Sources of Pesticide Losses to Surface Waters and Groundwater at Field and Landscape Scales

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Doctoral Thesis
Swedish University of Agricultural Sciences
Uppsala 2009

Acta Universitatis agriculturae Sueciae
2009:50

Cover: Pesticide application in Dalby Gräna. (Photo: Anna M.L. Lindahl)

ISSN 1652-6880
ISBN 978-91-86195-97-7

Print: SLU Service/Repro, Uppsala 2009

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Abstract

Pesticide residues in groundwater and surface waters may harm aquatic ecosystems and result in a deterioration of drinking water quality. EU legislation and policy emphasize risk management and risk reduction for pesticides to ensure long-term, sustainable use of water across Europe. Different tools applicable at scales ranging from farm to national and EU scales are required to meet the needs of the various managers engaged with the task of protecting water resources. The use of computer-based pesticide fate and transport models at such large scales is challenging since models are scale-specific and generally developed for the soil pedon or plot scale. Modelling at larger scales is further complicated by the spatial and temporal variability of agro-environmental conditions and the uncertainty in predictions. The objective of this thesis was to identify the soil processes that dominate diffuse pesticide losses at field and landscape scales and to develop methods that can help identify 'high risk' areas for leaching. The underlying idea was that pesticide pollution of groundwater and surface waters can be mitigated if pesticide application on such areas is reduced. Macropore flow increases the risk of pesticide leaching and was identified as the most important process responsible for spatial variation of diffuse pesticide losses from a 30 ha field and a 9 km^2 catchment in the south of Sweden. Point-sources caused by careless handling of pesticides when filling or cleaning spraying equipment were also a significant source of contamination at the landscape scale. The research presented in this thesis suggests that the strength of macropore flow due to earthworm burrows and soil aggregation can be predicted from widely available soil survey information such as texture, management practices etc. Thus, a simple classification of soils according to their susceptibility to macropore flow may facilitate the use of process-based models at the landscape scale. Predictions of a meta-model of the MACRO model suggested that, at the field scale, fine-textured soils are high-risk areas for pesticide leaching. Uncertainty in pesticide degradation and sorption did not significantly affect predictions of the spatial extent of these high-risk areas. Thus, site-specific pesticide application seems to be a promising method for mitigating groundwater contamination at this scale.

Keywords: aggregate, classification tree, earthworm, leaching, macropore flow, modelling, pesticide, spatial variability, uncertainty & sensitivity analysis, upscaling.

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Dedication

To the women in my family history.

~ For my part I know nothing with any certainty, but the sight of the stars makes me dream.

Vincent van Gogh

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Lindahl, A.M.L., Kreuger, J., Stenström, J., Gärdenäs, A.I., Alavi, G., Roulier, S. and Jarvis, N.J. (2005). Stochastic modeling of diffuse pesticide losses from a small agricultural catchment. *Journal of Environmental Quality* 34(4), 1174-1185.

II 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* 93(1-4), 270-283.

III Lindahl, A.M.L., Söderström, M. and Jarvis, N. (2008). Influence of input uncertainty on prediction of within-field pesticide leaching risks. *Journal of Contaminant Hydrology* 98(3-4), 106-114.

IV Lindahl, A.M.L., Dubus, I.G. and Jarvis, N. (2009). Site classification to predict the abundance of the deep-burrowing earthworm *Lumbricus terrestris* L. *Vadose Zone Journal*. 8 (4). In press.

The contribution of Anna M.L. Lindahl to the papers included in this thesis was as follows:

I Planned the study together with Jarvis, Kreuger, Gärdenäs and Stenström and was responsible for all the simulations, the data analyses and most of the writing.

II Chose method for, performed, and contributed with text on the sensitivity analyses and the case study.

III Planned the study together with Jarvis and Söderström, performed field sampling, chose all the methods and was responsible for all the simulations, the data analyses and the writing.

IV Planned the study together with Jarvis and was responsible for all the analyses and most of the writing.

Abbreviation

K_{oc}	Partition coefficient to soil organic carbon

1 Introduction

Pesticides are applied to agricultural fields to combat weeds, pests and diseases that reduce crop yields. If pesticide residues are transported away from where they are intended to be active they may reach ecosystems such as groundwater or surface waters where they may harm non-target organisms (Murty, 1986; Schulz and Liess, 1999; DeLorenzo et al., 2001; Frankart et al., 2003; Vryzas et al., 2009) and impair drinking water quality for human consumption (WHO, 2008).

The risks of pesticide leaching to groundwater are assessed according to the Council Directive 91/414/EEC in the registration procedure of existing and new pesticides within the EU (European Union, 1991). Prior to any approval for agricultural use in Sweden, the National Chemicals Inspectorate (according to the Annex VI to the Directive 91/414/EEC) carries out refined leaching risk assessments for plant protection products that take the specific hydrological, geological and climatic conditions of Sweden into account. At both EU and national level, the assessments are performed by running computer-based pesticide fate and transport models for a selection of representative worst-case agricultural scenarios.

The recently adopted EU Groundwater Directive defines an environmental threshold for groundwater of 0.1 $\mu g\,L^{-1}$ for individual pesticides and their relevant metabolites and 0.5 $\mu g\,L^{-1}$ for their sum (European Union, 2006). These threshold concentrations are also the quality standard for European drinking water set by Council Directive 91/414/EEC (European Union, 1991). Environmental monitoring programs have detected residues of registered pesticides in groundwater at concentrations exceeding 0.1 $\mu g\,L^{-1}$ in Sweden (Törnquist et al., 2007) and other European countries (e.g. Lapworth et al., 2006; Schipper et al., 2008). Surface waters have also been found to be contaminated with pesticides at concentrations that are toxic to aquatic organisms (e.g. Schulz and Liess, 1999). Several

studies have found that careless handling of pesticides can explain some of the pesticide detections in surface waters (Kreuger and Nilsson, 2001; Gerecke et al., 2002; Müller et al., 2002; Neumann et al., 2002; Leu, 2004a), but diffuse pesticide losses from especially susceptible areas, due to vulnerable soils and/or the prevailing climate, are also a significant source of contamination (Leu et al., 2004a).

Swedish and EU legislation and policy emphasizes risk management and risk reduction for approved products. For example, the Water Framework Directive establishes a legal framework to protect and restore clean water across Europe and ensure its long-term, sustainable use (European Union, 2000, 2006). Clearly, risk assessment and management of pesticide impacts on water resources in the agricultural landscape is needed if the ambitions of the Water Framework Directive are to be realized, but there is presently a lack of suitable tools for this purpose. Funded by the European Commission, the FOOTPRINT research programme (FOOTPRINT, 2009) is developing such modelling tools. Different tools are required since a range of different end-users, working at farm, catchment, national and EU scales, are engaged with the task of managing and protecting water resources. Apart from dealing with the issue that pesticide fate and transport models are scale-specific, these models must address the spatial and temporal variability of agro-environmental conditions and the uncertainty in predictions.

1.1 Pathways of pesticide transport – from machine to recipient

Pesticides (and their metabolites) reach groundwater and surface waters through a number of transport routes (Fig. 1). The pesticide can either be surface applied or incorporated into the soil directly. When surface applied, pesticide droplets may be caught up by the wind and transported to surface waters by spray drift (van de Zande, 2006). A fraction of the application will be intercepted by the growing crops. Depending on the chemical composition of the molecule, the pesticide may be taken up by the plant (Schmidt and Pestemer, 1980). Volatilization (i.e., evaporation of pesticide to the atmosphere) may be a significant transport process for some pesticides (Hance, 1980). If it is not decomposed, pesticide vapour in the air may adsorb to aerosols and reach surface water by dry or wet deposition. The remainder of the applied pesticide and pesticide that is washed off the plants, by irrigation or precipitation, will reach the soil. Heavy rain or excessive irrigation may result in surface runoff in which pesticides, in solution or adsorbed to soil particles, can be lost to surface waters (Flury, 1996).

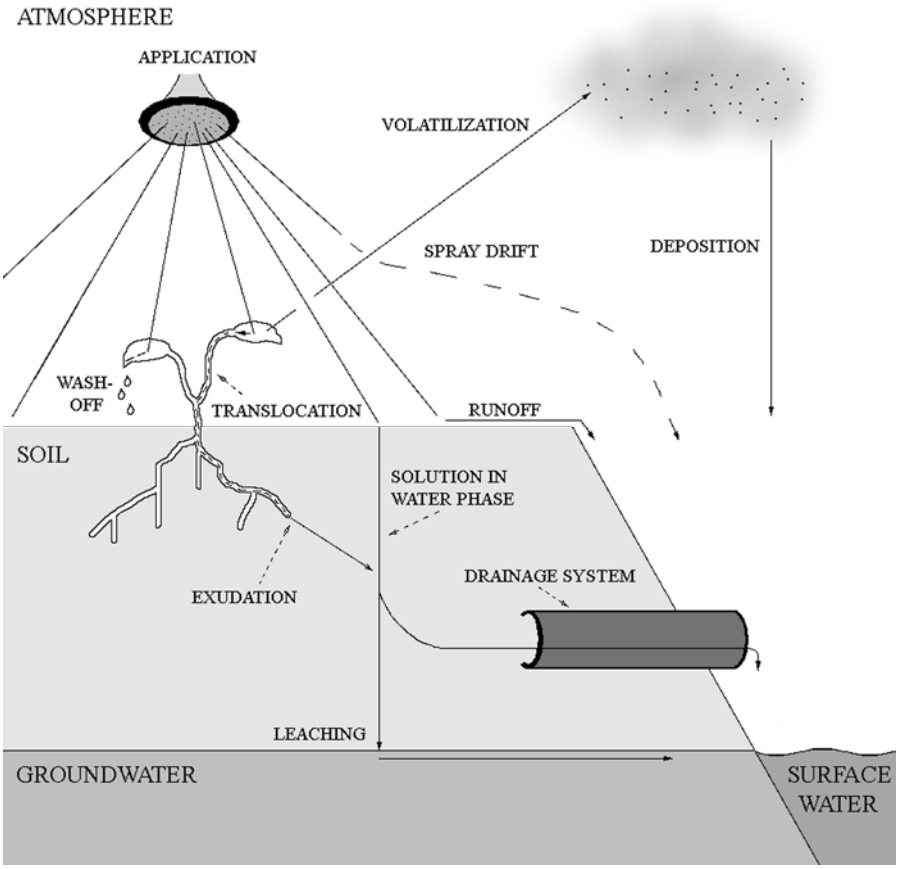


Figure 1. Diagrammatic representation of pesticide transport routes to groundwater and surface waters.

Water is the dominant transport medium in soil, although pesticides may also be re-distributed by soil fauna or translocated through plant roots (Greaves et al., 1976). During advective transport, pesticides can be taken up by plant roots (Schmidt and Pestemer, 1980) or transformed by chemical or biological degradation (Torstensson, 1980; Alexander, 1999). Pesticide molecules are also temporarily immobilized by adsorption to stationary solids (Alexander, 1999). This sorption 'retardation' may strongly reduce pesticide losses to water recipients. The rate of soil water flow is controlled by the sizes of the conducting pores (Leistra, 1980). The flow within pores is generally laminar (i.e., increasing with distance from the pore wall) but large pores may even exhibit transitional to turbulent flow (Jarvis, 2007). Due to different water flow rates, the pesticide is dispersed as it flows through the soil (Leistra, 1980). Transverse diffusion (i.e., substance exchange due to

differences in concentration) reduces the extent of dispersion. However, for very large pores (so-called macropores, including shrinkage cracks, inter-aggregate voids, root holes and earthworm channels), this transverse mixing is very slow compared with vertical advective flow velocities. 'Non-equilibrium' or preferential transport therefore often dominates pesticide leaching in structured soils (Flury, 1996; Jarvis, 2007), especially if the topsoil is by-passed rapidly since this part of the soil is the most active concerning sorption (Wauchope et al., 2002) and degradation (Pothuluri et al., 1990; Charnay et al., 2005; Rodríguez-Cruz et al., 2006). Soil water entering a drainage system will flush transported pesticide into surrounding surface waters. Any remaining pesticide residue will leach to groundwater.

1.2 Spatial and temporal variability of pesticide fate and transport processes

Soil formation is a long-term and complicated process (Webster, 2000). Soils are continuously subjected to spatial and temporal variability in physical and chemical conditions and biological activity that can amplify even small differences in the parent material. Additionally, for cultivated soils, agricultural management practices treat the soil in a spatially variable manner across fields. Soils therefore often exhibit spatially heterogeneous physical, chemical and biological properties and are also temporally dynamic (e.g. with respect to soil moisture and temperature). Since transport velocities, degradation rates and sorption depend on these variable factors, pesticide leaching may show a large spatial and temporal variation within a soil. At larger scales the variation can be extensive since new sources of variability are introduced (e.g. changing parent material, relief, vegetation type, soil management practices, weather and climate).

1.2.1 Sorption

The spatial variability of the adsorption process at the field (Elabd et al., 1986; Vink, 1996) and catchment scale (Coquet, 2003; Coquet and Barriuso, 2002) is due to the spatial variability in soil constituents that adsorb pesticides (i.e., soil organic carbon, clay minerals and sesquioxides). Changes in pH are also important for the sorption of substances with ionic equilibrium constants close to the range of soil pH since the proportion of ionized and non-ionized species will vary (Nicholls and Evans, 1991a,b). Adsorption of non-ionic pesticides (i.e., hydrophobic adsorption) will generally be insensitive to changes in soil pH.

Soil organic matter is usually the dominant soil solid phase for adsorption of most pesticides (Wauchope et al., 2002). It is therefore common to characterise adsorption of pesticides by the partition coefficient to soil organic carbon (K_{oc}), a coefficient that relates the pesticide concentration sorbed onto the organic carbon fraction to its soil solution concentration. For soils in which adsorption is dominated by organic matter, site-specific probability density functions of K_{oc} values can be used together with measured spatial variation of soil organic carbon to predict the spatial variation of adsorption of non-ionic pesticides. Due to the costs of obtaining local information of such data, single measured K_{oc} values or K_{oc} values from literature databases are often used in pesticide risk assessment procedures. Such an approach however neglects the effect of pH, other adsorbing surfaces, possible nonlinear sorption isotherms and the variability in quality (i.e., the structure and chemistry) of soil organic matter (Wauchope et al., 2002). In a comparative study, pesticide leaching risks at catchment scale were predicted either by values of K_{oc} and degradation half-life from databases or from site-specific measurements (Coquet et al., 2005). The approach in which database values were used was found to be insufficient for catchment-scale risk assessment.

1.2.2 Degradation

It is well-known that the spatial variation of pesticide degradation rates can be considerable at the field scale (Walker and Brown, 1983; Walker et al., 2001, 2002; Bending et al., 2006; Rodrígues-Cruz et al., 2006). In a study by Parkin and Shelton (1992), it was shown that pesticide degradation half-lives may also vary in time. Spatial variation has been explained by the control of pH on degradation rate (Walker et al., 2001, 2002), through its influence on the rates of hydrolysis and chemical degradation and the proliferation of soil micro-organisms (Bending et al., 2003). The activity of soil micro-organisms is also influenced by many other spatially and temporally variable factors including the availability of nutrients, salinity, soil temperature, oxygen content and soil moisture content (Alexander, 1999). Soil contents of organic matter, or alternatively, organic carbon have been found to be both positively (e.g. Rodrígues-Cruz et al., 2006) and negatively correlated (e.g. Pussemier et al., 1997) to pesticide degradation rate. These contradictory findings might be explained by the conflicting effects of organic carbon. A high content of organic carbon can retard degradation since adsorbed compounds are less available to soil micro-organisms. But soil organic carbon may also be considered as a surrogate variable, which is positively correlated with microbial activity in nutrient-limited environments

(Pothuluri et al., 1990). Spatially variable degradation half-lives have been found to significantly influence predicted amounts of pesticide leaching (Leterme et al., 2007b). However, it seems impossible to predict the spatial pattern of degradation rate across fields or at the larger landscape scale since the effects of soil conditions on degradation are complex and still poorly understood.

1.2.3 Macropore flow

Macropore flow has been shown to dominate pesticide transport in structured, macroporous soil (Novak et al., 2001) especially for strongly adsorbed and quickly degrading compounds (Jarvis, 1995; Larsson and Jarvis, 2000). Macropores are of two basic types (Jarvis, 2007): i.) cylindrical biopores formed by plant roots or soil fauna such as earthworms and ii.) planar fissures and more irregular inter-aggregate voids caused by physical processes such as swelling/shrinkage or disruption due to soil tillage implements. The geometry and properties of individual macropores show high spatial and temporal variability, which makes it difficult to predict their impact on flow and transport processes (Beven, 1991; Jury and Flühler, 1992). The spatial variability of fissuring and aggregation across a field is due to the effects of faunal activity and soil properties (including texture, clay mineralogy and organic matter content) on macropore formation and degradation (Dexter, 1988; Oades, 1993; Watts and Dexter, 1998). Temporal variability is caused by seasonal variations of biological activity, tillage, compaction, soil crusting, and shrinking and swelling due to freeze-thaw and wet-dry cycles. The density of conducting earthworm burrows affects the degree of preferential flow in soil (Smettem, 1992), and consequently the risk of pesticide leaching. Such channels are created by anecic earthworms, i.e., large earthworms that live in deep permanent or semi-permanent vertical burrows in soil and feed from the surface litter (Edwards and Bohlen, 1996). The spatial distribution of anecic earthworm abundance, and therefore the spatial variability of water-conducting burrows (Chan and Heenan, 1993; Bouché and Al-addan, 1997; Chan, 2004) is controlled by factors influencing the availability of food and the physicochemical environment (e.g. soil temperature, moisture, pH, inorganic salts, aeration and texture) (Edwards and Bohlen, 1996). Many of these factors can be drastically altered by land use and soil management practices. Earthworm abundance can be affected by fertilizer type (e.g. organic manure versus inorganic fertilization) (Whalen et al., 1998), pesticide usage (Edwards and Bohlen, 1992; Edwards and Bohlen, 1996), water management (Barley and Klienig, 1964), and cultivation practices (e.g. tillage

intensity and intercropping) (Haukka, 1988; Edwards and Lofty, 1982b; Boström, 1995; Schmidt et al., 2001, 2003; Chan, 2001, 2004; Pelosi et al., 2009). Application of farmyard manure is favoured by earthworms since it provides an important food resource (Edwards and Lofty, 1982a) and conserves soil moisture (Lee, 1985). Tillage, especially mouldboard ploughing, is detrimental to anecic earthworms (Edwards and Lofty, 1982b) since it causes mechanical damage, disrupts burrows, buries the plant remains which serve as food for the animals and increases exposure to inclement weather conditions (Edwards and Bohlen, 1996; Chan, 2001) and predation (Cuendet, 1983).

1.2.4 Source areas

Whether field scale spatial variability of pesticide leaching is dominated by the variability in soil sorption and degradation or transport properties depends on the specific properties of the pesticide and the particular site. For example, sorption and degradation will have less influence on pesticide leaching when a pesticide is being transported with limited contact time to the soil matrix (i.e., by rapid flow through macropores) (Larsson and Jarvis, 2000; Dubus and Brown, 2002). Similarly, stochastic modelling approaches suggest that leaching of mobile pesticides is relatively insensitive to variations in organic carbon content compared with variations in hydraulic conductivity, pore water velocity and soil physical properties (Lafrance and Banton, 1995; Mulla et al., 1996). The processes that control pesticide losses to surface water at the small catchment scale have been investigated experimentally by Leu et al. (2004a,b) and Freitas et al. (2008). The spatial variation in losses was dominated by spatial differences in factors affecting soil susceptibility to surface saturation and thus rapid transport from the fields by surface runoff and/or preferential flow to field drainage systems. These differences in field characteristics (i.e., topography and soil profile properties) influenced the losses more than differences in the physical-chemical properties of the pesticides considered. The spatial heterogeneity of pesticide losses between different fields (Leu, 2004b) and even within single fields (Freitas et al., 2008) was found to be large. Even though pesticide losses obviously vary in time, the main contributing areas seemed to be the same under very different weather conditions (Freitas et al., 2008). If such high-risk areas for diffuse losses can be identified within fields and actively managed by site-specific application technologies, losses could be substantially reduced at the catchment scale without significantly affecting crop yields (Freitas et al., 2008). Management could, for example, involve reducing the dose of pesticides applied on vulnerable fields or parts of fields

or excluding application altogether on these areas. The feasibility of such an approach may depend on the scale of variability of soil properties responsible for high-risk source areas.

Site-specific pesticide application necessitates cheap and reliable approaches to map soil properties that are related to vulnerability to pesticide losses at field and farm scales. Potentially promising methods in this respect are frequency domain electromagnetic induction techniques. These are non-destructive measuring methods that enable rapid mapping of electrical conductivity (Jaynes, 1996). The electrical conductivity of a soil depends on water and salt content, clay content and mineralogy, and soil temperature (Brevik and Fenton, 2002). The relationship between soil texture and pesticide losses (Novak et al., 2001) indicates a potential for a correlation between measured variations in soil electrical conductivity and pesticide leaching risks. A cheap alternative for identifying areas susceptible to pesticide losses could be to locate saturated areas by visual inspection of the field during rain events. Precision application using digital image analysis to obtain spatial information on weed infestation levels is another promising approach for reducing herbicide loads to surface and groundwater (Gerhards and Oebel, 2006). Within such a site-specific weed control system, only areas with high infestation levels are sprayed, hence reducing the amount of herbicide used.

1.3 Simulation models

Simulation models are simplified descriptions of the full complexity of an environmental system (the conceptual model) translated to algorithms that will run on a computer (Beven, 2009). Several simplifying assumptions are inevitably introduced into the model during the development process, i.e., when formalising the mathematical descriptions and implementing numerical solutions for nonlinear partial differential equations. Models render it possible to study the environment at different time periods, scales and locations at a relatively low cost and high speed. They are developed and run for two purposes: to test current scientific understanding or to make use of predictions to support policy development and decision making (Beven, 2009). For example, a number of process-based modelling approaches have been developed that can simulate pesticide leaching in soil at the column or small plot scale including PELMO (Jene, 1998), PRZM (Carsel et al., 2003), PEARL (Tiktak et al., 2000) and MACRO (Jarvis, 1994; Larsbo et al., 2005). These models are widely used in pesticide risk assessment (e.g. registration). However, few studies have explored their potential as tools in

risk management at larger scales (e.g. to identify source areas) (e.g. Tiktak et al., 2004; Leterme et al., 2007b). In principle, fully distributed physically based models (e.g. MIKE SHE, Abbott et al. 1986) could be used to identify source areas at field and catchment scales. However, these models are computationally demanding and data intensive. They are therefore usually impossible to use for large scale application due to data scarcity. Experimental data for direct parameterisation of process-based models are not always available. This may be because the model requires input parameters which are difficult or impossible to measure (e.g. parameters regarding macropore flow) or that the measurements are only available at a different and inappropriate scale (e.g. rainfall intensity). Furthermore, it is very expensive and time-consuming to characterize a heterogeneous field. Intensive experimental investigations at larger scales are therefore very impractical. Instead of process-based models, index methods such as the GUS index (Gustafson, 1989) and DRASTIC (Aller et al., 1987) can be used for large scale applications. Index methods are easy to use since they require few input parameters. The drawback is that they often lack important process descriptions (e.g. macropore flow).

For spatial applications at large scales, empirical relationships between model parameters that are difficult to obtain and easily measured soil properties, i.e., pedotransfer functions (Bouma, 1989), offer a cost-effective way to estimate troublesome parameters required by process-based models. However, the advantages come at a cost of additional errors and uncertainty introduced by these functions (Espino et al., 1995; Wösten et al., 2001; Minasny and McBratney, 2002b). Simulation meta-models, supported by pedotransfer functions, are a way to simplify the use of process-based models (i.e., by speeding up the simulations and reducing the number of input parameters required) whilst maintaining a similar degree of process detail. This approach has been adopted in the FOOTPRINT research programme (FOOTPRINT, 2009).

2 Aims and objectives

The objective of this thesis was to develop methods to predict diffuse pesticide losses to surface waters and groundwater at field and catchment scales, with special emphasis on macropore flow. The modelling work in this thesis is based on the dual permeability model MACRO since it is one of only a few models that can account for the significant effects of macropore flow on pesticide leaching.

In the following chapter, MACRO is first briefly described and a meta-model of MACRO that was developed to overcome the parameterisation problems of the full model is presented. Chapter 4 discusses the use of pedotransfer functions to parameterise process-based models. The problems associated with scale-dependent models and techniques for transferring simulation results from one scale to another are discussed in chapter 5. Chapter 6 discusses uncertainties associated with models of environmental systems. Chapters 4 to 6 in this summary begin with some introductory text which describes 'the state of the art' and sets the context for the research. This is followed by brief descriptions of the contributions made by this thesis. The final chapter comprises a review of the conclusions drawn and recommendations on the focus of future research.

The thesis is supported by four papers. The main sources of variation in pesticide losses within a field and a small catchment in southern Sweden are identified in paper I using MACRO. In paper II a simulation meta-model of MACRO for groundwater exposure assessment of pesticide leaching is developed using artificial neural networks. Paper III investigates whether site-specific applications at the field scale can contribute to a reduction of pesticide leaching despite uncertainty in the underlying leaching risk map derived from meta-model predictions. A quantitative scheme to predict the abundance of the anecic earthworm *Lumbricus terrestris* L. in agro-ecosystems from easily obtained site and soil factors is developed in paper IV as part of a

wider soil classification scheme designed to predict susceptibility of soils to macropore flow.

3 The MACRO model

MACRO (Jarvis, 1994; Larsbo et al., 2005) is a model developed for simulating the field water balance and the fate and transport of pesticides at the column scale. MACRO is a process-based dual-permeability model, i.e., water flow and solute transport are simulated in two separate but interacting pore systems, micropores and macropores. Only the most relevant (in the context of this thesis) aspects of the model are briefly described here.

A "boundary" water potential constitutes the division between the two pore systems, thus also defining corresponding saturated micropore water content and saturated micropore hydraulic conductivity. Soil water retention in the micropores is given by the Brooks and Corey equation (Brooks and Corey, 1964) in MACRO version 4.3b. In version 5.1, a modified version of van Genuchten's (1980) equation (Vogel et al., 2000) that allows a greater flexibility in matching the model to measured hydraulic properties is implemented instead. Water flow in the micropores is calculated using Richard's equation. In the macropores, water flow is described by the kinematic wave equation (Germann and Beven, 1985), assuming the water flow to be gravity-driven only. The macropore hydraulic conductivity is given by a power law function of the macropore degree of saturation. When the pressure head in the micropores exceeds the boundary water potential, macropore flow is assumed to be generated instantaneously. Water flow in the reverse direction (from macropores to micropores) is calculated using a first-order approximation of a diffusion equation with gradients in water content as the only driving force. A surrogate parameter ('effective diffusion pathlength') related to aggregate size, macropore spacing and the influence of coatings on macropore and aggregate surfaces controls the rate of mass exchange. Water flow to field drains is calculated from saturated soil layers in the profile using seepage potential theory (Leeds-Harrison et al., 1986).

Solute transport in micropores is calculated using the advection-dispersion equation with source–sink terms for mass exchange between the two pore systems, lateral losses to drains and/or regional groundwater, uptake by plants, kinetic sorption, and biodegradation. The same expression is used for solute transport in macropores, with the exception that only equilibrium sorption is considered and that dispersion is neglected since solute transport is assumed to be dominated by convection. The mass transfer between macro- and micropores is described by a combination of convection and diffusion terms, again regulated by the effective diffusion pathlength.

The solute concentration in water, routed into macropores at the soil surface, is calculated assuming immediate equilibrium and complete mixing of infiltrating water with the water stored in a shallow surface soil layer, or 'mixing depth' (Steenhuis and Walter, 1980).

Pesticide degradation is assumed to follow first-order kinetics, with the rate coefficients given as a function of soil temperature (by a modified form of the Arrenhius equation as described by Boesten and van der Linden (1991)) and moisture content (by a modified form of Walker's (1974) equation). Pesticide sorption is given by a Freundlich isotherm and can either be simulated as an instantaneous (the only option in MACRO 4.3b) or kinetic process using a two-site model (Altfelder et al., 2000).

3.1 The meta-model of MACRO

A meta-model of the MACRO model version 5.1 (Larsbo et al., 2005), developed by Fredrik Stenemo, is described in paper II. The meta-model is intended to be included in decision-support systems to assess worst-case groundwater pesticide exposure at large scales and is applicable for the scenario of spring-applied pesticides in climates similar to that of southern and central Sweden. Representing a 'worst-case' scenario, the meta-model predicts the 80th percentile concentration of the annual average leaching at one metre depth.

To construct the meta-model, MACRO was parameterised using eight continuous pedotransfer functions (see chapter 4) derived from regression analyses. These pedotransfer functions were based solely on soil properties that are normally recorded in soil surveys. As a result, the meta-model requires no more than clay and sand contents of the topsoil and subsoil, the topsoil organic carbon content and the pesticide properties K_{oc} and pesticide half-life as input parameters.

A total of 23,760 MACRO parameter sets were run for a simulation period of 26 years (the first 6 years were discarded as a 'warm-up' period). For each simulation, the year with the fourth largest average leachate concentration was selected as the target output to be predicted by the meta-model. The final meta-model consists of four artificial networks built by using fully-connected feed-forward artificial neural networks (Haykin, 1994; Bishop 1994). A classification network classifies the input pattern as belonging to one of three classes of simulated leachate concentrations (<0.01 $\mu g\ L^{-1}$, 0.01-1 $\mu g\ L^{-1}$ and >1 $\mu g\ L^{-1}$), and three corresponding networks predict pesticide concentrations. The overall R^2 values for the regressions between target and predicted data were 0.98, and 0.22, 0.74 and 0.98 when the meta-model was applied for the three different classes of target variable (in the order of low to high concentrations). It remains to be seen how the uncertainties associated with MACRO model parameterisation affect meta-model predictions. If these have little influence, the meta-model should be suitable for mapping the relative leaching risks at field, farm and catchment scales since it is fast to run and only requires a few widely available input parameters and yet takes important process descriptions, such as macropore flow, into account.

4 Pedotransfer functions

Process-based models for pesticide leaching require parameters some of which are difficult or even impossible to measure. Pedotransfer functions deal with this issue by relating model parameters to soil properties frequently recorded in soil survey studies (e.g. texture, bulk density and soil organic matter) (Bouma, 1989). Since they reduce dependency on tedious field measurements and laboratory experiments, pedotransfer functions are indispensable when applying simulation models at larger scales such as catchments or regions. Pedotransfer functions can be derived through analysis of databases either by regression analysis (e.g. Vereecken et al., 1989, 1990; Wösten et al., 1999) or data-mining techniques (e.g. artificial neural networks (e.g. Pachepsky et al., 1996; Minasny and McBratney, 2002a; Minasny et al., 2004), group methods of data (Pachepsky et al., 1998), and classification and regression trees (e.g. McKenzie and Jacquier, 1997)). In contrast to data mining tools, regression techniques are limited by 'a priori' assumptions on the shape of the dependencies. If the data are grouped prior to pedotransfer function development the functions are termed 'class' pedotransfer functions (Wösten et al., 2001). Otherwise, the pedotransfer functions are of 'continuous' type. The idea with grouping is that similar processes are assumed to occur for the objects within a group. The correlation of the output variable with the input variables is therefore probably more stable and consistent within the group.

A disadvantage of pedotransfer functions is that they introduce additional uncertainty to the model parameterisation (Espino et al., 1995; Wösten et al., 2001; Minasny and McBratney, 2002b). This uncertainty originates from the errors of the pedotransfer function and the uncertainty in the pedotransfer function input parameters (Minasny and McBratney, 2002b). Additionally, as for all statistical models, the specific conditions under which

pedotransfer functions are derived generally limit their area of applicability (Mermoud and Xu, 2006).

Traditionally, pedotransfer functions have mostly been developed for hydraulic properties of the soil matrix (e.g. soil water retention characteristics and soil hydraulic conductivity). Model predictions of pesticide leaching are however usually more sensitive to macropore flow parameters related to soil structure (Dubus and Brown, 2002). Relationships between morphological observed soil structure and preferential solute flow have been shown in solute breakthrough experiments with bromide as a non-reactive tracer (Vervoort et al., 1999; Ersahin et al., 2002). However, very few studies have attempted to quantify these relationships by developing pedotransfer functions to estimate soil structure related parameters (Shaw et al., 2000; Gonçalves et al., 2001; Jarvis et al., 2007). Furthermore, all of these experimental and statistical studies suffer from being based on very limited datasets. With no suitable data and methods to obtain their values, default values are generally used for macropore hydraulic parameters (Šimůnek et al., 2003). In this thesis, pedotransfer functions have been developed and applied for macropore flow parameters in the MACRO model.

Continuous pedotransfer functions to parameterise MACRO

In paper I, losses of the herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) were simulated for the 900 ha agricultural catchment of Vemmenhög (55°26´ N, 13°27´ E) and Näsbygård, a field of 30 ha, located within the Vemmenhög catchment. The parameterization of the MACRO model version 4.3b was aided by six continuous pedotransfer functions. The pedotransfer functions were developed by applying least square regression to data acquired in soil surveys and measurement campaigns carried out in the catchment. The normally distributed regression error terms associated with the pedotransfer functions, reflecting the strength of the derived relationships, were used as stochastic variables in a Monte Carlo sensitivity analysis (see Chapter 6.3). The effective diffusion pathlength was found to depend exponentially on organic carbon content and the characteristic particle size. These dependencies probably reflect the effect these soil properties have on soil structure hierarchy and therefore macropore flow (Jarvis, 2007). The Brooks-Corey pore size distribution index is another important input parameter regulating macropore flow since it was used in the pedotransfer function to derive saturated matrix hydraulic conductivity. The estimated Brooks-Corey pore size distribution index is smaller in soils of smaller organic carbon content. Hence, macropore flow is predicted to be

much stronger and occur more frequently in soils of finer texture and smaller organic carbon content.

Class pedotransfer functions for macropore flow parameters

The pedotransfer functions developed in paper I are of continuous type and specifically developed for the catchment of Vemmenhög. In paper IV, a more general class pedotransfer function was developed with the objective to support predictions of macropore flow for all agricultural soils in Europe. This pedotransfer function was constructed to estimate the abundance of the anecic earthworm species *Lumbricus terrestris* (Fig. 2). The pedotransfer function was developed as a classification tree by applying the C4.5 data mining algorithm (Quinlan, 1993) to literature data on 86 agricultural sites across Europe. The derived scheme classifies agricultural soils into one of three abundance classes for *Lumbricus terrestris*, termed 'low' (< 3 m^{-2}), 'medium' (3-10 m^{-2}) and 'high' (> 10 m^{-2}).

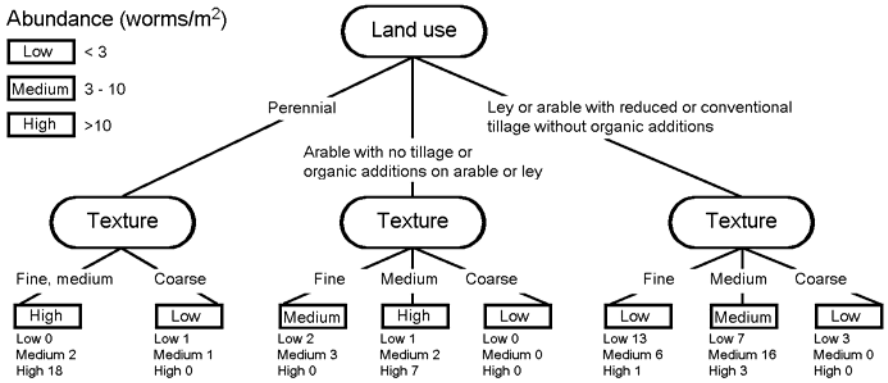


Figure 2. Classification tree for predicting the abundance of *Lumbricus terrestris* based on data from 86 agricultural sites in Europe. The text below each class denotes the number of training sites of different abundance sorted to that class.

Cross-validation showed that the expected accuracy of the classification tree is 65% when applied to other agricultural sites in Europe. The abundance of *Lumbricus terrestris* in agro-ecosystems was found to be strongly influenced by land use, soil management practices (e.g. manuring, tillage and cropping systems) and soil texture. According to the results, medium-textured soils are clearly most favourable for anecic earthworms, whereas coarse-textured soils appear to be least favourable. Sandy soils are thought to be abrasive to burrowing earthworms and are also drought prone (Lee, 1985). The classification tree also demonstrates that fewer earthworms are found in

clayey soils compared to medium-textured soils. This may be due to several different factors including a higher resistance to burrowing and a greater risk of waterlogging (Lee, 1985). The importance of the quantity, quality and availability of organic matter as food supply for anecic earthworms (Edwards and Bohlen, 1996) is reflected by the influence of land use and soil management practices on their abundance. Among the land use types included, grassland and orchards are the most favourable. The classification scheme also reflects the positive effect of organic additions and the negative effect of tillage.

Known limiting factors, that were not expressed in the classification tree, include the effects of extreme climates, low pH and the presence of restricting conditions in the soil profile (Lee, 1985) (e.g. hard rock or anoxic conditions below the water table). If they are to thrive, anecic earthworms require a certain soil depth that offers no restrictions to burrowing. These soil and site conditions could not be identified as significant factors in the analysis due to lack of supporting data. One reason may be that researchers rarely choose to investigate earthworm abundance at sites where they are not common.

Classification trees for predicting aggregation in agricultural soil were developed based on the SEISMIC database (Hollis et al., 1993), which contains data on basic soil properties and aggregation for 1399 typical or 'benchmark' soil horizons in the U.K. The same data mining techniques were applied for the development of these classification trees as for the earthworm classification tree described in paper IV. Soil structure in SEISMIC is described by the shape, grade and size of aggregates according to the FAO system (FAO, 2006). To simplify the analysis, soil structure descriptions were grouped into five classes according to their potential to support macropore flow, which is assumed to be stronger with coarser aggregation within a poorly developed structure hierarchy (Jarvis, 2007). The classes range from 'no-potential' (I) to 'high potential' (V), for which class 1 encompasses structureless soil (i.e., single grain or massive) or platy structures and class V comprises the largest and most strongly developed aggregates (Table 1 a,b). Predictor variables tested in the analyses were FAO master horizon designation and their subordinate characteristics (FAO, 2006), upper and lower depths of the horizon, organic carbon content, contents of sand, silt and clay, characteristic particle size and USDA (n.d.) texture class. Soil horizon designation was the most important predictor variable. To avoid creating a complex tree that is difficult to understand and interpret, five trees were developed separately, one for each horizon type (B or BC, C, O, E and A or AC).

Table 1a. *Aggregate class (I-V) for blocky and prismatic aggregates according to the size of the aggregates and the FAO (2006) structure grade.*

	Aggregate class								
Grade	*Weak and very weak*			*Moderate*			*Strong and very strong*		
Size (mm)	*< 20*	*20 - 50*	*> 50*	*< 20*	*20 – 50*	*> 50*	*< 10*	*10 – 20*	*> 20*
	II	III	IV	III	IV	V	III	IV	ff

Table 1b. *Aggregate class (I-V) of the FAO (2006) structure type, grade and size classes.*

	Aggregate class											
Grade	*Weak and very weak*				*Moderate*				*Strong and very strong*			
Size[1]	*VF/ F*	*M*	*C*	*VC*	*VF/ F*	*M*	*C*	*VC*	*VF*	*F*	*M*	*C/ VC*
Type												
Blocky	II	II	III	IV	III	III	IV	V	III	III	IV	V
Prismatic	II	III	IV	IV	III	IV	V	V	III	IV	V	V
Granular	II →											
Platy, massive and single grain	I →											

[1] Very fine (*VF*), fine (*F*), medium (*M*), coarse (*C*) and very coarse (*VC*).

The classification tree placed all C horizons into class I (Fig. 3a). This is in accordance with FAO (2006), which defines C horizons as little affected by pedogenic processes. O horizons were classified as I or II, depending on the depth of the horizon and the organic carbon content (Fig. 3b). The strength and/or size of aggregation in E horizons increased with increasing clay content (Fig. 3c). A similar effect of texture was found for A and B horizons (Fig. 3d and 4). Organic carbon content was the most important predictor variable for aggregation in B horizons (Fig. 4, Table 2), although its effects were complex and difficult to explain. A higher organic carbon content gave finer/weaker aggregation for silty and loamy soils, but had the opposite effect for clayey soils and loamy sand. Any influence of hydrological conditions on soil structure development (Vervoort et al., 1999; Roulier and Jarvis, 2003), as expressed in the FAO subordinate horizon designation (FAO, 2006), could not be identified in the classification trees developed.

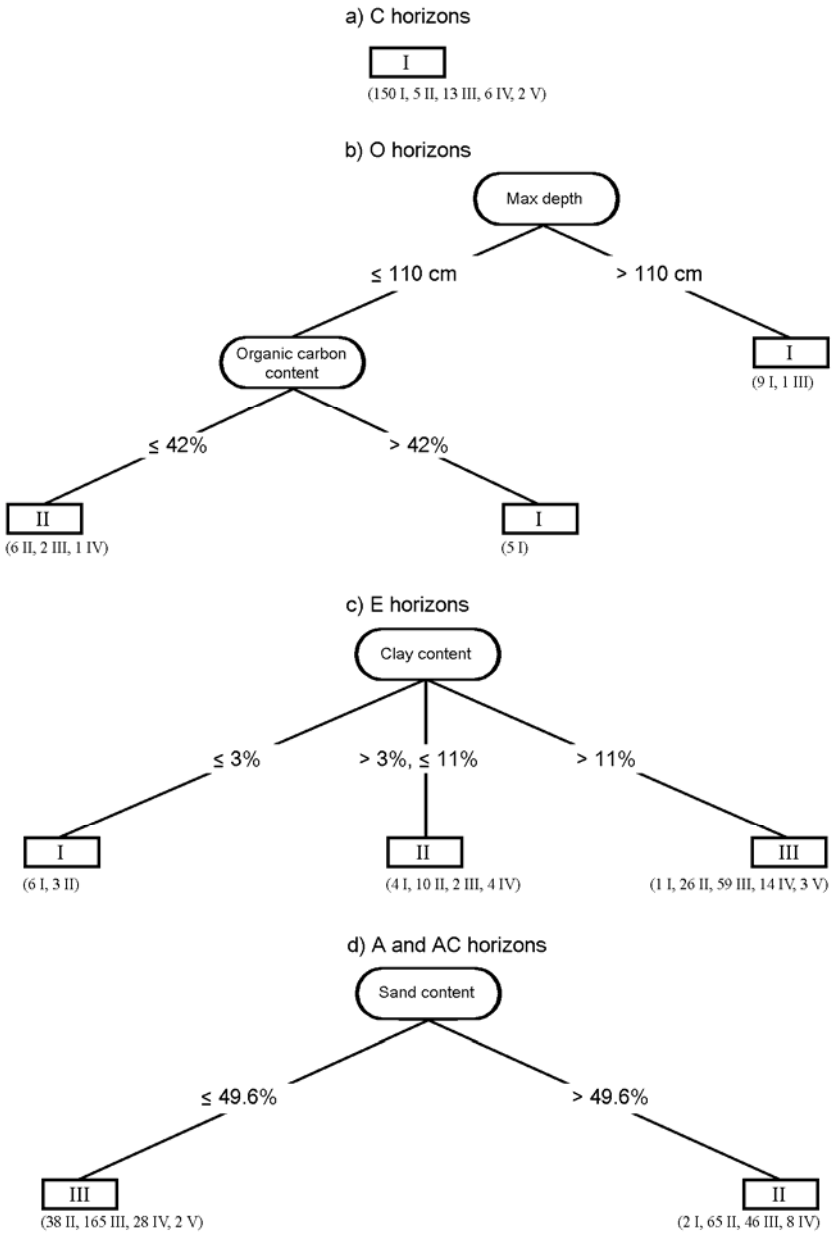


Figure 3. Classification trees for predicting aggregate type in horizons of designation C (a), O (b), E (c) and A and AC (d) based on agricultural soils in the U.K. (SEISMIC; Hollis et al., 1993). Horizon designations follow FAO (2006). The text below each class denotes the number of training sites of different aggregate classes sorted to that class.

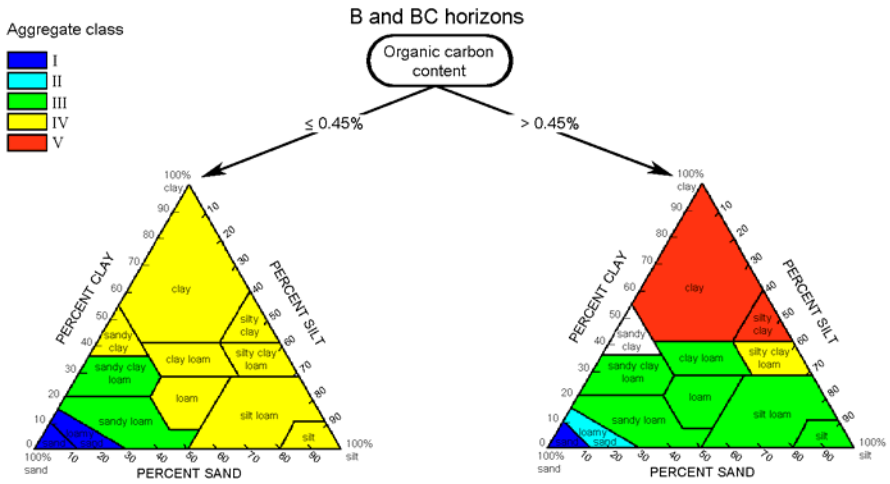


Figure 4. Classification tree for predicting aggregate class in FAO (2006) B and BC horizons based on agricultural soils in the U.K. (SEISMIC; Hollis et al., 1993). Uncoloured combination of organic carbon content and texture class was not represented for B and BC horizons.

Table 2. *Number of horizon designation* B *and* BC *training sites of different aggregate classes sorted to each predicted aggregate class*.

	Distribution of training classes	
Organic carbon content (%)	≤ *0.45*	> *0.45*
Predicted class		
I	32 I, 6 II, 3 III, 3 IV	8 I, 3 II, 1 III
II		9 II, 4 I, 1 III
III	37 III, 23 I, 15 II, 11 IV, 5 V	112 III, 50 II, 33 IV, 15 V, 14 I
IV	64 IV, 37 III, 36 I, 34 V, 20 II	15 IV, 10 III, 5 V, 2 II, 1 I
V		42 V, 29 IV, 24 III, 5 II, 4 I

The classification trees for predicting earthworm abundance (paper IV) and aggregation were used to support the development of an overall scheme to predict the susceptibility of soil profiles to macropore flow from easily available soil properties and site factors (Fig. 5, 6 a,b; Jarvis et al., 2009). The branch that concerns the abundance of earthworms was slightly modified by introducing additional restrictions for limiting soil horizons and inhospitable climates to the classification tree (Fig. 5). The effect of tillage and traffic compaction on soil structure was also integrated in the decision tree (Fig. 6 a,b). The decision tree classifies soil horizons into one of four susceptibility classes ranging from 'no potential' to 'high potential' for water flow and solute transport in macropores. The predictive scheme is model-

independent and thus enables users to link each class to specific parameter values of any suitable solute transport model using class pedotransfer functions. The purpose of the scheme is to support predictions of site susceptibility to macropore flow within a broader risk assessment for pesticide leaching at farm, catchment and national scales in the EU (FOOTPRINT, 2009). A test of the model against tracer breakthrough experiments on undisturbed soil columns assembled from literature data (n = 52) suggested that the classification tree can be useful to predict the integrated effects of macropores on solute transport at the landscape scale (Jarvis et al., 2009).

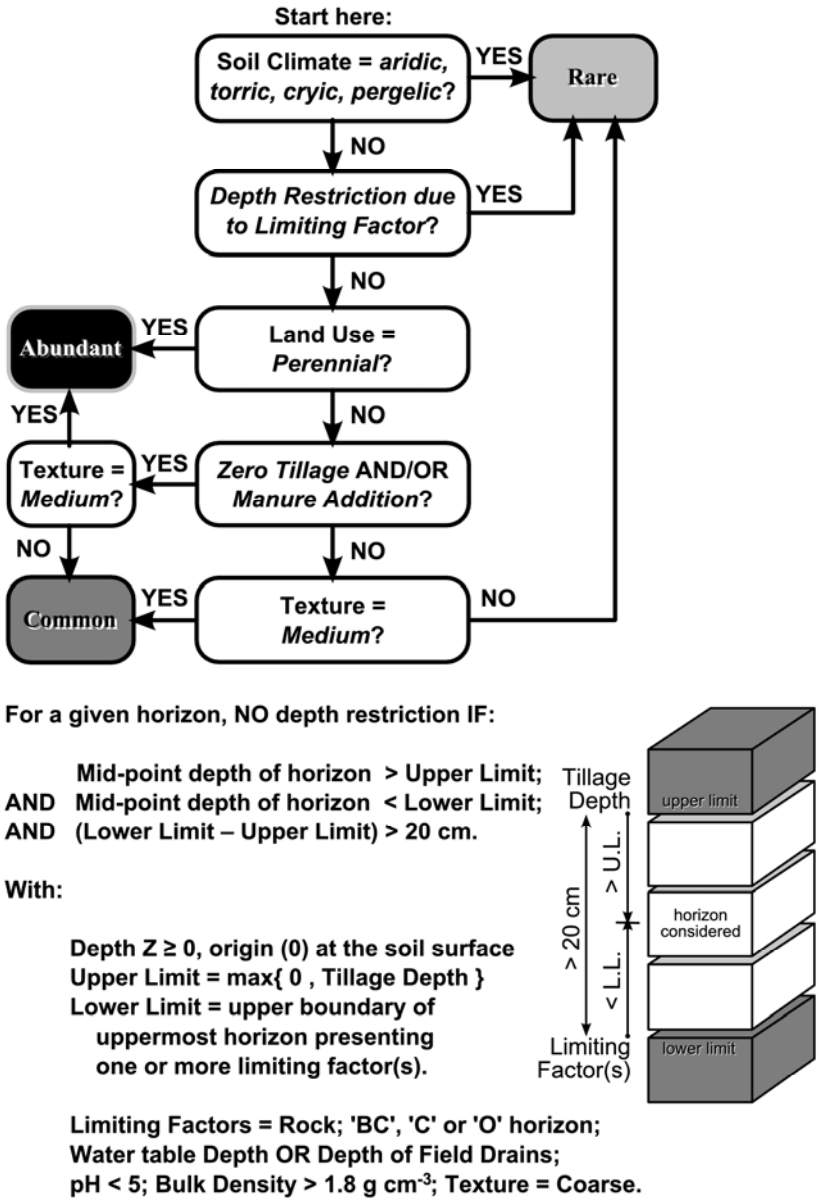
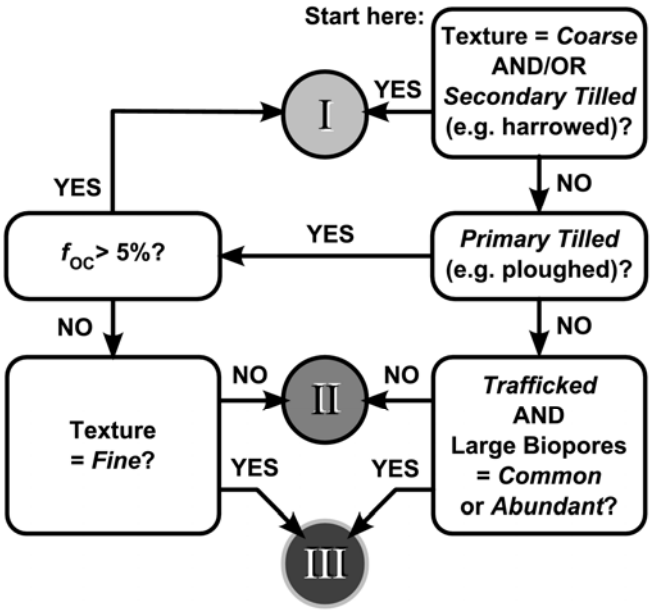


Figure 5. Decision tree for predicting the abundance of anecic earthworm biopores. Climate terms are defined according to the USDA (2003) soil moisture and temperature system. Horizon designations follow the FAO (2006) definitions. 'coarse' texture = sand or loamy sand; 'fine' = clay, silty clay, clay loam or silty clay loam; 'medium' = all other texture classes. Texture classes are defined according to the system of USDA (n.d.). Figure reproduced from Jarvis et al., 2009, with the permission of the Soil Science Society of America.

a)



b)

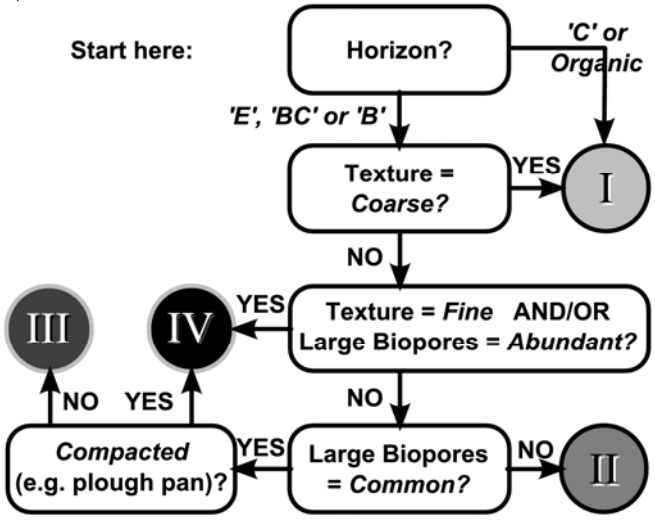


Figure 6. Scheme for classifying susceptibility to macropore flow in topsoil (a) and subsoil (b) horizons. Class I = none, II = low, III = moderate and IV = high. f_{oc} is the soil organic carbon content, 'coarse' texture = sand or loamy sand, 'fine' = clay, silty clay, clay loam or silty clay loam and 'medium' = all other texture classes. Texture classes follow the system of USDA (n.d.) and horizon designations the FAO (2006) definitions. Figure reproduced from Jarvis et al., 2009, with the permission of the Soil Science Society of America.

5 Upscaling

Our understanding of soil processes is generally derived from experiments on soil columns in laboratories or small research plots. Models of these processes are therefore usually developed at such small spatial scales, in this text referred to as the point scale. Consequently, a horizontal homogeneity is assumed for these one-dimensional models. In practice there is a need to model soil processes at larger scales (FOOTPRINT, 2009; Mulla et al., 2003) such as the field scale, catchment or regional/national scales. As an example, the MACRO model predicts pesticide leaching at the scale of one m^2 whereas farmers, agricultural advisors and water managers are interested in predicting the quality of surface water and groundwater at scales of the size of hectares or larger. But models cannot be assumed to remain valid when applied at scales other than the ones they were developed for. Heuvelink (1998) specify three reasons why models are scale-specific. The first reason originates from the simplification step in model development, which focuses on capturing dominant processes while less important ones are ignored. However, the scale of interest will determine which processes are dominant (Wagenet, 1998). As an example, the dominant hydrological process may change from macropore flow to surface runoff when shifting from pore to catchment scale. The second reason is that large scale models are often less complex than small scale models (Heuvelink, 1998). This difference is due to the availability of input data. Much of the input data for small scale models are available through measurements. The MACRO model, for example, requires soil physical and chemical properties that are measured in soil cores of a volume of the order of one dm^3. Large scale models, on the other hand, often have to rely on low quality input data derived from general information sources (e.g. soil survey, agricultural statistics and expert judgment) and pedotransfer functions (Heuvelink, 1998). Low quality data are intrinsically associated with large uncertainty. To develop simpler models

for large scale applications can therefore be theoretically justified (Jansen, 1998). The third reason is that model input and output variables are generally scale dependent (Heuvelink, 1998) since they represent some kind of average of point-scale values derived within the area of interest. The relationships between variables derived at one scale therefore do not necessarily hold for a change in extent, and model formulations thus often differ with scale. Topography, vegetation and soil properties are some examples of common model variables that vary with extent due to their scale dependent heterogeneity.

Scaling techniques have been developed to change model scales either upward (i.e., upscaling) or downward (i.e., downscaling). The issue of upscaling soil processes and properties is highly complex (Pachepsky et al., 2003). Some of the difficulties in upscaling arise due to the inherent spatial variability of soil properties and their often nonlinear dependence on state variables (Vereecken et al., 2007). A lot of research remains to be done before a more complete understanding of the scale dependencies of soil variability is reached and soil processes can be successfully simulated across large scales (Pachepsky et al., 2003). The challenge of downscaling methods is to introduce a spatial pattern or statistical distribution on a landscape from large scale data at relatively poor spatial resolution (Seyfried, 2003). Downscaling has proven to be even more difficult than upscaling and has been less studied (Wagenet, 1998).

5.1 Characterizing spatial variability

Several upscaling techniques for hydraulic properties and transport parameters require information regarding the spatial variation in hydraulic properties (Vereecken et al., 2007). The degree of knowledge required about the spatial variation (ranging from measures of central tendencies to the actual spatial relationships) depends on the heterogeneity of the area under study, and the upscaling technique applied. Even though the spatial correlation structure of hydraulic parameters in the direction of mean flow has a critical control on flow transport processes, information on the spatial variability of soil properties in the vertical direction is generally much less common than information on the lateral direction (Vereecken et al., 2007). Due to the spatial heterogeneity of soil properties, it is generally impossible to know their true values at every location. Interpolation techniques offer a way to estimate values at locations where no measured values are available based on a collection of observed data points. These techniques rely on the assumption that the variable is continuous over space and spatially dependent

(i.e., that samples collected close to one another are more likely to be similar than samples collected further apart). In soil science, geostatistical interpolation methods are typically used (Heuvelink and Webster, 2001). Geostatistics comprise several tools for improving estimation under different conditions (Ellsworth et al., 2003). At field scale, kriging is frequently used as it is generally assumed that soil spatial variation can be predicted with a statistical model describing random stationary variation. Even though soils in reality are neither random nor stationary, the models might still be reasonable for some situations (Webster, 2000). However, models that assume stationary spatial differences definitely become untenable when the scale is increased beyond the field scale. Kriging uses an assumed or estimated covariance function, called the variogram, to aid predictions (Ellsworth et al., 2003). As a consequence, variation is underestimated and the estimated pattern will therefore be smoother than the true pattern. Co-kriging is a useful interpolation technique that makes use of spatial dependencies between variables (e.g. the effect of topography and soil properties on soil moisture) to greatly improve interpolation estimates of the primary variable if the secondary variable is sampled more intensely (Goovaerts, 1997).

Prior to the advent of geostatistical techniques, soil patterns in the landscape were described by the spatial distribution of qualitatively and empirically defined soil classes (Heuvelink and Webster, 2001). In soil classification, soil is partitioned into more or less discrete classes in which the soil is relatively homogeneous. A disadvantage of soil classification is the crisp boundaries between the soil classes and the lack of variation within them. These make it impossible to depict the commonly occurring situation of gradual spatial variation of soil properties. Since both sharp boundaries and gradual transitions may be present within an area, some attempts have been made to merge soil classification and geostatistical approaches. One method that aims to depict continuous and discrete soil spatial variation is to incorporate fuzzy set theory with soil classification. This allows a soil to be a member of multiple classes, achieving a gradual transition from one soil type to another across the mapped region. Heuvelink and Webster (2001) suggest that further improvements can be achieved by inter-disciplinary studies that integrate knowledge of all relevant processes, including soil forming factors. Collaboration between pedologists, soil physicists and hydrologists constitutes an interdisciplinary field of research termed hydropedology (Lin, 2003). Hydropedology can facilitate translation of data attained in soil surveys into soil hydraulic information and link the phenomena occurring at the scale of pores and aggregates to the scales of pedons and catenas and

further on to catchment, regional and global scales. In this way, a hydropedological approach has great potential to describe variations in soil-water interactions across spatial and temporal scales for a variety of issues, including water quality and contaminant fate.

5.2 Upscaling approaches

Two different upscaling approaches can be distinguished: to increase the degree of aggregation of model quantities or to increase the model extent (Heuvelink and Pebesma, 1999; Vereecken et al., 2007). An increased degree of aggregation means that a heterogeneous area is replaced with a homogeneous one that produces the same response with the help of effective large scale model input parameters (Vereecken et al., 2007). Such parameters are generally estimated either by inverse modelling or by forward approaches (for which in some methods effective equations are also derived). Inverse modelling is a data driven technique that deduces effective parameters for a certain scale from information gathered at various scales. Forward upscaling approaches, on the other hand, are process-oriented techniques that transfer mechanistic understanding developed at one scale to another, using information only gathered at the small scale. One such method is the 'scaleway' (Vogel and Roth, 2003) in which the smaller scale random heterogeneities are replaced by average effective descriptions. Deterministic structure, on the other hand, is thoroughly characterized since connectivity of so-called structural units or elements is of great importance for transport processes at any scale of observation (e.g. for the pore scale (Ewing and Horton, 2003) and for the catchment scale (Frey et al., 2009)).

Upscaling methods that increase the model extent involve spatial aggregation of point-scale model outputs (Heuvelink and Pebesma, 1999). The performance of such techniques does not seem to depend as much on the magnitude of upscaling as on the relative similarity between the smaller unit that is upscaled and the larger unit. If the spatial distribution of the output is needed, strategic spatial scaling should be used (Leterme et al., 2007a). This type of scaling includes spatial interpolation to generate areal coverage from point-scale inputs and running the model prior to a final aggregation step (Heuvelink and Pebesma, 1999). In strategic spatial scaling, the model can either be executed on all available inputs followed by interpolation of the model outputs, or the model can be run with input parameters generated in preceding interpolations. At present no single theory for ideal strategic spatial scaling is available. Different studies have reached different conclusions regarding which approach performs best (e.g.

Stein et al., 1991; Bosma et al, 1994; Heuvelink and Pebesma 1999) and a comparative study (Leterme et al 2007a) showed that the approaches produced dissimilar outputs for non-linear models. To enable a more efficient use of the spatial distribution characteristics of individual inputs, Heuvelink and Pebesma (1999) recommend that the input parameters should be interpolated. However, it could also be argued that interpolation should be used as a last resort (i.e., for output values) since it is a tool to 'fill in the missing information' (Leterme et al., 2007a). Leterme et al. (2007a) suggest that the relevance of either approach depends on the available input information. A potentially key feature in favour of interpolating outputs lies in the additional computational costs involved in the alternative approach, especially for process-based models and if uncertainty analysis is to be performed.

All upscaling techniques result in a loss of precision relative to the point scale because spatial variability increases with scale (Seyfried, 2003). Another scaling effect is a loss in accuracy as a result of deterioration in parameter estimation (e.g. achieved through calibration or interpolation techniques) and a failure to account for how dominant processes are affected by scale changes. Moreover, interpolation of environmental variables conditionally involves a reduction in heterogeneity, a scaling effect that needs to be assessed in an uncertainty analysis when interpolation-based approaches are employed (Leterme et al., 2007a). Both the unknown value and the uncertainty of the predicted value are estimated by kriging (Ellsworth et al., 2003). The uncertainty due to the random component of geostatistical analyses can be assessed by calculating several stochastic realisations of the spatial distribution of the variable (Heuvelink and Webster, 2001). These realisations maintain the correlation described by the variogram, while the pattern is smoothed by the kriging procedure.

Upscaling MACRO to field and catchment scales

In paper I, drain flows and leaching of MCPA, simulated using the MACRO-model version 4.3b (Jarvis, 1994), were upscaled for the 900 ha agricultural catchment of Vemmenhög and the 30 ha field at Näsbygård. The aim was to compare the results of these simulations with aggregated drain flows and concentrations of MCPA measured for one year at the main outlet of the Näsbygård field and for seven years in a stream draining the catchment. A prior analysis of the pesticide and water input and transport routes suggested that there is very little surface runoff, negligible groundwater inflow and due to culverting, no spray drift input. Moreover, the field drainage systems in the Vemmenhög catchment create a rapid connection between field

leaching and the catchment outlet. The conclusion drawn from this analysis was that processes that influence pesticide loadings and concentrations in the stream correspond closely to the ones included in the MACRO model. However, upscaling was required since MACRO is a one-dimensional model. A Monte Carlo approach was chosen as the method for upscaling. The input distributions regarding soil properties and MCPA degradation rates were obtained through soil sampling campaigns. Model input parameters regarding crops grown and pesticide handling and usage on individual fields were based on information gathered annually through interviewing the local farmers. However, to achieve a complete parameterization, thirteen input parameters were treated deterministically either because they were considered a priori less sensitive, or because insufficient data were available to estimate their variation. At the catchment scale, upscaling was performed by dividing each field into parcels of 0.96 ha and randomly assigning a sampled input parameter set to that parcel. In the final upscaling step, the outputs from the 620 simulations (in total) were aggregated. At the field scale, two alternative upscaling approaches were performed. The first involved aggregating the outputs from 200 stochastic simulations, each nominally representing an area of approximately 0.15 ha. The second upscaling alternative was simply a single deterministic model execution using the means of the input parameter distributions. Obtaining parameters that describe the ensemble behaviour of heterogeneous formations by averaging, as was the case with the latter alternative, can give errors in the prediction (Vereecken et al., 2007). This problem with upscaling input parameters became apparent in this study, as the output of the second upscaling approach gave a smooth attenuated drainage response that failed to capture measured peak outflows (Fig. 7). The hydrologic responses of the field and the catchment were, on the other hand, successfully predicted by the stochastic simulations. The resemblance between simulated and measured MCPA concentrations in the field outlet was also good. Regarding the catchment scale, the true loads in the stream and the concentrations in 97% of the measured samples were underestimated by the corresponding simulations (Fig. 8). These dissimilarities may be partly explained by model structural errors, boundary condition errors, modeller subjectivity, or the fact that one or more input parameter distributions did not accurately reflect conditions in the catchment. However, the main reason is probably that the model does not include point sources. Several of the samples with large MCPA concentrations were collected from the stream during recession flows with no connection to flow peaks and thus clearly originated from point-source pollution from filling or cleaning spraying equipment. This is an

illustrative example of an upscaling error. The error is intrinsic to the upscaling approach performed in paper I, since point-source pollution is relevant at the farm or larger scales but irrelevant at the point scale.

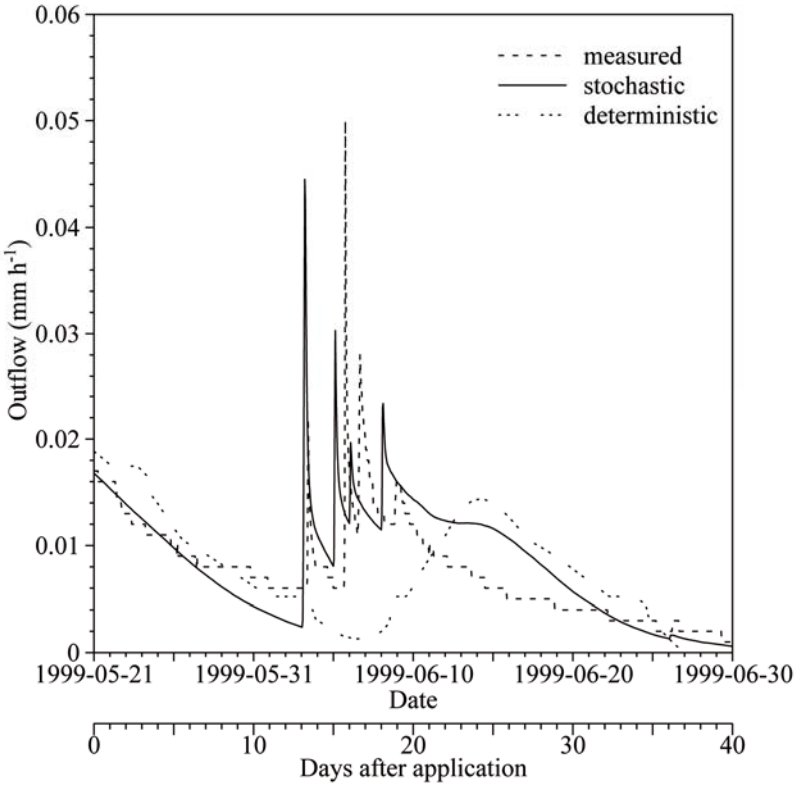


Figure 7. Measured and predicted (stochastic and deterministic) outflows from the Näsbygård field site for a 40-day period following pesticide application on 21st May 1999.

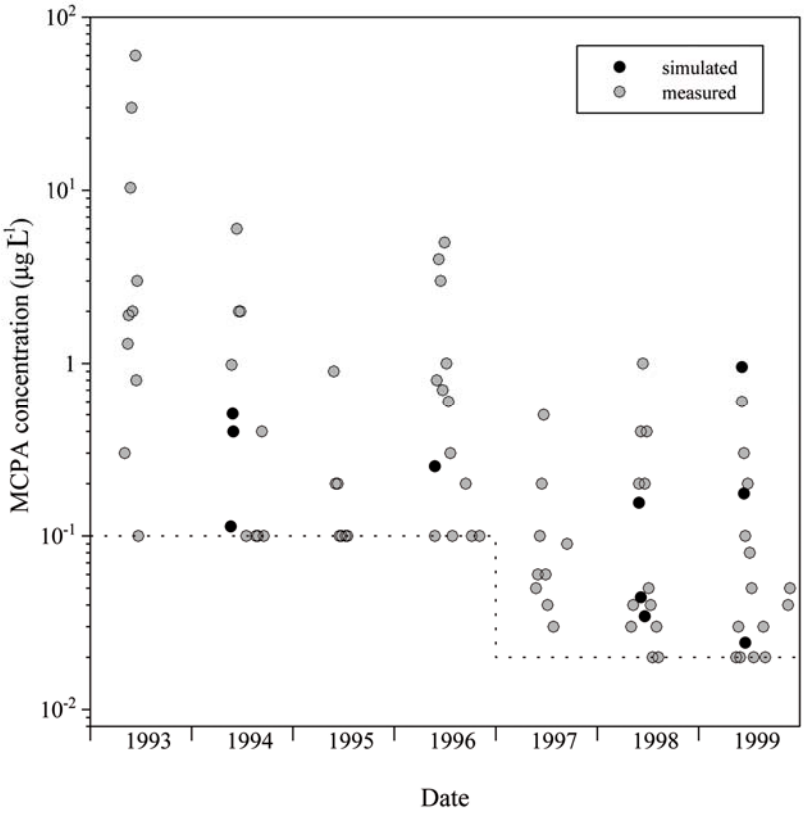


Figure 8. Measured and predicted concentrations of MCPA at the catchment monitoring station. The dotted line marks the limit of determination. Simulated concentrations were averaged to match the time resolution in the measurements (composite samples taken once or twice weekly).

Source areas for leaching at the field scale

In paper II, the spatial distribution of pesticide leaching within a 144 by 144 m grid at the Näsbygård field was predicted with the meta-model of MACRO. The grid consisted of 77 measurement locations spaced at distances of 6 to 24 m. Topsoil was collected from all sampling sites. Subsoil, however, was only sampled at 14 of the locations, at a spacing of 24 m. The soil samples were analysed for the input parameters required by the meta-model (sand and clay content in topsoil and subsoil and soil organic carbon content in the topsoil). For the 63 measuring locations that had not been sampled in the subsoil, clay and sand contents were estimated by co-kriging with topsoil clay content, topsoil sand content and elevation as secondary variables. In this way, all sampled soil information was efficiently utilized to produce a

spatially dense (high resolution) leaching prediction. The meta-model was run for all measurement locations for two hypothetical pesticides of contrasting leachability, with respect to degradation and adsorption properties. Ordinary kriging was applied to upscale the 77 point-scale leaching outputs of the meta-model to the spatial extent of the grid. For comparative reasons, ordinary kriging was also carried out to produce maps to visualize the spatial distribution of soil properties across the grid. The resulting leaching patterns were dissimilar (Fig. 9). For the more leachable pesticide, slightly larger concentrations were predicted to leach from areas of coarser-textured soil (Fig. 9 a). Due to the effects of macropore flow, predicted concentrations of the less-leachable pesticide are up to 1 order of magnitude larger for areas of finer-textured soil compared with concentrations for other areas of the field (Fig. 9 b). These kinds of interactions between compound properties and the effects of macropore flow on pesticide leaching have been demonstrated in other studies (e.g. Larsson and Jarvis, 2000; McGrath et al., 2008).

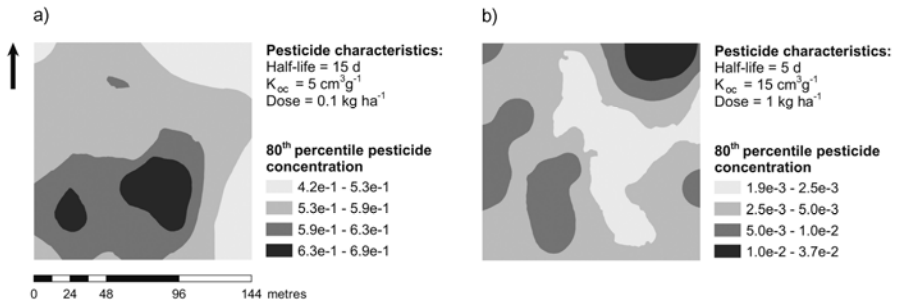


Figure 9. Spatial variation of predicted leaching for a leachable 'low-dose' pesticide (a) and a less leachable 'normal-dose' pesticide (b) at Näsbygård. Note the difference in scale.

In paper III, the techniques of strategic spatial scaling were used to localise high-risk areas for pesticide leaching and calculate the field average leachate concentration for a 46.9 ha field located at Bjertorp in south-west Sweden (58°13´ N, 13°08´ E). Soil samples were collected for the topsoil at a density of four per hectare, giving a total of 162 sampling sites. Ordinary kriging was carried out to visualize the spatial distribution of soil texture and soil organic carbon content across the field. Pesticide leaching was first predicted for each measurement location and then interpolated by ordinary kriging to visualize and compare the spatial distributions resulting from four alternative scenarios accounting for different patterns of spatial variation of pesticide degradation half-lives and K_{oc}. Increasing the resolution of the input data by interpolating the input parameters might seem like a feasible alternative

approach since the meta-model yields results almost instantaneously and requires few input parameters. However, uncertainty analyses were also carried out in paper III so the computational effort and additional work-load would therefore still have been extensive with such an approach. According to the meta-model, the largest leaching occurred on areas of fine-textured soils, which are more prone to macropore flow, and which also had smaller organic carbon contents and therefore weaker sorption. This relationship between soil texture and macropore flow is supported by the results of leaching experiments carried out on undisturbed soil columns sampled at Bjertorp (Jarvis et al., 2007). The results of the scenario-based uncertainty analyses are discussed in the following chapter.

To achieve a reliable interpolation from point-scale measurements, the sampling sites must be sufficiently densely distributed. At Vemmenhög, for example, only 1 soil sample was gathered for every 16 ha to 46 ha (depending on sample depth), which is clearly insufficient to support interpolation of spatially variable soil properties. Therefore, only the aggregated responses of the catchment were investigated and no attempt was made to locate any source areas. It may perhaps be possible to improve interpolation of limited measurements of clay content and organic carbon content, by utilizing apparent electrical conductivity as a secondary variable in co-kriging. Another potential approach that could make soil sampling schemes more efficient is to utilize measurements of apparent electrical conductivity (and possibly topography) within a field for defining zones of varying degrees of leaching risk. In such an approach, cost-effective and accurate interpolation for relevant field areas can be achieved even though the number of samples is reduced. A preliminary study was carried out to investigate whether measurements of apparent electrical conductivity can support model parameterization to locate areas susceptible to pesticide leaching at the field scale. The spatial distribution of apparent electrical conductivity was measured with an EM-38 electromagnetic induction meter at Näsbygård and also at the 46.9 ha field located at Bjertorp, A moderate correlation was found for apparent electrical conductivity (EC_a) and soil and site properties relevant for leaching, i.e., clay content (C_c), organic carbon content (f_{oc}) and topography (H, elevation in metres above the lowest point in the field). The best regression found for the Näsbygård site was:

$$EC_a \text{ (mS m}^{-1}) = 18 + 80 \star C_c \ (R^2 = 0.40)$$

and for the Bjertorp site:

$$EC_a \text{ (mS m}^{-1}) = -2.4 + 29 \star C_c + 0.22 \star H - 300 \star f_{oc} \quad (R^2 = 0.51)$$

A strong correlation with topsoil properties was not to be expected since the EM-38 conductivity meter senses deeper into the soil. But even a moderate correlation could be useful in mapping the spatial variation of pesticide leaching at field and farm scales. However, the reliability of identified source areas based on a method combining frequency-domain electromagnetic induction meters and simulation models still needs to be determined. An analysis of the uncertainties involved in utilizing measurements of apparent electrical conductivity either for co-kriging or for directing soil sampling is thus a research task for the future.

6 Uncertainty and sensitivity

Modelling of environmental systems is complicated by the presence of uncertainties that originate from the limited knowledge about the system for a particular place or application brought into the modelling procedure (Beven, 2009). The end result of these uncertainties may be untrustworthy model predictions. It is therefore important to consider modelling uncertainties so that the reliability of predictions can be determined. The robustness of model outputs can be assessed by methods of uncertainty analyses. A considerable work load is generally required to incorporate uncertainties in the modelling process, but valuable information may be gained (Beven, 2009). Such information can, for example, aid in decision making when assessing risks of environmental contamination. Subsequent to an uncertainty analysis, a sensitivity analysis can be carried out to explore how the different uncertainties influence model output (Chan et al., 1997).

6.1 Types and origins of uncertainty

Depending on the origin, uncertainty in environmental modelling can be classified as uncertainty about model form, uncertainty in the model operations, uncertainty about model completeness or adequacy and uncertainties in model quantities (van Asselt and Rotmans, 2002). Uncertainty about model form refers to uncertainty concerning model structure, i.e., functional relationships and choices of algorithms. The uncertainties that arise due to accumulation of uncertainties propagated through the model and due to unknown errors in the implementation of the model (e.g. hard- and software errors and numerical errors), are classed as model operation uncertainties. Uncertainties about model completeness or adequacy pertain to how well the model represents the system under study. Parameters, driving data and initial states are model quantities. Spatial and

temporal variability of environmental variables, either due to natural conditions or imposed on the system under study, will cause uncertainty in the model quantities (Dubus et al., 2003). Uncertainty will also arise from sampling procedures and from laboratory analyses for determination of model quantities. These measurements may be subjected to 'systematic' as well as 'random error'. Furthermore, uncertainty is introduced for model quantities that cannot be directly measured (e.g. surrogate parameters) but must be either set at their default values, derived by expert judgement, extracted from existing databases or estimated using pedotransfer functions. Model results can also be significantly influenced by modeller subjectivity since the choices and assumptions made regarding model quantities vary among modellers (Boesten, 2000; Beulke et al., 2006).

Two types of uncertainty can be distinguished; epistemic and aleatory (O'Hagan and Oakley, 2004). Epistemic uncertainty is due to incomplete scientific knowledge. This type of uncertainty includes systematic measurement errors, lack of observations or measurements, conflicting evidence and processes not observed nor theoretically imagined (van Asselt and Rotmans, 2002). Aleatory uncertainties arise from inherent variability or randomness in systems. Even though quantum physics suggests that there is true randomness in some phenomena, we do not know whether this randomness extends to the operational scales of our models (O'Hagan and Oakley, 2004). Webster (2000) argues that soil is not random but deterministically chaotic. Soil, however, appear to us as random (at some scale) due to the incompleteness of our knowledge. Since we can not explain some of the variation, we are forced to treat the soil as if it were truly random. Fortunately, stochastic techniques work equally well regardless of whether the randomness is real or apparent. Nevertheless, the distinction is useful because epistemic uncertainties can, in principle, be reduced by gathering additional information and filling knowledge gaps, whereas aleatory uncertainties are irreducible (O'Hagan and Oakley, 2004). Uncertainty about model form, uncertainty about model completeness or adequacy and uncertainty in the model operations are clearly epistemic. Model quantities, on the other hand, can include both epistemic and aleatory components of uncertainty.

6.2 Uncertainty analysis

Uncertainty analyses seek to quantify the reliability in model predictions. Alas, only a few uncertainties are easy to quantify, many are difficult to quantify (e.g. model structure and model subjectivity) and several are

impossible to quantify (Dubus et al., 2003). Methods for analysing uncertainty therefore usually only address uncertainties associated with model quantities and generally assume that the model is structurally correct, modeller subjectivity is negligible and that the model can be sufficiently parameterised. Uncertainty regarding model completeness is commonly addressed in a validation phase (van Asselt and Rotmans, 2002). The term validation is however seldom used when testing environmental model performance since a complete validation of such complex systems is impossible due to inherent uncertainty.

The reliability of model predictions is evaluated from a set of alternative model realisations, commonly derived using some Monte Carlo technique (Beven, 2009). Such techniques involve running the model repeatedly for a large number of model quantities sampled from assumed probability distributions. The confidence that should be assigned to the model output is then analysed statistically. Classical set theory and probability theory are the two most widely used approaches for representing uncertainty (Beven, 2009). In classical set theory, the uncertainty arises from the non-specificity inherent in a set of alternatives out of which only one is sought. One major disadvantage of set theory is the crisp boundary of a set, i.e., alternatives initially not contained in the set will be left outside the set and hence not considered. In probability theory, on the other hand, any alternative within the universal set of alternatives can be studied. For each given alternative, the likelihood that it is the one that is wanted is expressed by a measure ranging from 0 to 1. Both probability theory and classical set theory assume that uncertainty is primarily aleatory. Uncertainty analysis methods that include elements of epistemic uncertainty are fuzzy set theory, rough set theory, fuzzy measure theory and the info-gap approach of Ben-Haim (2006).

Uncertainty analysis of source areas at the field scale

According to the Monte Carlo simulations performed in paper I, 1 to 17% of the Vemmenhög catchment area contributed 90% of the annual amount of leached MCPA (Fig. 10). If such 'hot-spots' for diffuse leaching were identified, pesticide leaching could be significantly reduced by site-specific pesticide application. But the efficiency of site-specific application strategies may be adversely affected by uncertainty in the leaching predictions. Since it is costly and time-consuming to make measurements with a high spatial resolution, pesticide characteristics can generally be expected to be collected from existing databases and assumed to be constant for all locations in the field. As a consequence, uncertainties about these model quantities are

introduced in the modelling procedure. Any correlation between pesticide degradation half-life and soil organic matter will also be uncertain. As mentioned before, degradation half-life and soil organic carbon content have been found to be both negatively and positively correlated. Furthermore, the model quantities associated with the variogram may involve large uncertainties when interpolating by kriging (Jansen, 1998). It would therefore be important to consider this uncertainty for precision-application systems based on interpolated risk maps.

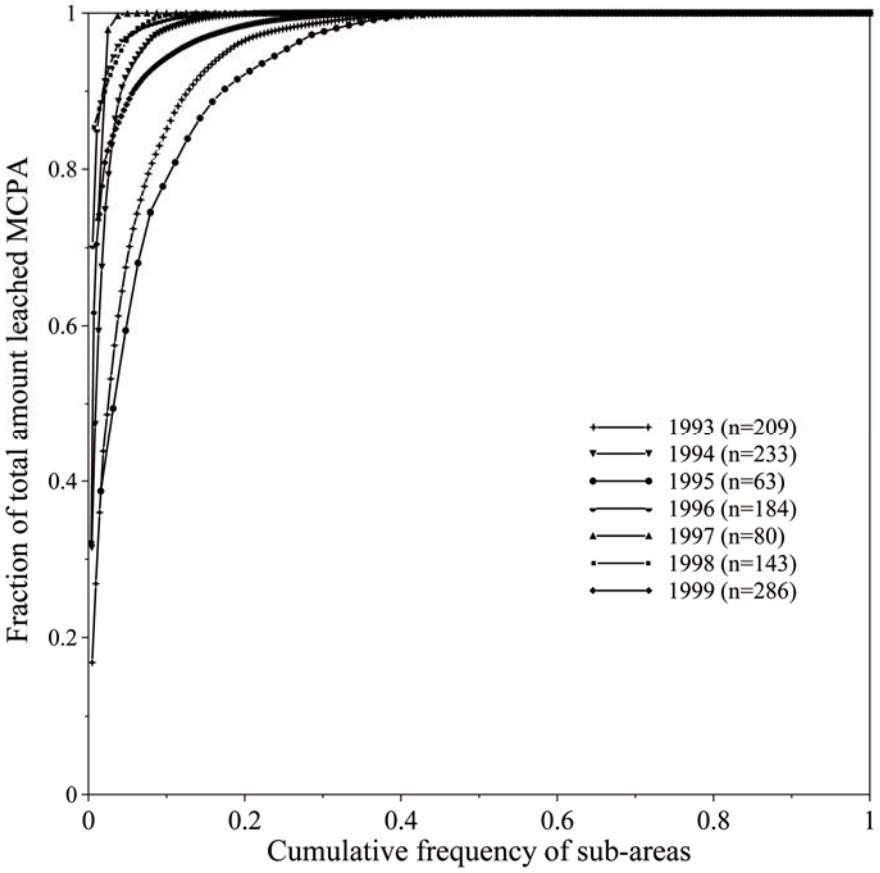


Figure 10. Cumulative frequency of the contribution of 'sub-areas' to the fraction of accumulated leaching of MCPA for different years.

Whether site-specific application at the field scale can contribute to a reduction of pesticide leaching despite uncertainty in the underlying model-based leaching risk map was investigated in paper III. The meta-model of

MACRO was applied to the 46.9 ha field at Bjertorp. The study addressed uncertainties regarding two meta-model input parameters concerning pesticide characteristics, namely degradation half-lives and K_{oc}, and the spatial interpolation. The measurement errors of the input parameters (i.e., organic carbon content and soil texture) were however assumed to be negligible in relation to the uncertainty of spatial interpolation. Three scenarios which differed with regard to whether degradation half-life was assumed to be negatively correlated, positively correlated or uncorrelated to organic carbon content were considered in the analyses. A standard scenario that assumes spatially constant pesticide properties was also addressed since it was assumed that, in practice, such a scenario will constitute the template for site-specific application. The uncertainty analyses were carried out by applying classical set theory. With the exception of the standard scenario, values of degradation half-life and K_{oc} for locations within the field were sampled from probability density functions using a Monte Carlo technique. The assumed distributions for these pesticide characteristics were chosen based on the findings of previous research at the field scale (e.g. Novak et al., 1997 for K_{oc}, and Walker et al., 2001; Rodrígues-Cruz et al., 2006 for half-life). For each scenario, this procedure was repeated 500 times producing realisations describing different spatial patterns of degradation half-life and K_{oc}. For each scenario, the realisation with the 5^{th} percentile correlation with the predictions of the standard scenario was identified as a 'worst-case' and selected for further study. To account for interpolation uncertainty, maps of predicted pesticide leaching risk were produced by the method of sequential Gaussian simulation (Rautman and Istok, 1996). The method involves Monte Carlo sampling from probability density functions of multivariate Gaussian form. The procedure was repeated 1000 times for each scenario resulting in a set of stochastic images from which leaching risk maps, visualizing the probability of exceeding a threshold concentration of 0.1 $\mu g\ L^{-1}$ in leachate at 1-m depth, were created.

According to the results, the patterns of leaching risk were similar for all scenarios, despite considering the uncertainties. Larger reductions of predicted leaching could therefore be achieved by site-specific application than by a comparable uniform dose reduction. All in all, precision agriculture seems a promising approach for reducing pesticide losses to groundwater at the field scale. The potential for minimizing pesticide impacts by precision agriculture may be larger for surface water than for groundwater since losses are dominated by fast transport processes (preferential flow to drainage systems and surface runoff) occurring shortly after pesticide application (e.g. Leu et al., 2004 b; Freitas et al., 2008).

6.3 Sensitivity analysis

Sensitivity analyses show how predictions of a model are related to the input parameters (Chan et al., 1997). The methods can be used to identify influential and insignificant factors and (groups of) parameters that interact with each other. By determining the main sources of model output uncertainty (or variability), a sensitivity analysis identifies research areas that should be prioritised or which parameters that need to be measured more accurately for improving model performance. Another area of application is evaluating whether all observed effects can be physically explained.

Sensitivity analysis is generally conducted as an uncertainty analysis with the addition of an extra final step in which the influence of each input parameters on the output variable is assessed. There are two different kinds of sensitivity analyses: local and global (Saltelli et al., 1999). Local sensitivity analyses try to determine the impact that individual input parameters have on the model response by computing the derivative of the output with respect to the input parameters. One input parameter at a time is varied within a small interval around a nominal value, hence the term 'local'. The input-output relationship is assumed to be linear, which is rarely satisfied by environmental models (Campolongo et al., 1999). For non-linear models, a global sensitivity method should be used instead. Global sensitivity analyses seek to assign the variation in the output variable(s) to the variation of the input parameters (Saltelli et al., 1999). The input parameters are allowed to vary simultaneously over their entire ranges (Soutter and Musy, 1999). For each input parameter, global sensitivity analyses usually generate an average measure of the overall sensitivity. These measures render it possible to compare and rank the influence of input parameters on model output.

There are several sensitivity analysis techniques available and the choice of method depends on the problem addressed, the characteristics of the model and the computational effort required (Campolongo et al., 1999). There is a trade-off between computational cost and information gained. Methods that quantify how much a given parameter is more important than another are computationally expensive (i.e., they require a large number of model runs, usually in the range of thousands). Qualitative methods that rank the input parameters in order of importance are relatively simple and quick (usually requiring tens to hundreds of model executions). Qualitative methods are usually used for computationally expensive process-based environmental models with many input parameters. However, with the continuous enhancement of computer power, quantitative methods will become practical for many process-based environmental models (Saltelli et al., 1999).

Sensitivity analysis of the MACRO model

In paper I, sensitivity analyses were performed to identify the MACRO-model version 4.3b input parameters that contributed most to the variation in two 'target' model outputs: the maximum concentration of MCPA and the total loss of MCPA to surface waters. The influence of input parameters related to degradation, sorption and water flow on pesticide loss to drainage was investigated at both field and catchment scales. The catchment scale sensitivity analyses also included the influence of precipitation and pesticide management practices. Weather data, soil properties, information on crops grown, handling and usage of the herbicide MCPA were collected for the 900 ha agricultural catchment of Vemmenhög and the 30 ha field at Näsbygård. For the catchment study, some of the input parameters in the simulation setup were correlated. It was therefore appropriate to choose partial rank correlation coefficients (Kendall and Stuart, 1979) as a global method for analysing sensitivity. This technique ranks the input parameters in order based on the degree of correlation between model output and any input parameter by removing the effects that originate from correlations with any other input parameter (Conover, 1980). Being a linear estimator, partial correlation coefficients applied to the non-linear MACRO model would be strongly sensitive to the values at the upper tail of the output distribution (Saltelli and Sobol, 1995). To give equal weight to all values in the distribution, rank transformation of the input parameter values and the output values was performed. Hence, analyses based on partial rank correlation coefficients are qualitative. The technique only account for first-order terms and are therefore incapable of revealing the importance of input parameters that influence model output mainly through interactions. A sensitivity analysis based on partial rank correlation coefficients can only succeed if the relationships between input parameters and the model output variable are monotonic. The requirement of a monotonic model was found to be not completely met by the MACRO model. This indicates that the resulting mutual order of ranking of input parameters with similar partial rank correlation coefficients is uncertain.

The resulting sensitivity analyses showed that variations in soil properties controlling the water flow through macropores influenced total pesticide losses and peak concentrations the most. At the catchment scale, precipitation following pesticide application was also highly ranked in the sensitivity analysis. Adsorption was also found to be relatively important at both field and catchment scales. Moreover, the variation of pesticide application timing over the catchment also had a relatively large influence on the pesticide losses. This is an illustrative example of an additional and

significant source of variability introduced as the study area is enlarged. The sensitivity analyses revealed that the regression error terms of the pedotransfer functions used to estimate bulk density, Brooks-Corey pore size distribution index, effective diffusion pathlength and saturated matrix hydraulic conductivity were among the most influential variables. This result illustrates the importance of minimizing the uncertainties associated with pedotransfer functions. Since the effective diffusion pathlength is impossible to measure, a substantial part of the pedotransfer error may originate from the uncertainty introduced when estimating effective diffusion pathlength from calibration procedures (Roulier and Jarvis, 2003). The pedotransfer function error terms related to dispersivity and saturated hydraulic conductivity were among the least influential variables. It could therefore be concluded that any further research to elucidate what their unexplained variations depend on is of low priority.

Sensitivity analysis of the meta-model of MACRO

In paper II, extended Fourier amplitude sensitivity tests (extended FAST) (Saltelli et al., 1999) were used to quantify the influence of the input parameters of the meta-model of MACRO. Since it was the model itself that was evaluated, the probability distributions of the input parameters were chosen so that the sensitivity analyses were performed for the entire domain of applicability of the meta-model. Extended FAST is independent from assumptions about the model structure, and thus does not require the model to be linear or monotonic. The technique can be considered a truly quantitative global sensitivity analysis, as it provides the exact percentage of the total output variance that each factor (or group of factors) is responsible for (Chan et al., 1997; Saltelli et al., 1999). Both the fractional contribution to the total variance of each factor alone (the first order term), and the overall contribution of the factor due to interactions with the other input factors (the total order term) are calculated (Saltelli et al., 1999). A severe limitation of extended FAST is that it only applies for independent input factors (Crosetto et al., 2000). The meta-model input parameters sand and clay content are correlated. However, extended FAST can treat sets of factors as single factors, so this limitation could be overcome by sampling clay content and an independent measure of the sand and silt distribution from which sand content was calculated. The sensitivity analyses were then performed by partitioning the contribution of clay content and the measure of texture distribution in a subgroup so that the effect of texture as a whole (for each horizon) was studied rather than the separate effects of the different texture classes.

The sensitivity analysis showed that the model output was sensitive to all input parameters. The two input parameters describing pesticide characteristics (half-life and K_{oc}) were the most influential, but topsoil texture was also quite important. The sensitivity to soil texture is probably mainly due to its influence on parameters controlling the mass exchange coefficient that regulates the strength of macropore flow. This behavior is in strong contrast to leaching models that do not account for macropore flow, and thus are relatively insensitive to soil texture and hydraulic properties (e.g. Boesten, 1991).

Extended FAST could not be used for the catchment scale study carried out in paper I since the simulations incorporated several correlated parameters. Furthermore, the simulations were computationally very expensive. We therefore had to be economic and reuse the Monte Carlo based simulations carried out to reproduce the pesticide losses from the field and the catchment when performing the sensitivity analyses. Such a strategy is not compatible with extended FAST since it has its own sampling scheme (Chan et al., 1997; Saltelli et al., 1999).

7 Conclusions and future research

A method of upscaling is required if point-scale simulation models are to be used for large scale applications. Important non-linear and highly intermittent processes such as macropore flow will not become sufficiently expressed in a deterministic upscaling approach based on average parameter values within the area under study. Such an approach failed to reproduce both water flows and pesticide losses from a 30 ha field within a 900 ha catchment in the south of Sweden. Using a stochastic upscaling approach instead, the point-scale process-based MACRO model was capable of reproducing the hydrologic response and pesticide losses from the field. Macropore flow was shown to be the most important process influencing predicted diffuse pesticide losses. In comparison to the field scale, catchments are subject to greater internal and external variation in a wider range of factors that can affect pesticide losses. Thus, when stochastic upscaling was carried out to the entire catchment, the resemblance of simulated and measured water flows was still good but pesticide losses were underestimated due to point-source pollution, most likely caused by careless handling of pesticides when filling or cleaning spraying equipment.

Difficulties associated with the parameterisation of point-scale process-based models generally restrict their use for identifying source areas at the scale of fields or catchments. Instead, the simulation meta-model of MACRO may prove a useful tool for this purpose. The area of the field that contributes most to leaching depends on the properties of the compound applied. The meta-model predicted that sandy soils are slightly more vulnerable for highly leachable compounds, whereas finer-textured soils represent a worst-case scenario for 'non-leachers' due to the dominant effects of macropore flow. To mitigate groundwater contamination at the field scale, these high risk areas need to be identified and managed. In a simulation case-study, it was shown that despite uncertainties in spatial

variation of degradation half-life and K_{oc} and interpolation of predicted leaching, site-specific application resulted in larger reductions of predicted leaching than that achieved by a comparable uniform dose reduction. Providing that the model approach gives reasonable estimates of the spatial pattern of pesticide leaching, the results demonstrate that site-specific applications may be a feasible method to reduce pesticide leaching at the field-scale.

The issue of how to identify source areas that significantly contribute to pesticide contamination of catchment water resources is yet to be resolved. The difficulties in estimating model input parameters, the large datasets required to represent the highly heterogeneous nature of landscapes and the difficulties of upscaling point-scale measurements, especially to account for processes that are missing at the point scale, suggest that current day simulation models may be inadequate to resolve this issue. New, simpler models which can locate source areas and identify dominant contamination pathways (e.g. macropore flow or surface runoff) from input data that are easily obtained at low cost are thus required. The development of new models would benefit from a hydropedological approach, involving a close collaboration with hydrologists (Lin, 2003). The schemes developed in this thesis for predicting soil structure effects on susceptibility to leaching may have potential in this respect, since they only require knowledge of readily available soil properties and site factors. Data from remote sensing (Seyfried, 2003), and obtained or inferred from soil maps and other survey data, farmer interviews, and data from tractor-mounted soil sensors (e.g. penetration resistance and electrical conductivity) (Morgan et al., 2003) could also be used to improve the spatial resolution of risk mapping.

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Acknowledgements

I gratefully acknowledge the financial supporters of this study; the European Union Commission for the projects 'CAMSCALE: Upscaling, predictive models and catchment water quality' (ENV4-CT97-0439) and 'FOOTPRINT: Functional tools for pesticide risk assessment and management' (Project no. SSPI-CT-2005-022704), the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) in the project 'Understanding the variability of pesticide losses to surface waters and groundwater at field and catchment scales' and the Swedish Farmers' Foundation for Agricultural Research (Stiftelsen Lantbruksforskning) in the project 'Mapping pesticide leaching risks at the field scale'.

My deepest thanks go to:

- My main supervisor *Nicholas Jarvis,* for your unfailing trust and support. At all times you have been kind and encouraging. You always made time for me when I needed guidance, sharing your scientific expertise and other valuable secrets about the academic world. The enthusiasm you have shown for my project has been truly infectious. I have very much enjoyed working with you!

- The co-authors, *Ghasem Alavi*, *Igor Dubus*. *Annemieke Gärdenäs*, *Nicholas Jarvis*, *Jenny Kreuger*, *Stéphanie Roulier*, *Fredrik Stenemo*, *John Stenström* and *Mats Söderström*, without your efforts there would not have been any thesis!

- My life companion *Mikael Söderman,* for building computer programs that facilitated my work, keeping my computers in good shape, serving me countless numbers of cups of tea and being completely wonderful.

❖ My mother *Anita Lindahl,* for taking care of Ilon so marvellously well, whenever I needed it.

❖ My father *Lars-Åke Lindahl,* for always being ready to unravel mathematical quandaries.

❖ All former and present colleagues at the Department of Soil and Environment, for creating such a friendly workplace atmosphere. In particular I want to mention:
- *Karin Blombäck,* for taking me under her wings, providing me good friendship and support.
- *Christina Öhman,* for excellent laboratory work that saved me many hours and the nice chit-chats we shared.
- *Lave Persson,* for enthusiastically solving any kind of technical problem I did encounter.
- *Gunnel Alvenäs, Lisbet Lewan, Mats Larsbo, Anne Ohlsson* and *Lovisa Stjernman Forsberg,* for always being friendly and helpful.
- *Ragnar Persson,* for allowing me to use the department computer room during nights and weekends.
- *Julien Moeys,* for bringing me interesting articles.
- *Ingvar Nilsson*, *Johan Arvidsson* and *Olle Andrén,* for reading and commenting on this thesis.

❖ My faithful friends *Karolina Bergström* and sister *Matti Ridenfeldt,* for so convincingly believing in me and in so doing boasting my spirit. My friend *Mia Olsson,* for always being enthusiastic about new experiences, even soil sampling. My friend *Marika Nestor,* for entertainingly coaching me during the process of writing this thesis.

❖ *Bilbo*, *Lukas* and *Viggo*, for your companionship on the many walks in the forest that I have needed to clear my mind.