (defined by the regression shown in Fig. 5) to account for the uncertainty due to pedotransfer function errors. Effectively, this transforms the predictions to an 80^{th} percentile 'worst-case' estimate. If the goal is to rank pesticides at one location, the uncertainty factor has no value since it does not influence the relative ranking. If, on the other hand, a specific concentration is used as a vulnerability indicator for regulatory decisions (i.e. the EU drinking water limit), the uncertainty factor should be used to provide a measure of safety that satisfies the pre-cautionary principle.

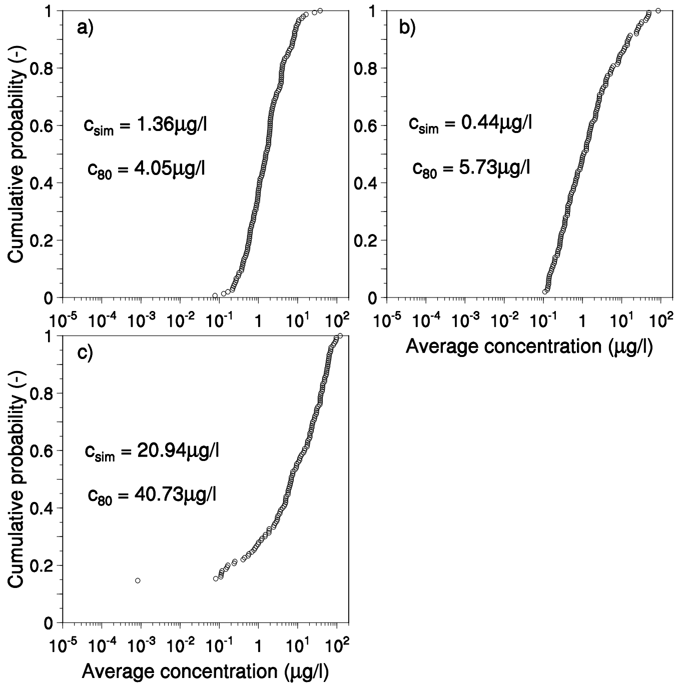

Fig. 4. Cumulative probability distributions for 3 scenarios with autumn application for a pesticide with $t_{1/2}$ = 10 days and K_{oc} = 30 cm^3/g: a) coarse-textured soil, b) medium-textured soil, c) fine-textured soil. C_{sim} denotes the simulated concentration without any pedotransfer function errors, and C_{80} the 80^{th}-percentile concentration in the Monte-Carlo simulations.

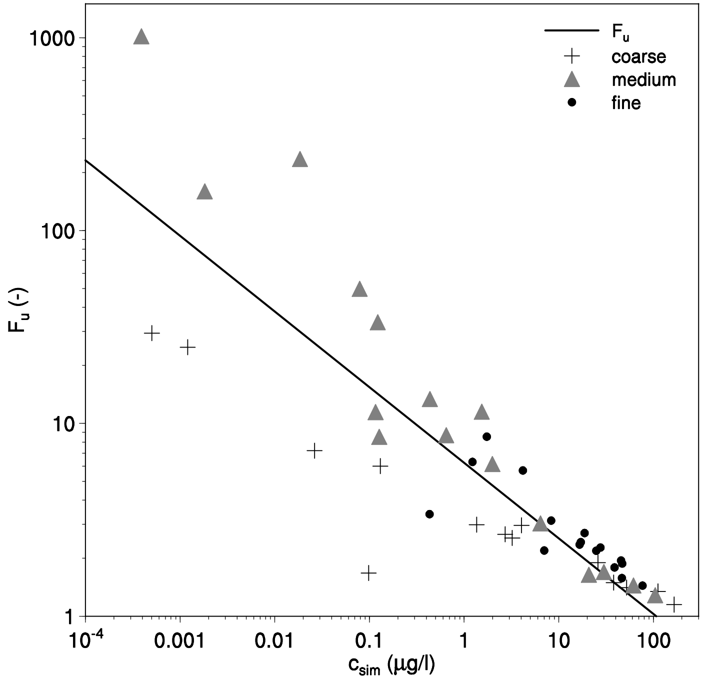

Fig. 5. The uncertainty factor, F_u, as a function of the simulated concentration, c_{sim}, (two scenarios with $c_{sim} < 10^{-4}$ µg/L are not shown on the figure).

Vulnerability assessment for deep groundwater underlying fractured till

In Paper III, the MACRO model was loose-linked to the three-dimensional unsaturated/saturated flow and transport model FRAC3DVS (Therrien and Sudicky, 1996) to investigate leaching of the pesticide mecoprop to shallow and deep groundwater in fractured till at Havdrup, Denmark. The objective of this modelling exercise was to develop a tool that could be used by water managers to evaluate pesticide leaching to deeper groundwater aquifers and wells. For example, it could be used predict the economic consequences of contamination as a function of self-remediation times.

Linking two models introduces an artificial boundary at the linkage depth, which has significant effects on the simulation results. This is potentially important for the studied site, where fracture flow has been shown to be important (Jørgensen et al., 1998, 2002). So, one additional objective of Paper III was to evaluate the effect of different boundary conditions (spatially variable, spatially constant, constant in time or transient) used for the groundwater model and to evaluate the effects of different assumptions concerning the connectivity of fractures at the interface between the two models.

The uncertainty of the simulations in Paper III was not evaluated, but it could be expected to be large. Therefore, Paper III must be considered as a preliminary feasibility study to develop recommendations for a suitable methodology. Further studies would be needed to determine a suitable vulnerability indicator and to assess the uncertainty in the predictions.

The FRAC3DVS model

FRAC3DVS uses Richards' equation and the advection-dispersion equation to describe water flow and solute transport in the matrix. Discrete fractures are defined as parallel plates and water and solute transfer between fractures and matrix is modelled. Linear sorption and first-order degradation can also be simulated. FRAC3DVS has been used to model solute and water flow for columns and pesticide leaching in field studies (Jørgensen et al., 1998, 2002, 2004a, 2004b).

Model linkage

The rationale for using two linked models was that each of the models provides a better description of the governing processes in the part of the system for which they are applied. For example, MACRO is a one-dimensional model and although it can simulate coupled unsaturated-saturated flow and a fluctuating groundwater table, it can only be used where the groundwater fluxes are predominantly vertical. FRAC3DVS simulates fracture flow, but it is not possible in practice to explicitly describe the geometry of individual macropores in the soil root zone, where the macropores are more densely distributed and of different types (e.g. fissures, earthworm channels, voids between clods produced by tillage). Furthermore, a high spatial resolution of the computational nodes would be necessary to accurately capture the highly transient nature of the transport processes close to the soil surface, which would result in prohibitively long execution times. Combining the two models results in a tool that can simulate a system that each of the two models alone cannot describe. Ideally, one single model should have been used to avoid the drawbacks of the linkage approach, but the adopted strategy provides a practical way forward by combining two existing models.

MACRO and FRAC3DVS were linked using a one-way approach, where output from the MACRO model provided FRAC3DVS with its upper boundary condition of water and solute fluxes. There was no feed-back from the groundwater model to MACRO and the models were run separately. This modelling set-up is limited to locations where either the groundwater table is sufficiently deep so as not to influence the zone simulated by MACRO, or situations where the groundwater table fluctuations can be reasonably well simulated with MACRO.

Modelling

The simulation models were parameterized with site-specific data (Jørgensen et al., 1998, 2002, 2004b), pedotransfer functions and by calibrating the parameter in MACRO that regulates the water table position. Havdrup is situated south-west of Copenhagen, and is a fractured till extending from the soil surface to a limestone aquifer at 16 meters depth, with a local sand aquifer at between 5 and 5.5 meters depth with lateral groundwater flow (Jørgensen et al., 1998, 2002). A spatially-variable upper boundary was created from MACRO simulations where the pesticide half-life, the topsoil organic carbon content, and two parameters regulating simulated macropore flow (the aggregate half-width, and the saturated matrix hydraulic conductivity) were sampled using Latin Hypercube sampling (McKay et al., 1979). The MACRO simulations were randomly distributed at the upper boundary of FRAC3DVS. Simulated pesticide concentrations in the local sand aquifer at 5 meters depth using the spatially variable boundary were compared to the simulated concentration using a spatially aggregated boundary, and a boundary using 'effective' MACRO parameters. No major differences were found, although the differences were greatest between the spatially aggregated and the 'effective' parameter cases.

The effect of a transient vs. a constant upper boundary condition was investigated in plot-scale simulations, together with the effect of the connectivity of macropore flow and transport between the models. Diverting the pesticide loads simulated by MACRO preferentially to the fractures seems reasonable, given that most of the pesticide leaching in column experiments has been shown to be transported along fractures and macropores (Jørgensen et al., 1998, Jørgensen et al., 2002). The simulations showed a clear influence of using transient boundary conditions, and diverting pesticide preferentially to fractures, on the simulated mecoprop leaching to the regional aquifer (Fig. 6). It was concluded that a spatially constant but transient, upper boundary with pesticide leaching preferentially diverted to fractures represents a ‘reasonable worst-case’ for assessing the vulnerability of shallow and deep groundwater at this, and similar, sites.

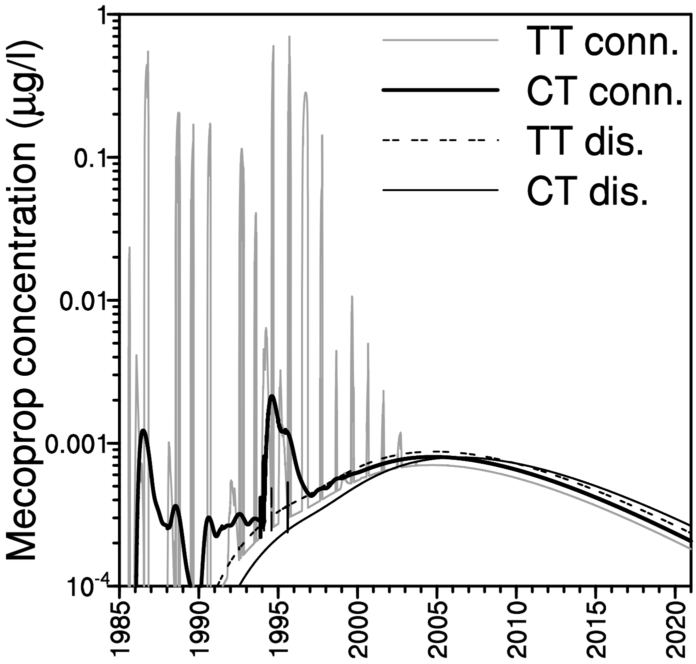

Fig 6. Mecoprop flux concentrations impacting the regional aquifer at 16 meters depth for the plot-scale simulations for the connected (conn.) and disconnected cases (dis.) using different upper boundary conditions (TT = transient water and solute flux, CT = constant water flux and transient solute flux).

Strengths and weaknesses

The advantages of process-based simulation models are that they can account for the most important processes that affect the fate and transport of pesticides in the soil. Furthermore, they are flexible in that a wide range of conditions with respect to for example soil properties, hydrological situations, management regimes and climate may be investigated. They may also be used to evaluate the effect of different management and mitigation options on reducing pesticide losses to water bodies.

The main limitation of simulation models in the context of groundwater vulnerability assessments is their extensive data requirements. For example, the soil data required to parameterize the MACRO model are time-consuming and expensive to obtain. Therefore, detailed simulation models cannot easily be used for routine groundwater vulnerability assessments in practice, except for a fixed and limited number of typical or 'worst-case' scenarios. The FOCUS scenarios used in pesticide regulation in the EU are one example of this kind of application. Another example was presented in the modelling work described in Paper III. The use of a detailed simulation model also requires in-depth knowledge of the model and its various parameters and available options, although this restriction can be circumvented by designing user-friendly interfaces with fixed pre-defined simulation settings (Paper II; FOCUS, 2000).

The data requirements of simulation models can be met by using pedotransfer functions, although this introduces additional uncertainty in the simulation results (Paper II). However, this may be acceptable for relative vulnerability assessments where the actual simulated concentrations are of no interest. If a specific concentration is used as a vulnerability indicator in the simulation tool, then uncertainty in the model predictions due to the pedotransfer function errors should be accounted for, for example by using the approach presented in Paper II.

Simulation models are also relatively slow to execute. This is a serious practical limitation in regional leaching assessments where many simulations must be run. Running a simulation model may also be considered too cumbersome and time-consuming in other potential model applications, for example, in direct discussions between extension advisors and farmers.

Meta-models

There are only a few examples of the development and application of meta-models for predicting pesticide leaching. A meta-model may be constructed using various techniques, for example linear or non-linear regression, artificial neural networks, and ‘look-up’ tables. Using non-linear regression, Bouzaher et al. (1993) constructed a meta-model of the RUSTIC modelling system (Dean et al., 1989) to predict herbicide concentrations in groundwater and surface water from soil properties (organic matter content, sand content, dry bulk density, water retention capacity) and pesticide properties (Henry’s constant, degradation rate and the soil organic matter partition coefficient). Bouzaher et al. (1993) used the meta-model in an integrated environmental/economic modelling system designed for policy evaluation at a regional scale, and concluded that meta-modelling is useful for such a purpose. Holman et al. (2004) constructed an ‘emulator’ of the MACRO model to predict pesticide concentrations at one metre depth using a ‘look-up’ table approach. The emulator, or meta-model, linked to a substrate attenuation factor model, was found to predict realistic regional patterns of pesticide leaching for some selected pesticides. Padovani et al. (2001) used a stepwise regression procedure to create a meta-model of a one-dimensional simulation model (LEACHP) to assess the spatial distribution of potential pesticide contamination of groundwater. They concluded that the approach seemed useful for this purpose. Tiktak et al. (2006) constructed a meta-model of the spatially distributed pesticide leaching model EuroPEARL (Tiktak et al., 2004) by using an analytical expression. This meta-model uses four spatially variable parameters, calibrated to fit model predictions, to predict the 80th percentile concentration of the annual average leaching at one metre depth for a 20 year simulation.

The first steps in developing a meta-model are to determine the goal of the meta-model, identify the inputs, specify the domain of applicability, and select the output variable of interest (Kleijnen and Sargent, 2000). The simulations that will form the basis of the meta-model are then determined and executed. This involves selecting a way to parameterize the simulation model for the selected domain, and choices of parameter values that are kept constant. Finally, the meta-model is constructed using, for example regression, artificial neural networks or a look-up table.

Meta-modelling of the pesticide fate model MACRO

A meta-model of MACRO was developed for 'worst-case' groundwater vulnerability assessments in southern Sweden (Paper IV) using the same set-up and parameterization routines underlying the simulation tool described in Paper II. MACRO was parameterized for combinations of soil and pesticide properties, selected to give a good coverage of the likely input space in further applications. For example, soil properties were selected to give a representative coverage of Swedish agricultural topsoils and pesticide properties were selected to cover the likely range of properties of substances approved for use. The meta-model was constructed from 23760 combinations of 6 input variables (topsoil half-life, K_{oc}, sand and clay contents in topsoil and subsoil). A spring sown crop combined with spring application of pesticide was simulated. The simulated 80th percentile average yearly concentration for a twenty-year simulation (i.e. the fourth largest yearly average concentration) was selected as the target variable for the meta-model, in order to agree with FOCUS procedures (FOCUS, 2000).

The meta-model was built using fully-connected feed-forward artificial neural networks (Haykin, 1994; Bishop, 1993). Artificial neural networks were considered suitable to construct a meta-model of MACRO since they are able to describe non-linear and non-monotonic relationships. Furthermore, they do not require any 'a priori' assumptions concerning the underlying model, and they are universal approximators for certain sets of functions (Funashi, 1989; Hornik et al., 1989).

The final meta-model was constructed by combining a network that classifies the input pattern into three groups, in combination with three neural networks trained to predict the target variable for each of the groups. The agreement between simulated and predicted concentrations was good across a range of different combinations of sand and clay content (Fig. 7). It was concluded that the meta-model introduced an acceptably small additional error compared to the full simulation model. Fig. 7b illustrates one of the strengths of artificial neural networks: for this pesticide, the non-linear and non-monotonic model response to texture was captured fairly well.

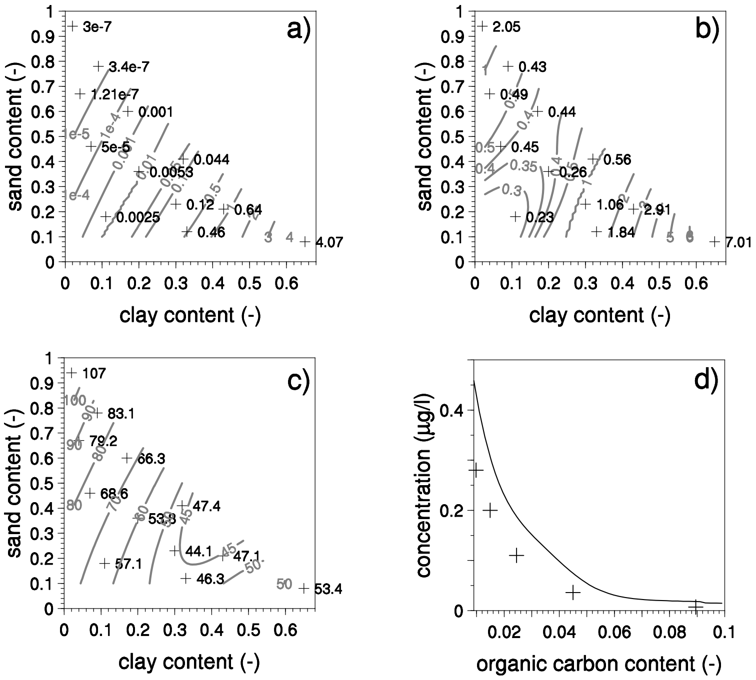

Fig. 7. Target (crosses) and predicted (lines) pesticide concentrations as a function of clay and sand content for three different pesticides with f_{oc} = 0.0245, a) $t_{1/2}$ = 10 days, K_{oc} = 300 cm^3/g b) $t_{1/2}$ = 10 days, K_{oc} = 10 cm^3/g and c) $t_{1/2}$ = 50 days, K_{oc} = 10 cm^3/g, and d) predicted concentrations as a function of organic carbon content for soil with a clay content of 20%, a sand content of 36% and a pesticide with $t_{1/2}$ = 10 days and K_{oc} = 30 cm^3/g.

The meta-model was used to predict leaching patterns for some hypothetical pesticides in a 2 ha grid at Näsbygård in southern Sweden. This showed that the predicted spatial pattern of leaching varied with pesticide properties (Fig 8). Larger concentrations for the more leachable pesticide were predicted for the coarser-textured parts of the field, whereas for the less leachable pesticide, predicted concentrations were larger for the finer-textured soil, where macropore flow was predicted to dominate pesticide transport. Thus, worst-case leaching scenarios with respect to soil properties are dependent on the pesticide properties. This means that intrinsic assessments of groundwater vulnerability that neglect compound properties are of limited value.

A FAST sensitivity analysis (Saltelli et al. 1999; Crosetto et al., 2000) was performed that showed that the meta-model was sensitive to all its input parameters. Pesticide characteristics (i.e. K_{oc} and topsoil pesticide half-life) were the most important parameters for model output. Soil texture was also quite influential, which is probably mainly due to its influence on parameters controlling macropore flow (equation 4). This behaviour is in contrast to leaching models based on Richard's equation and the advection-dispersion equation, which are relatively insensitive to soil texture and hydraulic properties (e.g. Boesten, 1991).

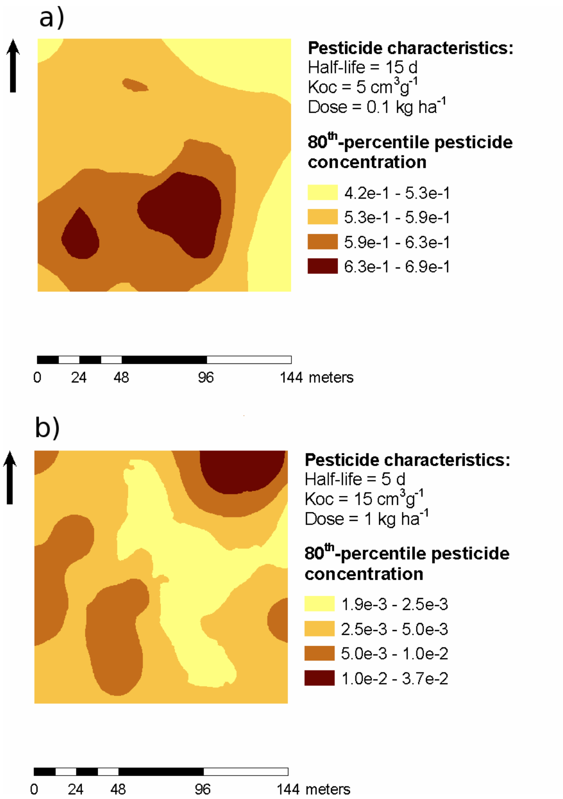

Fig 8. Spatial variation of predicted leaching for a leachable 'low-dose'pesticide (a) and a less leachable 'normal-dose' pesticide (b) at Näsbygård. Note the difference in scale.

Strengths and weaknesses

One advantage of a meta-model compared to the full simulation model is that it yields results almost instantaneously. This is important for several potential end-users, including extension service advisors in their discussions with farmers, and water managers and policy-makers interested in mapping pesticide leaching potential across large areas. In addition, a meta-model requires less input data and is easily incorporated into larger decision-support and geographical information systems. Compared to the attenuation factor used in Paper I, the main advantage of the meta-model is that important processes and factors excluded in the simpler index are implicitly taken into account (e.g. dispersion and preferential flow). Meta-models are easy to use and do not require expert knowledge, although it is important for the user to be aware of their limitations and domain of applicability. The advantages mentioned above can only be realised if the additional errors introduced by the meta-model are acceptable

The main drawback of meta-models is that they are not as flexible as the full simulation model and cannot be applied for conditions other than those for which they were developed. For example, this limits the meta-model described in Paper IV to spring applications of pesticide in the climate of southern Sweden. However, this is a practical problem, which can be addressed by running additional simulations and incorporating these into new or improved meta-models, should the need occur.

Discussion and conclusions

Process-based simulation models can be used to predict pesticide leaching for specific fields making use of comprehensive field data, both as direct parameter inputs and also to calibrate the model. Such an approach should reduce parameter uncertainty, although the uncertainties in predictions may still be large. For example, leaching losses are very sensitive to pesticide properties, which are also likely to vary significantly within a field (Walker and Brown, 1983; Lennartz, 1999). The modelling presented in Paper III was based on field and laboratory experiments. However, no data of pesticide leaching were available to evaluate the simulation results and the parameterization of the MACRO model was partly based on pedotransfer functions and personal judgement. Therefore, the predicted concentrations of the pesticide modelled (mecoprop) are highly uncertain. Approaches based on calibrated simulations for a typical or representative field site are potentially useful in many applications. For example, the set-up described in Paper III could be used by water managers to evaluate the vulnerability to pesticide contamination of drinking water aquifers underlying the till regions of Denmark and southern Sweden that underlie intensively farmed agricultural land.

Pedotransfer functions can be used to parameterize simulation models in the absence of site-specific data. This is exemplified by the vulnerability assessment tool presented in Paper II, which uses pedotransfer functions to parameterize the MACRO model by using easily available data (texture and organic carbon content). The tool is simple to use and flexible, enabling simulations of many different active ingredients, crops and application patterns. Thus, it can be used as an educational tool to evaluate common crop-pesticide scenarios. For example, the simulation tool described in Paper II has been used by the Swedish Board of Agriculture to compare the potential leaching risks under Swedish conditions of plant protection products that have identical agronomic uses and to illustrate the effects of various management options (i.e. application timing) on leaching (Ö. Folkesson, pers comm.). The results have been summarized in an information pamphlet that is used to train extension specialists in plant protection and to support their discussions with farmers on how to reduce pollution arising from diffuse sources. By simulating a range of pesticides and comparing the simulation results with monitoring results, a qualitative evaluation of the simulation tool has been performed (Ö. Folkesson, pers. comm.). The meta-model of MACRO developed in Paper IV could also be used for these kinds of assessments, although it lacks some of the flexibility of the simulation tool. However, the meta-model is faster to run and is therefore better suited to groundwater vulnerability assessments at catchment and regional scales. For example, the meta-model described in Paper IV has been included in a decision-support system developed to assess pesticide leaching risks from point sources in Denmark (A.P. Mortensen, pers comm.)

Decisions based on groundwater vulnerability assessments require some criterion with which the model prediction may be compared. The easiest approach is just to rank pesticides with respect to their predicted leaching potential. Such a ranking may serve as a basis for farmers to select which pesticide to use, all else being equal but their leaching behaviour, or as a basis for regulators to practice the substitution principle. Another common approach is to compare predictions with a specific value of a vulnerability measure, for example a given concentration. This approach is used in the FOCUS (2000) groundwater scenarios, where a safe usage of the pesticide is considered to exist if the 80th percentile simulated concentration is less than the EU drinking water limit (0.1 µg/l) in at least one of the scenarios. A similar philosophy underlies the simulation tool designed for local exposure assessments in drinking water abstraction districts in Sweden (Paper II). A third alternative, used in Paper I, is to compare the model predictions of leaching for the active ingredient of interest to that for a pesticide for which the leaching behaviour has been established (reference chemicals). This is a potentially useful approach that integrates measured data on the environmental fate of pesticides into the analysis, provided that sufficient monitoring data is available.

Simulation models are needed for groundwater vulnerability assessments where predictions of absolute concentrations are required and where different management options are to be explored (e.g. application timings). However, given the uncertainties and prohibitive data requirements associated with the use of process-based simulation models, it is legitimate to question whether they provide any clear advantage over the simpler index methods for use in relative assessments of leaching potential. For many scenarios, a relative ranking of pesticide leaching risk would probably be the same using either the attenuation factor or the simulation tool or meta-model based on MACRO. However, this will not always be the case. For example, the ranking may be affected by application timings (i.e. spring vs. autumn). As illustrated in Paper IV, the effects of macropore flow may also influence the relative ranking of pesticide leaching risk among different soils. If macropore flow occurs, a clay soil may represent the worst-case scenario for pesticides that the attenuation factor would classify as “non-leachers”. On the other hand, a sandy soil may represent a worst-case scenario for pesticides that are persistent and weakly sorbed. The ability of the modelling tools based on MACRO to capture this complexity represents a significant advantage.

The meta-model seems to represent a reasonable trade-off between the simplicity and lower data requirements of index-based approaches and the capability and flexibility of the full simulation model. The main drawback of the meta-model is that it is strictly limited to situations that match the simulation set-up used to derive it (boundary conditions, application timing, climate etc.). However, this is only a technical limitation, and it may be addressed by creating new meta-models from more simulations carried out for various agricultural and environmental scenarios with a suitable modelling set-up and appropriate output data. This is time-consuming, but once done, the results may provide a valuable database of simulation results for various applications that may be included in tools to assess groundwater vulnerability.

The main objective of this thesis was to develop tools for groundwater vulnerability assessments of pesticide leaching that are suited to the needs of different end-users. The simulation tool and the meta-model in papers II and IV were designed and developed with different end-users and purposes in mind, but they also have some characteristics and limitations in common. Both tools predict the pesticide concentration in soil water at one metre depth as a measure of groundwater vulnerability. This may be adequate for some conditions but not for others, depending on additional site factors such as the groundwater depth and the subsoil geology. Without additional data and information, the tools cannot identify whether it is groundwater or surface water (via subsurface saturated flow) that is at risk. Therefore, it is important to develop methods to account for these additional factors in the assessment. For example, the meta-model could be incorporated into a geographical information system and combined with additional data (e.g. soil survey information, subsoil geology, extent of groundwater resources, groundwater depth, cropping and pesticide usage statistics) to perform catchment or regional scale assessments of groundwater vulnerability.

More research to evaluate and, in the long-term, reduce the uncertainty in model predictions is needed to build confidence in the tools among the various end-users and stakeholders. In the case of MACRO, this implies that further development and functional evaluation of the pedotransfer functions to predict macropore flow parameters in the MACRO model is an important area of future research. One way forward would be to link standard data in soil surveys together with structural descriptions to the macropore flow parameters. Such a scheme could be validated and refined by making use of the results of existing column, lysimeter or field leaching experiments. In addition to this, groundwater monitoring data would be useful in large-scale evaluations of the simulation tool.

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