

# Modelling Climate Change Impacts on Pesticide Leaching

Uncertainty and Scenario Analysis  
at Field and Regional Scales

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# Modelling Climate Change Impacts on Pesticide Leaching. Uncertainty and Scenario Analysis at Field and Regional Scales

## Abstract

Climate change projections for Sweden indicate increases in both temperature and precipitation. In a warmer and wetter climate, weed and pest pressures are likely to increase, which might in turn trigger an increased use of pesticides. This thesis analysed potential impacts of climate change on pesticide losses from Swedish arable soils under present (1970-1999) and future (2070-2099) climate conditions. The pesticide fate model MACRO was used to evaluate the direct effects of climate change on pesticide losses to tile-drains at the field scale accounting for uncertainties related to model structure (i.e. the description of temperature dependent processes), parameters and climate input data. At the regional scale, MACRO-SE was used to assess the direct and the indirect effects of climate change (i.e. changes in cropping patterns and herbicide use) on the leaching of herbicides towards groundwater in southern Sweden.

At the field scale, the results showed that differences in model structures affected predictions of pesticide losses under climate change, despite large parameter uncertainty. The effect of climate input uncertainty was more important than the effect of parameter uncertainty for predicted changes in pesticide losses between present and future climates, while it was the opposite for simulated absolute pesticide losses. The direction and magnitude of predicted changes in pesticide losses depended on pesticide properties, application season and climate scenario. In the regional scale study, the area at risk of groundwater contamination was only slightly affected by direct effects of climate change, whereas the area at risk doubled due to the indirect effects of climate change that were included in the analysis.

The main conclusions are that (1) the relative importance of different sources of uncertainty depends on the pesticide properties, application season and whether the focus is on absolute losses or predicted changes, (2) ensembles of climate scenarios are necessary for robust assessments and (3) indirect effects need to be considered alongside the direct effects as predictions can be significantly affected. Despite large uncertainties, this thesis highlights the need to strengthen policies, to adopt improved mitigation measures and to implement management strategies that will limit pesticide use and minimize the risks of contamination of ground- and surface waters.

*Keywords:* soil; water; pesticide; modelling; MACRO model; climate change; regional scale; uncertainty; ensemble modelling; direct and indirect effects;

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# Dedication

To my grandmother.

*Predictions are uncertain, especially about the future.* (ATTRIBUTED TO NIELS BOHR)

*All models are wrong, but some are useful.* (GEORGE E.P. BOX)

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## List of Publications

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

- I Steffens, K., M. Larsbo, J. Moeys, N. Jarvis, and E. Lewan (2013). Predicting pesticide leaching under climate change: importance of model structure and parameter uncertainty. *Agriculture, Ecosystems and Environment* 172, 24-34.
- II Steffens, K., M. Larsbo, J. Moeys, E. Kjellström, N. Jarvis, and E. Lewan (2014). Modelling pesticide leaching under climate change: parameter vs. climate input uncertainty. *Hydrology and Earth System Sciences* 18, 479-491.
- III Steffens, K., N. Jarvis, E. Lewan, B. Lindström, J. Kreuger, E. Kjellström, J. Moeys (2015). Direct and indirect effects of climate change on herbicide leaching – a regional scale assessment in Sweden. *Science of the Total Environment* 514, 239-249.

Papers I-III are reproduced with the kind permission of the publishers Elsevier (I, III) and Copernicus Publications (II).

The contribution of Karin Steffens to the papers included in this thesis was as follows:

- I Planned the study together with the co-authors, performed the study (input data preparation, model simulations, data analysis and interpretation) and the writing with some assistance of the co-authors.
- II Planned the study together with the co-authors, performed the study (input data preparation, model simulations, data analysis and interpretation) and the writing with some assistance of the co-authors.
- III Planned the study together with the second, the third and the last author of the paper, performed the study (input data preparation, model simulations, data analysis and interpretation) and the writing with some assistance of all co-authors.



# Abbreviations and Glossary

## Abbreviations

Aut	Autumn
CKB	Centre for Chemical Pesticides
CS	Climate scenario
EF	Model Efficiency
EPC	Ensemble of Parameter Combinations
FST	FOOTPRINT soil type
GCM	Global Climate Model (usually General Circulation Model)
GHG	Greenhouse gas
GIS	Geographic Information System
GLUE	Generalized Likelihood Uncertainty Estimation
GSS	Southern plains of <i>Göteborg</i> (sv: <i>Götalands Södra Slättbygder</i> )
IPCC	Intergovernmental Panel on Climate Change
LOD	Limit of detection
MA	Maize
Ms	Moderately sorbed compounds
MV	Model version
OM	Organic matter
PAS	Pesticide Application Scenario
PB	Peas (and beans)
PCB	Polychlorinated biphenyl
PPDB	Pesticide Properties DataBase
PT	Potatoes
RCM	Regional Climate Model
RCP	Representative Concentration Pathway; see 3.1.1 and IPCC (2013b)
SB	Sugar beets
SC	Spring cereals
Spr	Spring

SR	Spring rape
SRES	Special Report on Emission Scenarios (Nakićenović & Swart, 2000)
Ss	Strongly sorbed compounds
WC	Winter cereals
WR	Winter rape
Ws	Weakly sorbed compounds

## Glossary

Climate projection	Estimates of future climate derived with climate models and the help of scenarios. It can be considered an conditional expectation reflecting what can be expected if this or that happens (WMO, 2015).
Climate Scenario (CS)	Climate model projections downscaled to local (or regional) scale that can be used to drive an impact model.
Downscaling	Transfer of large scale outputs of climate models to local or regional scales.
Ensemble modelling	Use of different models, scenarios or downscaling methods in parallel to illustrate and account for uncertainties.
Epistemic uncertainty	Uncertainty due to imperfect knowledge; see Walker et al. (2003) or Curry & Webster (2011).
Impact model	Refers to any model that is used within a climate change impact study, driven with climate time series (e.g. a pesticide fate model such as MACRO).
Pesticides	Chemical substances used to control weeds, pests and diseases in order to secure yields; also called plant protection products. Herbicides are pesticides specifically used to control weeds.
Pesticide Application Scenario (PAS)	A unique combination of a pesticide applied on a certain crop at a certain time with a certain dose.
Prediction scenarios	Simulation runs with calibrated versions of MACRO for present and future climate conditions.
Scenario	Scenarios provide plausible descriptions, i.e. based on coherent and internally consistent assumptions, of how the system or its driving forces (e.g. atmospheric GHG) may develop in the future (Walker <i>et al.</i> , 2003).

# 1 Introduction

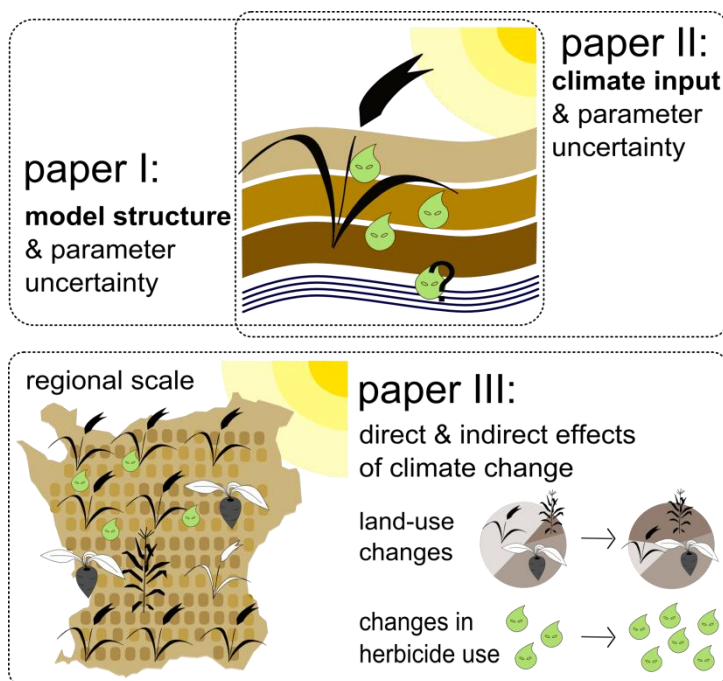
In the coming decades, we face the challenge of producing food to feed the growing world population with finite resources (Schneider *et al.*, 2011; Wirsenius *et al.*, 2010) in a socially, environmentally and economically sustainable way. The effects of climate change will add to the growing competition for water, energy and land resources (Godfray *et al.*, 2010). In Sweden, a warmer and wetter climate in the future is likely to improve conditions for crop production (e.g. Olesen *et al.*, 2011; Trnka *et al.*, 2011), but also to increase pest and weed pressures (e.g. Patterson *et al.*, 1999). Pesticides, which are used to control pests, weeds and diseases and secure yields, can have harmful effects on the environment and pose a threat to human health due to contamination of drinking water or food that contains pesticide residues (Tirado *et al.*, 2010; Miraglia *et al.*, 2009). Pesticides are regularly found in groundwater and surface waters in Sweden and around the world (e.g. Balderacchi *et al.*, 2013; Malaguerra *et al.*, 2012; Holvoet *et al.*, 2007; Kreuger, 1998) and negative effects on non-target organisms in the environment are frequently reported (e.g. van der Sluijs *et al.*, 2015; Malaj *et al.*, 2014; Moschet *et al.*, 2014). Since the remediation of contaminated groundwater is difficult and very slow (Vonberg *et al.*, 2014), future drinking water resources need to be protected already today.

Climate change might lead to increased pesticide use (Delcour *et al.*, 2015), is likely to strongly impact pesticide exposure (Schiedek *et al.*, 2007) and the distribution of pesticides in the environment (Noyes *et al.*, 2009), might increase their toxicity (Noyes *et al.*, 2009; Schiedek *et al.*, 2007) and degrade drinking water quality (Delpla *et al.*, 2009). The effects of climate change on pesticide fate and transport to ground- and surface waters are very diverse and might be difficult to predict (Bloomfield *et al.*, 2006). Very few studies have previously attempted to quantify the effects of climate change on pesticide fate and transport (e.g. Ahmadi *et al.*, 2014; Henriksen *et al.*, 2013; Beulke *et al.*, 2007) and only one European-wide study has assessed some potential effects

under Swedish conditions (Kattwinkel *et al.*, 2011). Thus, more quantitative research is needed to explore the direct and indirect effects of climate change on pesticide fate and impacts on water bodies in Sweden. Direct effects refer to natural responses and indirect effects to human-mediated responses to changes in climate that would lead to changes in pesticide fate, transport or use.

Modelling is an effective tool to assess the effects of various influential factors on system behaviour at different scales. However, pesticide fate modelling in the light of climate change is laced with uncertainty related to e.g. climate scenarios, model structure or parameters and not least the modeller. It is essential to account for these uncertainties in order to provide an appropriate scientific basis and realistic, well-founded background information for decision-making.

This PhD-thesis analyses several aspects of the modelling of pesticide leaching in a changing climate. This involves both the generation of climate scenarios as input data, pesticide fate modelling at different scales, and the evaluation of the uncertainties inherent to the process. The sketch in *Figure 1* gives an overview of how the three studies reported in this thesis are inter-related and which aspects and uncertainties were considered in each study.



*Figure 1.* Overview of how the three studies reported in this thesis relate to each other and which modelling aspects and uncertainties were considered. The combination of climate-soil-crop-pesticide (marked for paper I, II) can be considered a modelling base unit in all three studies.

## 2 Aims

- To assess whether pesticide leaching is likely to increase or decrease in Sweden in a future climate. (papers I, II, III)
- To analyse the relative importance of different sources of uncertainty in modelling pesticide leaching under climate change at the field scale: model structure, parameters, and climate input data. (papers I & II)
- To assess and contrast direct and indirect effects of climate change on herbicide leaching to groundwater and to analyse the relative contribution of different factors influencing herbicide leaching under climate change at the regional scale. (paper III)



## 3 Background

### 3.1 Climate Change Projections and Impact Studies

#### 3.1.1 Climate Change Projections

The climate system is unequivocally warming resulting in global climate change, for which human activities are *extremely likely*<sup>1</sup> to be responsible (IPCC, 2013a). For Sweden, climate change projections indicate an overall increase in both temperature and precipitation (Kjellström *et al.*, 2014; IPCC, 2012; Kjellström *et al.*, 2011). They furthermore project a strong correlation between increased precipitation and temperature (Kjellström *et al.*, 2011), an increase in climate variability (Olesen *et al.*, 2011) and changes in the frequency of extreme events (IPCC, 2012; Nikulin *et al.*, 2011). The uncertainty in climate model projections is large, especially for summer precipitation and extremes (Kjellström *et al.*, 2014; Kjellström *et al.*, 2011). Warm temperature extremes are likely to increase and cold temperature extremes to decrease. The frequency of dry spells might not increase, but periods of drought might increase due to increased temperatures and higher evapotranspiration in combination with potentially reduced precipitation amounts (Kjellström *et al.*, 2014). *Figure 2* shows projected average monthly changes for southern Sweden (55° - 60° N) for 2071-2100 compared to 1961-1990 based on projections from 23 global climate models (GCMs).

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1. *Extremely likely* means with at least 95% certainty according to the IPCC assessment.

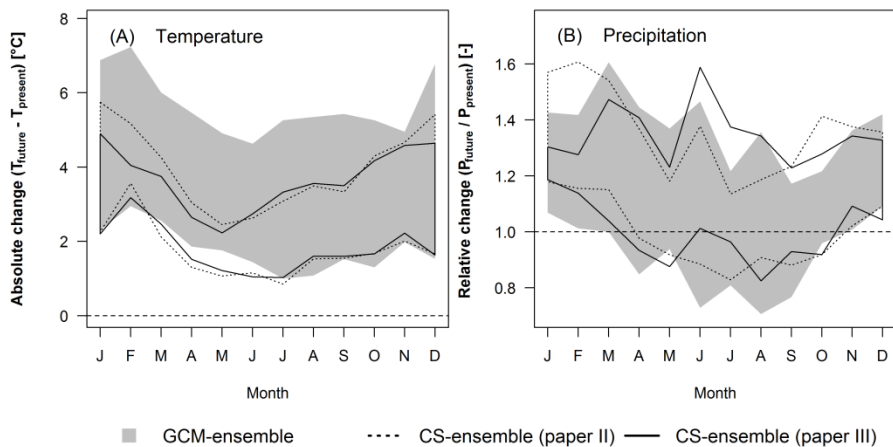


Figure 2. Projected monthly changes for southern Sweden based on an ensemble of 23 different Global Climate Models (GCMs) all under the greenhouse gas emission scenario A1B (taken from Lind & Kjellström, 2008). Additionally, the change factors from the ensemble of climate scenarios (CS) used in the studies for the region in *Västra Götaland* (paper II) and for the region in Scania (paper III) are presented. The dashed lines denote “no change”.

A climate projection refers to estimates of future climate derived with climate models and the help of scenarios, which can be seen as conditional expectations that reflect what can be expected, if this or that happens (WMO, 2015). Scenarios provide plausible descriptions of how the climate system or its driving forces (e.g. atmospheric greenhouse gases) may develop in the future and indicate what *might* happen in the future rather than forecasting what *will* happen (Walker *et al.*, 2003). If a variety of scenarios is used together, they represent a range of possibilities that reflect uncertainty and increase the robustness of projections (IPCC, 2015).

Climate model projections are commonly produced by General Circulation Models (GCMs; here referred to as Global Climate Models), with a spatial resolution of 100-300 km simulating the climate system for the entire globe. The older generation of GCMs were driven by emission scenarios as defined by the Special Report on Emission Scenarios (SRES; Nakićenović & Swart, 2000). These greenhouse gas (GHG) emission scenarios are based on assumptions about driving forces such as population growth, economic and technological developments. The SRES are grouped into four families that share a common storyline (called A1, A2, B1, and B2). They reflect the influence of more economic (A) or environmental (B) factors, while focusing more on global (1) or regional (2) solutions. The scenario A1B, which has been widely used (ENSEMBLES project; van der Linden & Mitchell, 2009), is a subset of the A1-family that assumes a balance across all energy sources. For the Fifth



Assessment report of the IPCC (IPCC, 2013a), climate models were run with four different ‘Representative Concentration Pathways’ (RCP) that define the total radiative forcing pathway until the year 2100 (Moss *et al.*, 2010). The radiative forcing is a cumulative measure of anthropogenic GHG emissions from all possible sources and the pathways can be described by a wide range of possible socio-economic and technological developments. Although the procedure for generating climate model projections differs between the SRES-driven simulations and the RCP-driven ones, the results for Sweden in terms of average monthly change factors for temperature and precipitation are in similar ranges (Kjellström *et al.*, 2014). In this thesis, only SRES-driven climate simulations were used as input to the climate change impact studies on pesticide leaching.

### 3.1.2 Climate Change Impact Studies

Studies that analyse the potential effects of climate change are called climate change impact studies. For Sweden, such studies have been performed for many different potential impacts, e.g. on catchment hydrology (Teutschbein & Seibert, 2012; Graham *et al.*, 2007a; Andréasson *et al.*, 2004), surface water quality (Arheimer *et al.*, 2005) or crop production (Eckersten *et al.*, 2012), but none of these studies has focused specifically on pesticide leaching. In all these studies, one or more impact models (such as a hydrological model or a crop model) were used, driven with climate projections relevant to the given location and scale of the study.

As the typical resolution of GCMs is usually too coarse for regional or local studies, the projections need to be downscaled. One way is to perform dynamical downscaling with the help of regional climate models (RCM) that have a typical resolution of 10-50 km, and sometimes down to 2-6 km. The higher resolution allows a better representation of the underlying topography and parameterization of regional and local scale processes. However, RCM outputs are often biased compared to observations (Fowler *et al.*, 2007) and therefore, bias correction methods have been developed to provide the required local scale input to the impact models such as distribution-based scaling (Wetterhall *et al.*, 2011; Yang *et al.*, 2010) or quantile-quantile mapping (Teutschbein & Seibert, 2012). The basic assumption behind all these approaches is that the bias is stationary (Teutschbein & Seibert, 2013; Maraun, 2012), which might not be valid (Christensen *et al.*, 2008). Reviews and comparisons of different methods are presented by for instance Wilby & Wigley (1997), Wilby *et al.* (2004), Fowler *et al.* (2007) and Teutschbein & Seibert (2012). Alternatively, statistical downscaling can be applied as described, for example, in Wilby *et al.* (2004). These methods include weather

classification schemes, regression models, and weather generators (Kilsby *et al.*, 2007; Semenov *et al.*, 1998).

The method used in this thesis is a simple and straight-forward alternative that is computationally inexpensive and widely applicable (e.g. by Eckersten *et al.*, 2012; Arheimer *et al.*, 2005). The so-called change factor method (Anandhi *et al.*, 2011), delta method (Graham *et al.*, 2007a) or delta change approach (Hay *et al.*, 2000) applies change factors to an observed time series to represent future climate conditions. Such a future time series is considered a *climate scenario*. The change factors are derived by comparing simulations for a future period with simulations for the reference period for which observations are available. The method can be applied to GCM-projections or RCM-outputs. It is based on the assumption that climate models are able to reproduce climate change signals better than absolute values of the climate variables. In its simplest form, average yearly or monthly change factors are calculated and applied directly to the observations. No change in the frequency of rainfall events is accounted for, but the intensity of rainfall events is changed and thereby the frequency of rainfall events above a certain threshold. More advanced methods have been developed that account for changes in the frequency of rainfall events (e.g. Olsson *et al.*, 2012) or vary the change factors according to rainfall intensity level (e.g. Olsson *et al.*, 2009).

### 3.1.3 Cascade of uncertainty

Climate change impact assessments are subject to various sources of uncertainty, the so-called *cascade of uncertainty* (Refsgaard *et al.*, 2013; Wilby & Dessai, 2010) consisting of the future society, GHG emissions, GCM, downscaling to regional (RCM) and local scales, impact model, local impacts and the implied adaptation responses. Uncertainty related to climate input data arises from the drivers of change (e.g. GHG), the response of the climate system to those drivers, natural variability and initialization of the GCM, the structure, accuracy, and parameterization of both GCMs and RCMs (Mote *et al.*, 2011; Giorgi, 2005). Which source of uncertainty dominates depends to some extent on the future period that is investigated: the differences between GHG emission scenarios are not so large in the middle of the 21<sup>st</sup> century, but increase towards the end, while uncertainty related to the natural variability in the climate typically decreases towards the end of the century (e.g. IPCC, 2013a; Kjellström *et al.*, 2011; Hawkins & Sutton, 2009). In addition to the uncertainty in the climate models, the downscaling approach introduces another source of uncertainty (e.g. Chen *et al.*, 2011; Teutschbein & Seibert, 2010) along with the chosen future period (Ledbetter *et al.*, 2012; Prudhomme *et al.*, 2010), while the impact model itself is subject to structural and

parameter uncertainty (e.g. Dobler *et al.*, 2012). Many studies have been performed to evaluate the relative importance of the different sources of uncertainty (e.g. Dobler *et al.*, 2012; Chen *et al.*, 2011; Kjellström *et al.*, 2011; Tebaldi *et al.*, 2005). Several studies concluded that the GCMs are a major source of uncertainty (e.g. Kjellström *et al.*, 2011; Déqué *et al.*, 2007; Graham *et al.*, 2007b), but other sources of uncertainty can be similar in magnitude (e.g. Dobler *et al.*, 2012; Chen *et al.*, 2011), depending on location, spatial scale and field of research.

#### 3.1.4 Ensemble modelling

Ensemble modelling is the use of different models or downscaling approaches in parallel to account for, or at least to illustrate, uncertainties (IPCC, 2001) (see also *Figure 2*). Ensembles can also be used to derive probabilistic information on climate change in a region (Kjellström *et al.*, 2011; Déqué & Somot, 2010). Ensemble modelling is common practice in weather forecasting and is widely adopted by the climate modelling community (e.g. IPCC, 2013a; van der Linden & Mitchell, 2009). For climate change impact studies, it is recommended to include an ensemble of climate models, especially GCMs (Maraun, 2012; IPCC, 2001); even a multi-model ensembles of both climate models and impact models (Teutschbein & Seibert, 2010) can be used.

### 3.2 Pesticide Fate in Soils

Pesticides found in ground- or surface water originate from both point sources (e.g. spills, accidents, sewage treatment plant effluent) and non-point (diffuse) sources arising from normal field application. Point sources may account for 20-80% of pesticide loadings in surface waters (Holvoet *et al.*, 2007), but are of less concern for groundwater. However, if groundwater is polluted, it may last very long. In this thesis, only non-point source pollution from agricultural land was considered.

Non-point source pollution of surface water occurs mainly due to surface runoff, drainflow and spray drift and to a lesser extent due to atmospheric deposition and groundwater seepage (Brown & van Beinum, 2009; Holvoet *et al.*, 2007). The main input pathway to groundwater is leaching through soils, while re-infiltration of surface water is a minor contributor to groundwater pollution (Balderacchi *et al.*, 2013). The major processes and pathways are presented in *Figure 3*.

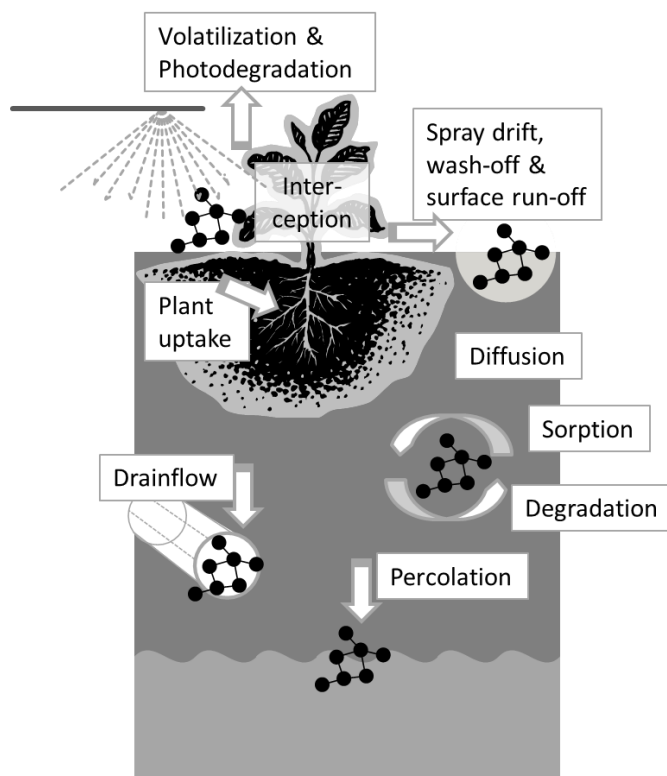


Figure 3. Sketch of the fate and transport of pesticides in agricultural soils.

Losses of pesticides to surface water are typically <2% of the amount applied in the catchment (Capel *et al.*, 2001; Kreuger, 1998). Losses to tile drains or groundwater are usually between <0.1 and 1% of the applied amount, but may occasionally exceed this (Brown & van Beinum, 2009; Kladviko *et al.*, 2001; Flury, 1996). If heavy rain occurs shortly after pesticide application, losses of up to 5% or 10% of the dose have been observed for leaching to groundwater (Flury, 1996) and tile-drains (Brown & van Beinum, 2009; Kladviko *et al.*, 2001).

### 3.2.1 Fate and Transport Processes

Pesticides are subject to microbial or chemical degradation and can sorb to clay, organic matter, and iron or aluminium oxides. These processes depend on both temperature and soil moisture and affect the availability of pesticides for transport with the soil water (Figure 3). Water flows in the soil matrix, but also as non-equilibrium preferential flow through pathways that only occupy a limited part of the soil (e.g. structural macropores; Jarvis, 2007; Worrall *et al.*, 1997).

Preferential flow can accelerate the transport of pesticides through the unsaturated zone to underlying groundwater or surface waters via subsurface drains (Jarvis, 2007; Kladvko *et al.*, 2001; Flury, 1996; Brown *et al.*, 1995) and explains why pesticides can be found in ground- or surface waters much earlier than expected according to the classical theory of equilibrium water flow and solute transport (Larsbo, 2005). Preferential flow can, however, also prevent leaching of mobile substances: with the first rainfall event after application, they might be washed into the soil matrix and, thus, might not be available for macropore transport afterwards (Larsson & Jarvis, 2000; Shipitalo *et al.*, 1990). The potential for non-equilibrium (macropore) water flow and solute (pesticide) transport at any site depends on the nature of the macropore network, which is determined by factors that affect soil structure formation and degradation, including the abundance and activity of soil biota (e.g. earthworms), soil properties (e.g. clay content), site factors (e.g. slope position, drying intensity, vegetation) and management (e.g. cropping, tillage, traffic) (Jarvis *et al.*, 2013; Jarvis, 2007). Rainfall patterns have been shown to play an important role for rapid transport of pesticides (McGrath *et al.*, 2010) and the relative timing of rainfall events in relation to pesticide application are especially relevant for drainage losses (Lewan *et al.*, 2009; Nolan *et al.*, 2008; Capel *et al.*, 2001), especially on structured soils (Johnson *et al.*, 1996).

Surface runoff is often considered a major pathway for pesticide losses to surface waters, especially for strongly adsorbing compounds, which are transported primarily in particulate-bound form (Holvoet *et al.*, 2007; Kladvko *et al.*, 2001; Wauchope, 1978). Particle-bound pesticides can also leach through soil macropores (Worrall *et al.*, 1999). However, these pathways were not further analysed in this thesis.

Many factors influence the fate of pesticides used in agriculture, many of which are interrelated (Balderacchi *et al.*, 2013) and influenced by climate. Site properties include land-use and soil type. The physicochemical properties of the pesticide not only influence the availability for transport, but are also a major factor determining the dominant transport pathways (Worrall & Kolpin, 2003). Weakly sorbed compounds are commonly transported in the soil matrix, moderately sorbed pesticides are more prone to macropore flow (McGrath *et al.*, 2010), while strongly sorbed pesticides might only be transported in particulate-bound form, either through macropores (Worrall *et al.*, 1999) or via surface runoff and erosion (Wauchope, 1978). Key agronomic practices that affect pesticide fate and transport include application timing and dose (e.g. paper III), tillage practices (Alletto *et al.*, 2010), crop rotations (Balderacchi *et al.*, 2008) and organic matter management (Larsbo *et al.*, 2009b).

### 3.2.2 Modelling Pesticide Fate and Transport

Models enable us to integrate knowledge on a specific system and to generalize concepts and results. They can be used to explore complex interactions, new environments or future conditions. Many models are available to simulate the fate and transport of pesticides in soils (Köhne *et al.*, 2009; Siimes & Kämäri, 2003; Jarvis, 2001). For the registration of pesticides at European and Swedish national level, one-dimensional models are used to evaluate the risks of groundwater or surface water contamination with pesticides. Only a limited number of models are used for these purposes, of which MACRO (Jarvis & Larsbo, 2012; Larsbo & Jarvis, 2005), described in chapter 4.2.2, is currently the only one that explicitly accounts for macropore flow<sup>2</sup>. Simulations that do not account for preferential flow will significantly underestimate leaching in structured soils (Moeys *et al.*, 2012; Herbst *et al.*, 2005).

As mentioned above, the major processes affecting pesticide availability for transport through soils are temperature dependent. According to Paraíba *et al.*, (2003), failure to account for temperature effects on pesticide degradation and sorption processes significantly affects the outputs of pesticide leaching models with regard to risks of groundwater or surface water pollution. Models commonly only account for temperature dependent degradation, whereas the temperature dependence of sorption and diffusion is usually neglected (Tiktak, 2000). In assessing climate change impacts on pesticide fate and transport, it is especially important to evaluate the effect of temperature dependent processes on the outputs. The available mathematical descriptions of temperature dependent sorption are (to my knowledge) only valid for linear sorption. Nevertheless, temperature dependent sorption and diffusion were included in the current version of MACRO for the purpose of this thesis as described in chapter 4.2.2.

### 3.2.3 Regional Scale Modelling

Regional scale modelling tools for pesticide fate and transport have been developed by coupling one-dimensional leaching models with geographic information systems (GIS), which may include several data layers describing, for example, crop and soil distributions (McGrath *et al.*, 2010; Holvoet *et al.*, 2007; Sood & Bhagat, 2005; Corwin & Wagenet, 1996). Pesticide leaching models range from simple models such as indicator or Attenuation Factor based (Rao *et al.*, 1985) models to physically-based dual-permeability models such as MACRO. As it is difficult to parameterize complex models due to lack

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2. This statement only refers to the FOCUS-versions of the pesticide fate models used for registration procedures. The research version of, for instance, the PEARL-model also includes preferential flow routines.

of data and the natural variability of soil properties in the landscape, simple models have often been preferred for large-scale assessments (McGrath *et al.*, 2010; Loague *et al.*, 1990). Nevertheless, complex preferential flow models have previously been implemented in GIS approaches for groundwater vulnerability assessments (e.g. Sinkevich *et al.*, 2005) and used in a GIS-context for studying the effects of crop rotations on leaching risks (Balderacchi *et al.*, 2008). The model tool MACRO-SE was used in the regional scale study described in paper III, which is based on a coupling of the one-dimensional pesticide fate model MACRO with GIS data and automated parameterization routines.

Several watershed-scale hydrological models have been developed that account for water quality and non-point source pollution (see e.g. Moriasi *et al.*, 2012; Quilbé *et al.*, 2006; Borah & Bera, 2003). Very few models, however, account for macropore processes in a spatially distributed way for an entire catchment. One example is MIKE SHE/DAISY, a coupling between the 3D watershed model MIKE SHE (Abbott *et al.*, 1986a; 1986b) and the 1D agroecosystem model DAISY (Abrahamsen & Hansen, 2000). Christensen *et al.* (2004) used MIKE SHE/DAISY and concluded that point-scale macropore processes were dominating processes for pesticide leaching at catchment scale, but not important for groundwater recharge and discharge. Furthermore, they noted that it might be sufficient to perform several single column simulations rather than running a comprehensive 3D model, if spatial and temporal variations in the groundwater depth in a catchment are adequately represented by the range of columns simulated.

At regional scales, the availability of suitable geographic input of soil, crop and climate data as well as the reliability of pedotransfer functions (PTFs) are important aspects. Additionally, information on pesticide use at an appropriate spatial resolution is essential (see Miraglia *et al.*, 2009; Boxall *et al.*, 2008). The (automated) parameterisation of the entire modelled region poses challenges and constitutes a large source of uncertainty. Furthermore, there are serious difficulties in validating such modelling approaches arising, for instance, from differences in the spatial and temporal scales of simulation outputs and measurements. This is discussed in paper III. Nevertheless, some watershed models have been tested (Holvoet *et al.*, 2007), at least for discharge predictions and water table level (e.g. Christiansen *et al.*, 2004) or against pesticide concentrations obtained by grab samples (Beernaerts *et al.*, 2005). Uncertainty analyses for regional scale assessments have been performed for GIS-based tools coupled with simple models (Loague *et al.*, 2012; Stenemo *et al.*, 2007; Loague, 1991) and for fully distributed models (e.g. Van den Berg *et al.*, 2012; Heuvelink *et al.*, 2010).

### 3.2.4 Uncertainty Analysis

Uncertainty in model predictions arises from many sources: driving data (e.g. weather or climate data), parameter values due to measurement errors or uncertainty in background supporting data used to estimate model parameters by pedotransfer functions (PTFs; Bouma, 1989), model structure (e.g. unknown processes, processes erroneously described or incompletely implemented), boundary conditions, unknown or incorrect initial conditions and modeller subjectivity (e.g. interpretation of input data or results; Boesten, 2000). In this thesis, uncertainty in the climate input data is merged with uncertainty in the generation of climate scenarios as described above. The uncertainty inherent in the predictions of the impact model is also part of the *cascade of uncertainty* described earlier. A detailed overview of the different sources of uncertainty in pesticide fate modelling is given in Dubus *et al.* (2003b) and those aspects which are relevant for this thesis are summarized in papers I and II.

An uncertainty analysis is essential for a reliable quantification of pesticide losses. Refsgaard *et al.* (2007) gives an overview of various methods for uncertainty assessments. Sensitivity analyses often serve as basis for estimating parameters and for uncertainty analysis. For many pesticide leaching models, parameters related to degradation and sorption are the most sensitive (Heuvelink *et al.*, 2010; Cheviron & Coquet, 2009; Dubus *et al.*, 2003a). In addition, parameters governing the generation of macropore flow and mass exchange between macropores and the soil matrix are of particular importance for preferential flow models like MACRO (Dubus & Brown, 2002).

Monte-Carlo methods are uncertainty assessment methods with stochastic application of deterministic models (Soutter & Musy, 1998). These methods calculate the distribution of the model output for a large number of realisations (deterministic simulations) with selected parameters (or input data) randomly sampled from prior distributions (Refsgaard *et al.*, 2007). Monte-Carlo-Markov-Chain methods update the prior distributions step-wise and search through the parameter space in a systematic and computationally efficient way, while making use of an explicit description of the error-model. Vrugt *et al.* (2009) summarized these approaches as formal Bayesian approaches.

The Generalized Likelihood Uncertainty Estimation (GLUE) method (Beven & Binley, 1992), on the other hand, is considered as an informal Bayesian approach, because the distinction between ‘behavioural’ and ‘non-behavioural’ parameter sets is subjective and different types of performance criteria (informal likelihood measures) can be used (Vrugt *et al.*, 2009; Smith *et al.*, 2008). GLUE is built on the philosophy that a strong assumption concerning the structure of the error model cannot be justified given the epistemic uncertainty of model structures in environmental models (Beven, 2006; Beven & Binley,



1992). Epistemic uncertainty refers to the uncertainty due to imperfect knowledge, which can potentially be reduced by more research and empirical data collections (Curry & Webster, 2011; Walker *et al.*, 2003). It is in contrast to uncertainty due to inherent variability or randomness (also called ontic or aleatory uncertainty; Curry & Webster, 2011). Despite intense discussion in the scientific literature on the advantages and disadvantages of the different philosophies (see e.g. Honti *et al.*, 2014; Vrugt *et al.*, 2009; Beven *et al.*, 2008; Mantovan & Todini, 2006), both methods seem to give similar results (Vrugt *et al.*, 2009; Beven *et al.*, 2008). The parameter identification method applied in paper I and II was based on GLUE, as it is conceptually simple, easy to implement and simulations can be easily run in parallel to reduce total simulation times (Vrugt *et al.*, 2009).

### 3.3 Direct and Indirect Effects of Climate Change on Pesticide Leaching

Climate change may affect the leaching of pesticides to ground- and surface waters both directly and indirectly. In the context of this thesis, direct effects summarize the natural responses of the soil-ecosystem to changes in climatic variables (mainly temperature, precipitation and potential evapotranspiration). Indirect effects refer to any changes in the use, fate and transport of pesticides that are triggered by human activities in response to climate change. Some changes can, thus, be considered either direct or indirect depending on the cause of the change (e.g. changes in soil organic carbon content).

#### 3.3.1 Direct Effects

The direct effects of climate change on the leaching of pesticides are diverse and often contrasting. *Table 1* summarizes the processes and transport pathways relevant for this thesis and the climatic drivers projected to be relevant for Sweden in a future climate (Kjellström *et al.*, 2014). Some effects are rather strong (e.g. faster degradation of pesticides), while others are rather weak (e.g. hydraulic conductivity for leaching to groundwater). For more details on how climate change might affect the source terms, transport pathways and receptors for pesticides, the reader is referred to the review by Bloomfield *et al.* (2006).

Table 1. *Direct effects of climate change on processes affecting pesticide fate and transport in soils and potential implications for leaching of pesticides under Swedish conditions. “+” indicates an increase in leaching, while “-” indicates a reduction in leaching.*

<b>Climatic driving force</b>	<b>Processes and effects in the system</b>	<b>Effect on pesticide leaching</b>
Increased temperature	Faster degradation	-
	Higher turn-over of organic matter (less sorption sites)	+
	Greater litter input due to improved growth and increased soil organic matter content	-
	Weaker sorption (for most compounds)	+
	Faster diffusion leads to faster mass exchange between micro- and macropores and to less transport via macropores	-
	More volatilization	-
	Increased hydraulic conductivity	+
	Increased potential (and actual) evapotranspiration leading to reduced drainflow and percolation	-
Increased winter temperatures	Changes in freezing-thawing cycles that can lead to changes in soil structure (e.g. crack formation, aggregation)	+/-
Increased precipitation amount	Increased volumes of drainflow/percolation	+
	Faster degradation due to increased soil moisture	-
	Reduced degradation, if soil moisture gets close to saturation	+
	Higher turn-over of organic matter (less sorption sites)	+
Higher precipitation intensities	Preferential transport triggered more often	+
Longer drought periods	Reduced degradation	+
	Faster gas diffusion	-
	Higher rate of volatilization	-
	Cracking of clay soils affects macropore flow	+

### 3.3.2 Indirect effects

The indirect effects of climate change on pesticide leaching are many and diverse and only a few can be discussed here. Conditions for crop growth in Sweden are likely to improve in a future climate mainly due to an extended growing period and milder winters (Eckersten *et al.*, 2008a). This is likely to change the cropping patterns and allow the cultivation of *new* crops (more maize, sunflower, grapes) and more autumn-sown crops (Harrison & Butterfield, 1996), which would require the use of pesticides adapted to these crops and conditions. It might also affect the timing of pesticide applications,

as sowing and harvest dates would be adapted to the growing conditions (Olesen *et al.*, 2012; Trnka *et al.*, 2011; Eckersten *et al.*, 2008b). However, the extent to which the soils are trafficable earlier in spring depends not only on temperature, but also on soil moisture conditions and the preceding rainfall amounts (Earl, 1997).

Warmer winters would favour the survival of pests and accelerate the development of weeds (Patterson *et al.*, 1999), which would lead to an increased need for plant protection, which could result in an increased use of pesticides (larger area sprayed or more frequent sprayings). Furthermore, the reduced efficiency of pesticides could require increased use (Bailey, 2004), as well as enhanced development of resistances against pesticides. The relationship between climate change and pesticide usage has been analysed for U.S. conditions with the conclusion that pesticide usage and the costs related to it are likely to increase in a future climate, partly due to increased inter-annual climate variability (Koleva *et al.*, 2010; Koleva & Schneider, 2009; Chen & McCarl, 2001).

Other indirect effects of climate change include socio-economic factors and political decisions (e.g. reduced pesticide use; Hossard *et al.*, 2014), which are typically difficult to assess as they are uncertain and might change rapidly, while having a strong impact on the agricultural system (Delcour *et al.*, 2015; Bloomfield *et al.*, 2006).

### 3.3.3 Previous Quantitative Assessments

Although the likely effects of climate change on pesticide losses to water recipients are qualitatively rather well understood, few studies have attempted to quantify these impacts. Beulke *et al.* (2007) analysed the impacts of climate change on the leaching of three representative pesticides to surface water via tile-drains. Their study suggested that losses of autumn-applied pesticides are likely to increase in the future resulting from increased volumes of drainflow and runoff and increased rain intensities in critical events. They accounted for some of the indirect effects of climate change (changes in crop development, application time, dose and frequency) and suggested that these and others could have larger impacts on leaching than the direct effects.

In a similar study, Henriksen *et al.* (2013) simulated the impact of climate change on the leaching of several different pesticides to groundwater and surface water for two different field sites and catchments in Denmark. They evaluated two different agricultural production systems and accounted for typical crop rotations and pesticide usage for present and future conditions based on estimates from locations further south in Europe (known as the analogue method or space-for-time substitution). Their results clearly indicate

the complex interplay of different factors that makes it difficult to draw general conclusions. Nevertheless, it seemed that both the direct and the indirect effects of climate change were stronger for loamy soils than for sandy soils, for which the effects were minimal or negligible. Depending on pesticide properties, projected increases in leaching were negligible for strongly sorbed herbicides, minor for *ordinary* herbicides such as MCPA or clopyralid and more pronounced for the newer low-dose herbicides such as florasulam. The catchment scale assessment they performed with MACRO coupled to MIKE-SHE showed that simulated pesticide concentrations were influenced by dilution in surface and groundwater and varied with soil and pesticide properties.

Kattwinkel *et al.* (2011) analysed the exposure of aquatic organisms to insecticides in a future climate at a European scale. They also accounted for changes in land-use and pesticide usage based on space-for-time substitution. They identified the insecticide application rate as the main driver for a change in the ecological risk and concluded that the combined impact of climate change was larger than direct or indirect effects considered separately.

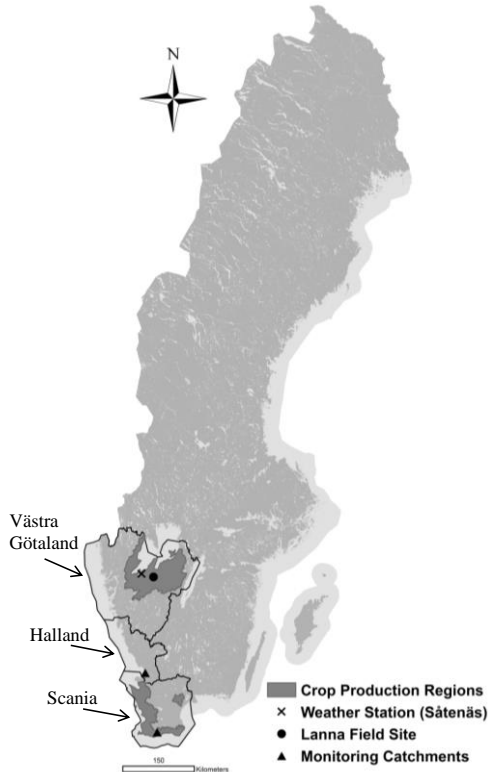
Two recent studies focused on direct effects of climate change and evaluated the uncertainty in such estimations. Ahmadi *et al.* (2014) performed a modelling study with the SWAT-model for a watershed in the US and evaluated the impacts of climate change on fate and transport of the herbicide atrazine. Variability and uncertainty increased in a future climate and changes in total atrazine loadings differed depending on the emission scenario (increases for the A2 scenario, no changes for A1B and B1). In a Monte-Carlo uncertainty analysis, Kong *et al.* (2013) assessed the effects of input uncertainty and variability on the modelled fate of the persistent organic PCBs (polychlorinated biphenyl) in the light of climate change. They concluded that the relative changes in concentrations in the soil and water bodies were dominated by climate uncertainty, while variation in degradation rates dominated the projections of the absolute values of those model outcomes.

## 4 Materials and Methods

### 4.1 The Study Set-ups

A unique combination of “climate-crop-pesticide-soil” forms the base simulation unit in all three studies (see also *Figure 1*). Pesticide fate simulations for this base-unit were run with MACRO for present climate conditions (1970-1999) and for a future climate representing the period 2070-2099. Each 30-year period was simulated with a preceding warm-up period of 6 years, the results of which were excluded from the analyses. The field scale

studies accounted for the direct effects of climate change and analysed the role of model structural differences (paper I) and climate input uncertainty (paper II) in relation to parameter uncertainty. In both papers, accumulated losses of pesticides to surface waters via tile-drains were simulated at the field site in Lanna (*Figure 4*). Both direct effects and indirect effects of climate change on the leaching of herbicides to groundwater were assessed at the regional scale for a major crop production region in Scania (*Figure 4*) focusing on concentration in leachate (paper III).



*Figure 4.* Map of Sweden, where the sites and crop production regions that are relevant for this thesis are marked.

## 4.2 Field Scale

The studies reported in paper I and II were set-up in a similar way and are therefore presented together here. In a first step, MACRO was calibrated against comprehensive field data from the field site at Lanna (*Figure 4*). This resulted in an ensemble of acceptable parameter sets, which was used in a second step, to run “prediction scenarios” of hypothetical compounds with different degrees of sorption strength leaching to field drains under present and future climate conditions.

### 4.2.1 Site

The field site at Lanna is located in the county of *Västra Götaland* in the south west of Sweden (see *Figure 4*). The soil is a silty clay (see Table 1 in paper I, II) that had been under no-tillage practice since 1988. In terms of pesticide leaching via preferential flow to drains, this soil represents a worst-case scenario, since it has a strongly developed and stable aggregate structure and abundant earthworm biopores. The field plot is 0.4 ha in size and tile-drained at 1 m depth and 13 m spacing. The field experiment was performed between October 1994 and December 1995 (Larsson & Jarvis, 1999). The weakly sorbed herbicide bentazone ( $2.5 \text{ kg ha}^{-1}$ ) was applied simultaneously with potassium bromide ( $44.4 \text{ kg Br}^{-} \text{ ha}^{-1}$ ; non-reactive tracer) on bare soil on October, 18<sup>th</sup> 1994. During the summer of 1995, spring-sown rape (*Brassica napus* L.) was grown. Drainflow and flux concentrations of bentazone and bromide were recorded continuously, while measurements of water content, resident bentazone and bromide concentrations in the soil were obtained from 1 m deep soil cores taken on 3-5 occasions during the experimental period. 8.5% of the applied amount of bentazone was lost to tile drains, 10.5% remained in the soil on the last measurement occasion, while the rest was either degraded or leached below the depth of measurements. Of the applied bromide, 31% was recovered in the drainflow, 22% was left in the soil at the end of the experiment and the remaining 47% was lost in deep percolation or in lateral shallow groundwater flow (Larsson & Jarvis, 1999).

### 4.2.2 Impact Model: MACRO

MACRO is a one-dimensional physically-based model that simulates water flow and solute transport in structured soils and explicitly accounts for non-equilibrium macropore flow with a dual-permeability approach. For a detailed description of the current version MACRO 5.2, see Jarvis & Larsbo (2012) and Larsbo *et al.* (2005). MACRO has been mainly used to simulate the impact of macropore flow on pesticide leaching (Jarvis & Larsbo, 2012), but it has also been used to simulate leaching of other solutes, such as

pharmaceuticals (e.g. Larsbo *et al.*, 2009a) and heavy metals (e.g. Moradi *et al.*, 2005). MACRO is driven with weather or climate data and crop growth is described with a simple approach. A complete water balance is simulated with root water uptake calculated using the model described by Jarvis (1989), flow and transport to drainage systems calculated by the Hooghoudt equation and seepage potential theory, and potential evapotranspiration is estimated with the Penman-Monteith equation (Larsbo & Jarvis, 2003).

Water flow in the soil matrix is calculated with Richard's equation and solute transport follows the convection-dispersion equation. Preferential flow in macropores is assumed to be gravity-dominated and modelled with the kinematic wave equation. The saturated hydraulic conductivity of the soil matrix ( $K_b$  [mm h<sup>-1</sup>]) governs the partitioning of water flow between matrix and macropore systems. The exchange of water and solutes between the two pore systems via diffusion and convection is controlled by the diffusion pathlength ( $d$  [mm]), a proxy parameter for the unknown geometry of soil macropore structure (Gerke & Van Genuchten, 1996).

Pesticide degradation is described by first-order kinetics, with the rate coefficient ( $\mu$ ; where  $\mu = \ln(2)$  divided by the half-life  $DT_{50}$  [days]) given as a function of soil temperature, according to the Arrhenius equation (Boesten & Van der Linden, 1991) and moisture content, following a modified Walker function (Walker, 1974). Sorption can be described with a linear isotherm or a non-linear Freundlich isotherm. In papers I and II, a linear sorption isotherm was used, with the sorption coefficient  $K_d$  [ml g<sup>-1</sup>] governing the partitioning of pesticides between solution and sorbed phase. As input to models like MACRO, the  $K_{oc}$  [ml g<sup>-1</sup>] is typically used, which is the  $K_d$  value normalized for the organic carbon fraction of the soil ( $f_{oc}$  [-]) according to Wauchope et al. (2002).

$$K_{oc} = \frac{K_d}{f_{oc}} \quad [1]$$

To study the effects of temperature on pesticide leaching in a future climate, optional functions were introduced into MACRO 5.2 to describe temperature dependent sorption and diffusion. The effect of temperature on sorption was simulated according to the van't Hoff equation for linear equilibrium sorption with a constant sorption enthalpy ( $\Delta H_s = -30$  kJ mol<sup>-1</sup>):

$$K_d = K_{d_{ref}} \exp \left[ \frac{-\Delta H_s}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad [2]$$

where  $K_{d,ref}$  is the sorption coefficient at reference temperature  $T_{ref}$  (20°C),  $T$  is the temperature [K] and  $R$  denotes the molar gas constant ( $=8.314$  J K<sup>-1</sup> mol<sup>-1</sup>).

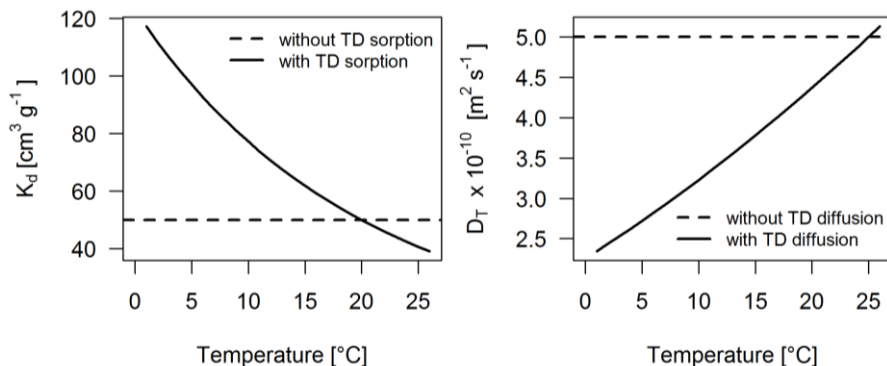


Figure 5. The effect of temperature on sorption (sorption coefficient  $K_d$ ) for a compound with a negative sorption enthalpy of  $-30 \text{ kJ mol}^{-1}$  and diffusion (molecular diffusion coefficient in water  $D_T$ ) as implemented in the model.

Temperature dependent diffusion was calculated as a function of viscosity at reference and actual (soil) temperatures and implemented as follows based on Korson *et al.* (1969) and Hayduk & Laudie (1974):

$$D_T = D_{ref} \left( \frac{\eta_{ref}}{\eta_{20}} \right)^{1.14} \left( 10^{((B(T-20)^2 - A(20-T))/(T+C)) * 1.14} \right) \quad [3]$$

where  $D_T$  and  $D_{ref}$  are the diffusion coefficients of the specific chemical in water at any temperature and at the reference temperature of  $25^\circ\text{C}$  ( $= 5 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ; FOCUS, 2000),  $\eta_{ref}$  ( $= 0.8904 \text{ g m}^{-1} \text{ s}^{-1}$ ) and  $\eta_{20}$  ( $= 1.002 \text{ g m}^{-1} \text{ s}^{-1}$ ) are the viscosities at  $25^\circ\text{C}$  and  $20^\circ\text{C}$ , respectively,  $A=1.1709$ ,  $B=0.001827$ , and  $C=89.93^\circ\text{C}$ . Paper I presents further details.

The effect of temperature on sorption and diffusion is illustrated in Figure 5 following equations 2 and 3, respectively. Implementation of these functions allowed the choice of four structurally different model versions (MVs; see Figure 6).

#### 4.2.3 Calibration

Figure 6 summarizes the approach used to calibrate the model and to identify an ensemble of acceptable parameter sets for MACRO that describes the observations sufficiently well. The approach is based on the GLUE-methodology described by Beven and Binley (1992). The basic principle is to run simulations with different sets of parameter combinations and evaluate their performance with respect to the measurements, in this case the field experiment described above. In order to test different model structures, we calibrated each of the four model versions (MVs) separately against the measurements (paper I). For paper II, we applied the same approach but only for MV4 with some modifications as mentioned below.



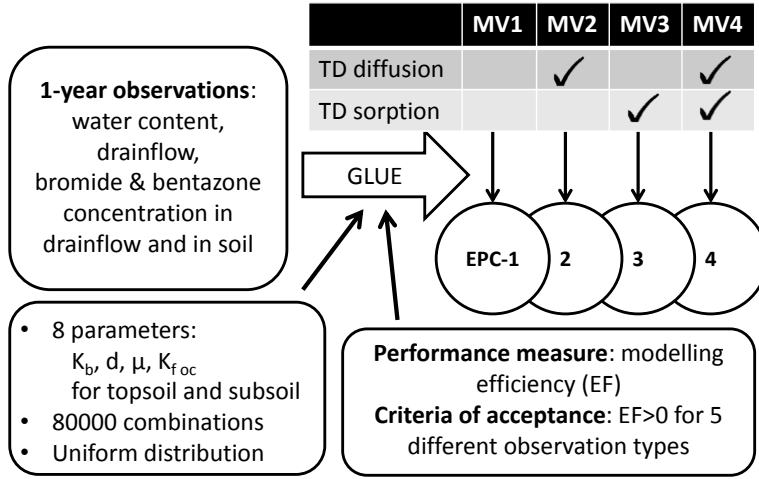


Figure 6. Sketch of the procedure to identify an ‘Ensemble of acceptable Parameter Combinations’ (EPC) for the four structurally different model versions (MVs) of the MACRO-model (paper I). TD stands for temperature dependent. For paper II, a slightly modified procedure was performed with only MV4, a reduced number of combinations (40000) and a criteria of acceptance that required an EF > 0 for all 6 different types of observations.

Four sensitive parameters in MACRO were included in the procedure based on previous sensitivity and uncertainty assessments (Larsbo & Jarvis, 2005; Dubus *et al.*, 2003a): the degradation rate coefficient ( $\mu$ ), the sorption coefficient ( $K_{oc}$ ), the diffusion pathlength ( $d$ ), and the saturated matrix hydraulic conductivity ( $K_b$ ). Values for topsoil and subsoil were sampled independently, which resulted in 8 uncertain parameters. 80000 and 40000 different parameter combinations were tested for papers I and II, respectively. Application date, application dose, soil properties and crop information were set according to measurements at the field site or previous calibrations of the model against the data (Larsbo & Jarvis, 2005; Larsson & Jarvis, 1999). The simulations were driven by on-site recorded meteorological time series of hourly precipitation, and daily data of temperature, solar radiation, wind speed and relative humidity.

The performance of the different parameter sets was evaluated based on the model efficiency (EF) (or Nash-Sutcliffe criteria; Nash & Sutcliffe, 1970), with

$$EF_i = \frac{\sum_{j=1}^n (O_{ij} - \bar{O}_i)^2 - \sum_{j=1}^n (O_{ij} - P_{ij})^2}{\sum_{j=1}^n (O_{ij} - \bar{O}_i)^2} \quad [4]$$

where  $i$  denotes the different types of observations,  $n$  is the number of observations in each group,  $O_{ij}$  and  $P_{ij}$  are the observed and simulated values and  $\bar{O}_i$  is the average of the observations for each group.

The criterion relates the variation in the observations to the variation in the simulations. It gives a value between  $-\infty$  and 1, where a value greater than zero means that the simulations are better predictors than the average of the measurements. All available measurements were included, i.e. measurements of dynamic fluxes and state variables, each of which produced one EF-value. Those simulations that gave EF-values larger than zero for all observation types were defined as *acceptable*. In paper I, bromide flux concentration data was excluded from this criterion because no parameter combination gave good simulations of both bromide flux concentration and bentazone resident concentration. For paper II, the prior ranges for  $K_b$  in top- and subsoil were narrowed in relation to the total number of samples taken, which gave a sufficient number of parameter combinations in the relevant range and much better simulations of bromide concentration in drainage.

#### 4.2.4 Prediction Scenarios

The calibrated ensemble of parameter sets was used to test different *prediction scenarios* under present and future climate conditions. We simulated six different pesticide application scenarios (PAS's) defined as a unique combination of a certain pesticide compound (with its specific properties) applied on a crop with a particular dose at a certain time of the year. We tested three hypothetical compounds differing in their sorption strength<sup>3</sup>, which were derived by multiplying the calibrated  $K_{oc}$  values with the factors given in Table 2. Pesticides were applied in spring (May, 1<sup>st</sup> to May, 16<sup>th</sup>) or in autumn (September, 29<sup>th</sup> to October, 15<sup>th</sup>) at a fixed annual application rate (0.45 kg ha<sup>-1</sup>) on winter cereals.

Table 2. Overview of the pesticide application scenarios simulated in papers I and II for present and future climate conditions. The calibrated  $K_{oc}$ -values were multiplied by the given  $K_{oc}$ -factors.

Scenario	Sorption properties	Application Season	$K_{oc}$ -factor
WsSpr	weakly sorbed	spring	1
WsAut		autumn	
MsSpr	moderately sorbed	spring	10
MsAut		autumn	
SsSpr	strongly sorbed	spring	50
SsAut		autumn	

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<sup>3</sup> see also Figure 9 in 4.3.3.

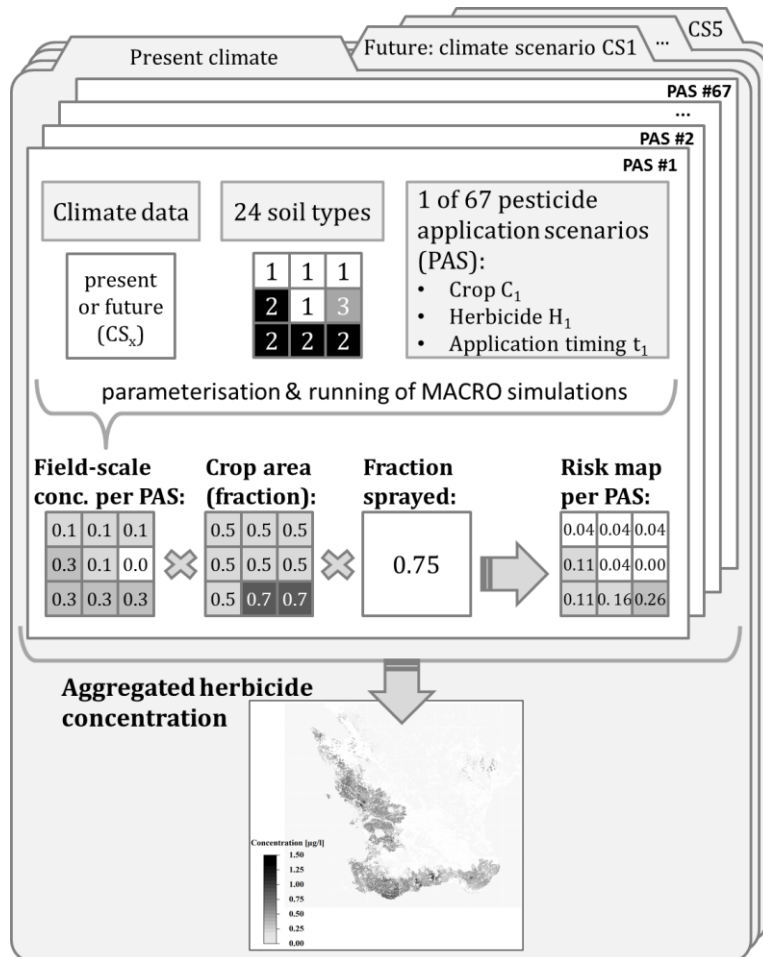
For present conditions, climate data from the weather station in Sâtenäs (58°26'N, 12°41'E, see *Figure 4*) was used, which is considered representative for the crop production region *Västra Götaland*. For future climate conditions, time series were generated with the simple delta-change method (see 3.1.2 and paper II). Thus, monthly average change factors were calculated for temperature, precipitation and solar radiation from the climate model projections (*Table 3*) and applied to systematically change the present climate time series. Additive change factors were used for temperature and solar radiation and multiplicative ones for precipitation (*Figure 2*). Wind speed and relative humidity were kept unchanged. In the case of wind speed, this was because projected changes are rather small and do not show systematic patterns (Kjellström *et al.*, 2014; Kjellström *et al.*, 2011), while models and experiments suggest that relative humidity will be unaffected in a future climate (Bengtsson, 2010). In paper I, only one climate scenario was included (CS9), while paper II included all nine climate scenarios (*Table 3*).

Table 3. Overview of the climate model projections forming the basis of the climate scenarios used in this thesis. SRES stands for the emission scenarios as described in Nakićenović & Swart (2000) and GCM for global climate model. All GCMs were dynamically downscaled by the regional climate model (RCM) developed by the Swedish Meteorological and Hydrological Institute, called RCA3 (Samuelsson *et al.*, 2011). For the ECHAM5-model, three simulations differing only in the initial states (denoted with r1, r2, r3) were used. References to the individual GCMs are given in paper II.

GCM	Short information about the GCM	SRES (initial state)	Climate Scenario	Paper		
				I	II	III
BCM	<i>Bergen Climate Model</i> is a coupled atmosphere–ocean–sea ice model consisting of the atmospheric model ARPEGE/IFS and a global version of the ocean model MICOM (Furevik <i>et al.</i> , 2003).	A1B	CS1	x	x	
CCSM3	<i>Community Climate System Model</i> is a coupled climate model for simulating the earth's climate system. It was created by the National Centre for Atmospheric Research (CO, USA), as a freely available model for the wider climate research community (CESM, 2015).	A1B	CS2	x	x	
HadCM3Q0	<i>Hadley Centre Coupled Model, version 3</i> is a coupled climate model developed at the Met Office Hadley Centre, UK (MetOffice, 2015). The model is run on a 360-day year, i.e. 12 months with 30 days each.	A1B	CS3	x	x	
IPSL	The IPSL Earth System Model was developed by the Institute Pierre Simon Laplace in France in a modular way with model components of the Earth system that can be used as standalone models or coupled to each other (IPSL, 2015).	A1B	CS4	x	x	
ECHAM5	The 5th generation of the ECHAM general circulation model, which was developed by the Max Planck Institute for Meteorology, Hamburg, Germany. It originates from developments based on the global numerical weather prediction model of the European Centre for Medium-Range Weather Forecasts (MPI-MET, 2015).	A1B (r1)	CS5	x	x	
		A1B (r2)	CS6	x		
		A1B (r3)	CS7	x		
		B1 (r1)	CS8	x		
		A2 (r1)	CS9	x	x	

### 4.3 Regional Scale

Field-scale studies can provide insights into processes that will affect pesticide leaching under climate change, but a proper appreciation of the likely overall impacts requires analyses at larger spatial scales such as catchments or regions. *Figure 7* gives an overview of the methodology adopted for the regional scale study reported in paper III, which analysed both direct and indirect effects of climate change on herbicide leaching to groundwater.



*Figure 7.* Sketch of the regional scale project. For each combination of climate, soil type, and pesticide application scenario (PAS), MACRO-SE parameterizes and runs simulations that produce field-scale concentrations. In a subsequent step, risk maps for each PAS are produced that account for soil distribution, fractional crop coverage and area sprayed with the herbicide. All the individual risk maps are then combined to obtain aggregated herbicide concentrations. This is done for both present and for each of the five climate scenarios separately.

#### 4.3.1 Study Region

The study focused on the southern part of the GSS crop production region in the county of Scania (GSS are the southern plains of *Götaland*; see *Figure 4*). This region is a major Swedish crop production region with agricultural land comprising 61% of the area, which is very high compared to the Swedish average of 7.6%. Scania contributes 50% of the total agricultural production in Sweden (SJV, 2014) on roughly 20% of the agricultural land with 60% of the national pesticide use (SCB, 2011). The dominant soils in Scania are developed in quaternary moraine (till) deposits. The climate in the simulated region is humid temperate with an annual precipitation of 706 mm and an annual average temperature of 7.8 °C (paper III, Table 1).

#### 4.3.2 Impact Model: MACRO-SE

MACRO-SE is a regionalized version of MACRO 5.2 (see chapter 4.2.2), currently under development by the Centre for Chemical Pesticides (CKB) at the Swedish University of Agricultural Sciences (SLU). It combines soil maps, detailed information on land-use, crop area and climate data with a set of empirical pedotransfer functions (PTFs) and other parameter estimation routines (Moeys *et al.*, 2012; Jarvis *et al.*, 2007), which provide a complete parameterization of MACRO 5.2 for an entire region in Sweden (cf. *Figure 7*). A previous test of the PTFs showed that water recharge, the general temporal pattern of solute leaching and the ranking of soils according to preferential solute transport indicators was reasonably well predicted (Moeys *et al.*, 2012).

The soil classification in MACRO-SE is based on the FOOTPRINT soil type (FST) classification (Centofanti *et al.*, 2008), but has been adapted to fit the available data for Swedish arable soils. The FST designation comprises four components: the soil hydrological class, the texture class in topsoil and subsoil, and the topsoil organic matter content class. The texture code is given by a number between 1 and 5 for coarse, medium, medium-fine, fine and very fine mineral soils, respectively (see also *Figure 8*), while bedrock in the subsoil is denoted with a 0 and peaty soils are denoted with a 6. The code for organic matter content (u, n, h, and t) represents topsoils with low (<3%), average (3-5%), and high (>5%) organic matter contents, and peaty soils, respectively. Four hydrological classes are distinguished that define the dominant flow pathways and the bottom boundary condition for MACRO (*Table 4*). Classes *W* and *Y* have recharge to groundwater via percolation as well as discharge to surface water, class *U* only discharges to surface water, while class *L* only recharges to groundwater. As an example: Y24n denotes a soil with hydrological class Y (discharge and recharge), a medium textured topsoil (2), fine textured subsoil (4) and medium organic carbon content (n).

Table 4. *Description of soil-geological conditions, modelled flow pathways and the definition of the bottom boundary condition in MACRO for the four hydrological classes in MACRO-SE.*

Hydrological class	Landscape feature or position	Flow pathways	Bottom boundary condition in MACRO
L	soils with free drainage to deep-lying groundwater	Only percolation towards groundwater	unit hydraulic gradient
W	soils with moderately permeable substrate; groundwater-table can reach into the soil profile, but not far	recharge to groundwater dominates, but discharge to surface waters via lateral flow occurs	percolation rate is defined as a linear function of the water table height
Y	soils with slowly permeable substrate; groundwater-table can reach far into the soil profile	discharge to surface waters via subsurface drains dominates, but recharge to groundwater occurs	percolation rate is defined as a linear function of the water table height
U	soils with impermeable substrate (i.e. very low hydraulic conductivity in the subsoil) or soils occupying low-lying discharge areas.	only discharge to surface water via subsurface drains	zero-flow

The default parameterization of MACRO-SE was used for all soils in the region. This means that the default version of MACRO 5.2 (MV1) was used, which does not account for the effects of temperature on sorption or diffusion. Sorption followed a Freundlich isotherm defined by the organic carbon sorption coefficient  $K_{foc}$  and the Freundlich exponent  $n_f$  and pesticide degradation was simulated with first-order kinetics as in paper I and II. More details on the data input to MACRO-SE are presented in the supplementary material to paper III.

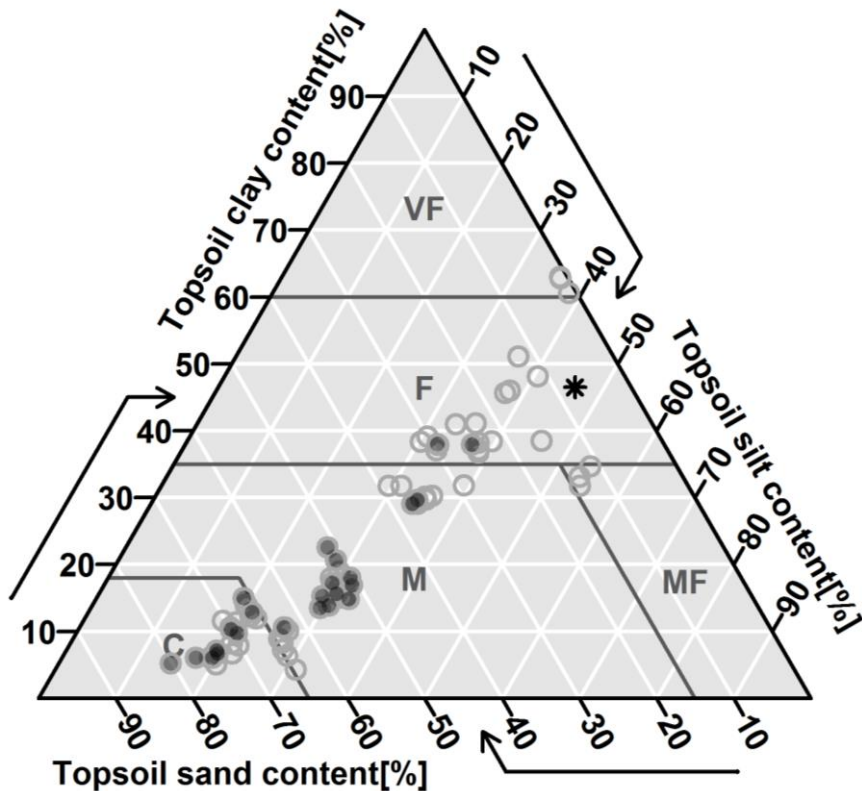
### 4.3.3 Input Data

#### *Climate*

For present conditions, measured data from a representative weather station in Barkåkra (56°29'N, 12°85'E) was used for the entire region. For future conditions, five different climate model projections were used to generate the climate scenarios with the same delta-change approach used in the field-scale studies (see 4.2.4; CS1-CS5 as described in Table 3). The change factors varied between climate scenarios (Figure 2) with an annual increase in temperatures of 2 to 3.5 °C and increases in annual precipitation of 12 to 25% (paper III, Fig. 2 and Table 1).

## Soil

The GSS region in Scania is dominated by medium-textured soils with a clay content of 10-20% in the topsoil and locally high clay contents of up to 40%. The organic matter (OM) contents are low to medium in the region (58% with <3% OM, 39% with 3-5% OM and 3% with >5% OM). 34% of the arable soils within the GSS-region were classified as *U*-soils with no recharge to groundwater and were, thus, not relevant for the study. The 24 most common *L*, *W* and *Y*-soils (filled circles in *Figure 8*) were simulated, which together accounted for 97% of the arable area with recharge to groundwater (unfilled circles in *Figure 8*). As an illustrative comparison, the topsoil (0-30cm) texture class of the field site in Lanna is also marked in *Figure 8*.



*Figure 8.* Topsoil texture triangle of the Soil Map of Europe, also called HYPRES texture triangle. The unfilled circles denote all soil types in the GSS region of Scania with recharge to groundwater, the filled dots are the 24 most common soils, which were included in paper III. The black star is the topsoil texture of the soil in Lanna (paper I and II). The letters mark the texture classes: C=coarse (FST-code 1), M=medium (FST-code 2), MF=medium-fine (FST-code 3), F=fine (FST-code 4) and VF=very fine (FST-code 5).



### *Crop*

The eight most important crop types in southern Sweden (winter cereals, spring cereals, winter rape, sugar beets, peas, potatoes, maize, and spring rape) were simulated. Grassland was also included in the study, but no simulations were run as the grassland area was considered as un-treated, while the water balance for grass was approximated by that of winter cereals. The fractional coverage of each crop was derived from a field scale database held by the Swedish Board of Agriculture, with the data aggregated to the catchment scale (see paper III, Fig. S3 and Table S1).

### *Pesticide application scenarios*

All herbicides that are currently allowed for use in Sweden on these eight crops were included, except for glyphosate and three additional compounds, for which the information was not sufficient to parameterize the simulations (bifenox, clomazone and picloram). The 37 herbicides (*Figure 9*) combined with the crops they are registered for use on, gave a total of 67 pesticide application scenarios (PAS's). For each PAS, application date and dose as well as the fraction of the specific crop sprayed with the particular herbicide was obtained from long-term monitoring data gathered in two catchments that are part of the Swedish national environmental monitoring program for pesticides (see *Figure 4*). In the monitoring programs, pesticide residues in surface water, groundwater, stream sediment, and rain water are collected regularly throughout the year. Additionally, the farmers are interviewed each year to gather information about field size, crops grown, and pesticide usage (i.e. substance, application day and rate). The pesticide properties ( $K_{loc}$ ,  $DT_{50}$ ,  $n_f$ ) were taken from the Pesticide Properties DataBase of the University of Hertfordshire (PPDB, 2013). For the complete list of all PAS's, including crop growth parameters, application dose and day of application, see Table S2 in paper III.

The study was performed as a two-step procedure (cf. *Figure 7*). From each simulation for soil type  $i$ , crop  $j$  and herbicide  $k$ , predictions of accumulated percolation in a depth of 2 m ( $W_{i,j}$  [m]) and the corresponding accumulated pesticide mass ( $L_{i,j,k}$  [mg m<sup>-2</sup>]) were obtained. For each location in the region ( $p$ ), these results were aggregated to an overall concentration of herbicides leaching to groundwater ( $\overline{C_{p(i)}}$ ) that accounted for the fractional coverage of the crop ( $f_{crop(j,p)}$ ), the fraction of the crop area sprayed with a particular herbicide ( $f_{sub(k,j)}$ ) and a factor for the relative changes in herbicide use compared to present conditions ( $f_{ind(j)}$ ):

$$\overline{C_{p(i)}} = \frac{\sum_{j=1}^{ncrops} \sum_{k=1}^{nsubs} (f_{crop(j,p)} f_{sub(k,j)} f_{ind(j)}) L_{i,j,k}}{\sum_{j=1}^{ncrops} f_{crop(j,p)} W_{i,j}} \quad [5]$$

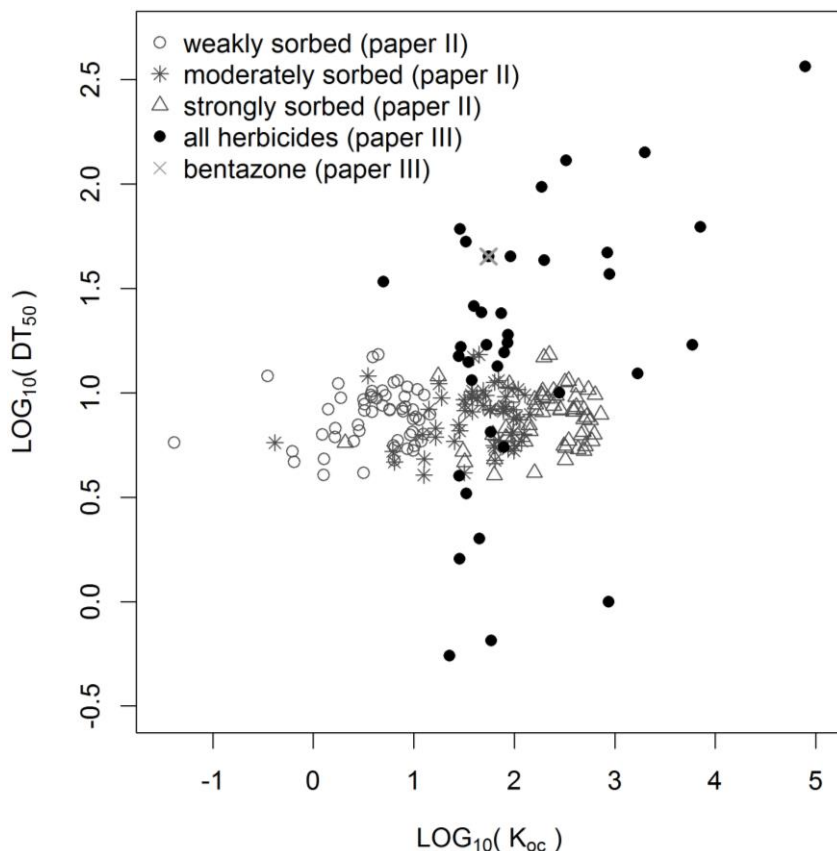


Figure 9. Pesticide properties for the simulated compounds in paper II and paper III. For the herbicides from paper III, the  $K_{\text{foc}}$  values are given, although  $K_{\text{oc}}$  is indicated in the axis label.

#### 4.3.4 Future Scenarios of Herbicide Use

Three scenarios of herbicide use in a future climate were explored. For each scenario, the five climate scenarios described above (Table 3) were included to represent climate input uncertainty.

- Scenario (A) only accounted for direct effects of climate change and assumed the cropping patterns and herbicide use to be unchanged compared to present conditions.
- Scenario (B) accounted for changes in climate and land-use. Land-use changes were represented by changes in the relative fractions of crops grown in the future. The area of spring sown cereals and spring sown oilseed rape were reduced by 60 and 100%, respectively, and replaced by autumn sown cereals and oilseed rape in a ratio of 3:2. The area of grassland was reduced by 50% in favour of maize.

- Scenario (C) accounted for changes in climate, land-use and herbicide use. In addition to the changes for scenario (B), the expected increase in weed-pressure is met by an increased use of herbicide. Change factors were calculated based on Wivstad (2010) and varied between 1.035 and 1.59 for the different crops, with an average increase of 45% (paper III, Table S1).

Only a few of the many possible indirect effects (cf. 3.3.2) could be assessed in this study due to a limited computational capacity and incomplete knowledge. The factors included in the analysis were considered as very likely to be relevant in the future and sensitive for herbicide leaching at regional scales, and they allowed the parameterization of the simulations within the given modelling framework. This aspect is further discussed in section 5.4.

#### 4.3.5 Model Evaluation against Monitoring Data

As discussed in paper III, a quantitative validation of MACRO-SE is difficult, so only a qualitative test of the regional scale modelling approach was performed. Simulations were compared with groundwater monitoring data to evaluate whether MACRO-SE could distinguish between *leachable* and *non-leachable* compounds. Results from four different monitoring campaigns in the region were available (see *Figure 4*): monitoring data collected from two catchments that are part of the Swedish national long-term environmental monitoring program for pesticides (CKB, 2014), monitoring campaigns carried out by the county boards in Scania (Virgin, 2012) and Halland (Löfgren & Tollebäck, 2012) and analyses of private groundwater wells in Halland (Larsson *et al.*, 2013). Based on these monitoring results, each herbicide was classified as *detected* when it was found at least once in any of the groundwater samples taken in any of the studies. In order to compare measurements with simulations, the simulations were censored based on a typical limit of detection (LOD) of  $0.01 \mu\text{g l}^{-1}$  and the herbicides were treated as *virtual detects* when simulated concentrations exceeded the LOD at any location in the area, and as *virtual non-detects* if simulated concentrations were always below the LOD.



## 5 Results and Discussion

### 5.1 Field scale

#### 5.1.1 Calibration Results

The comparison between the simulations with the ensemble of acceptable parameter combinations and the measured flux variables from paper II are shown in *Figure 10*. The corresponding results in paper I were similar for drainflow and bentazone concentrations in drainflow, but worse for bromide, partly because those observations were excluded from the performance criterion. The model failed to simulate the first peak of drainflow and consequently did not predict any solute transport in this period (papers I, II). This was most likely due to a lack of measurements below one meter depth, which led to wrong initial soil moisture conditions, especially with respect to the initial depth of the groundwater table. This is probably also the reason why the model underestimated the total amount of pesticide lost to drains (measured: 8.5%; simulated 3.1-6.2% of the applied dose). Nevertheless, the model described the remaining observations reasonably well. A comparison between simulated and measured state variables (water content, resident bromide and bentazone concentration in soils) showed that the variation in the replicated measurements was also reasonably well captured (paper I, Figs. 7-9).

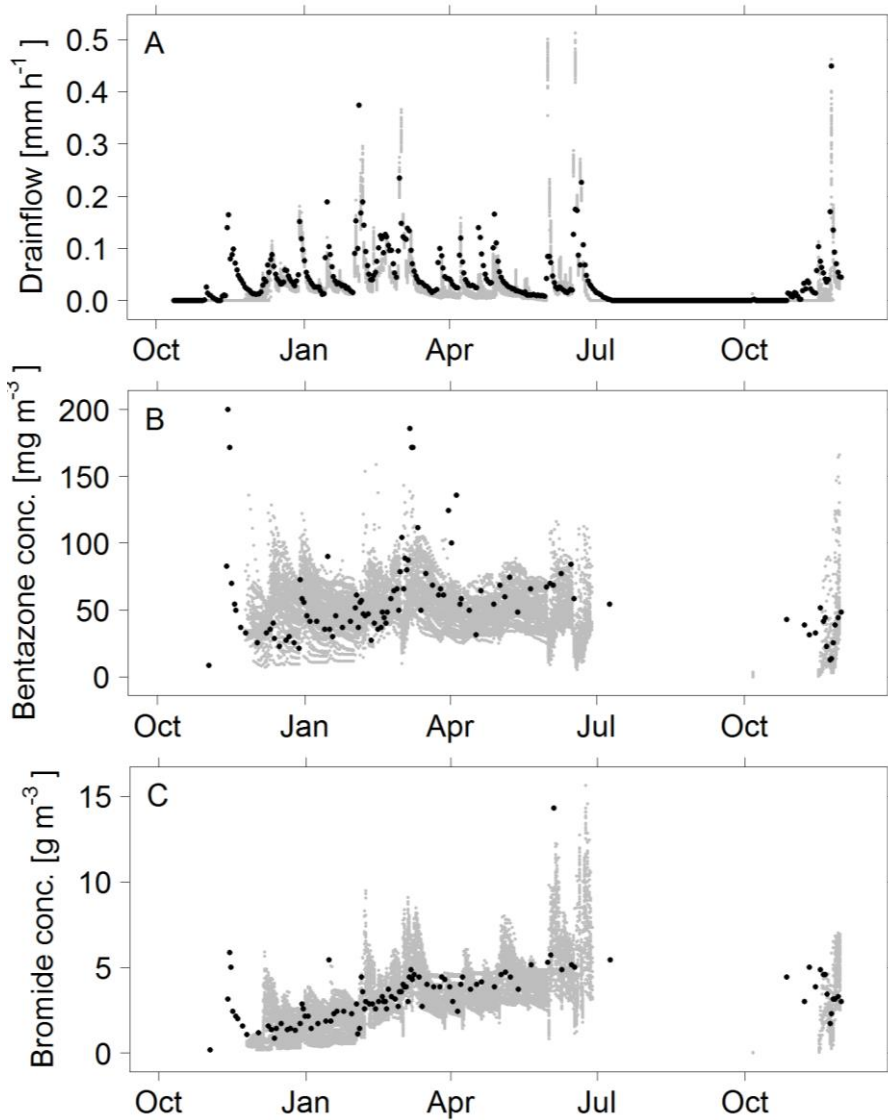
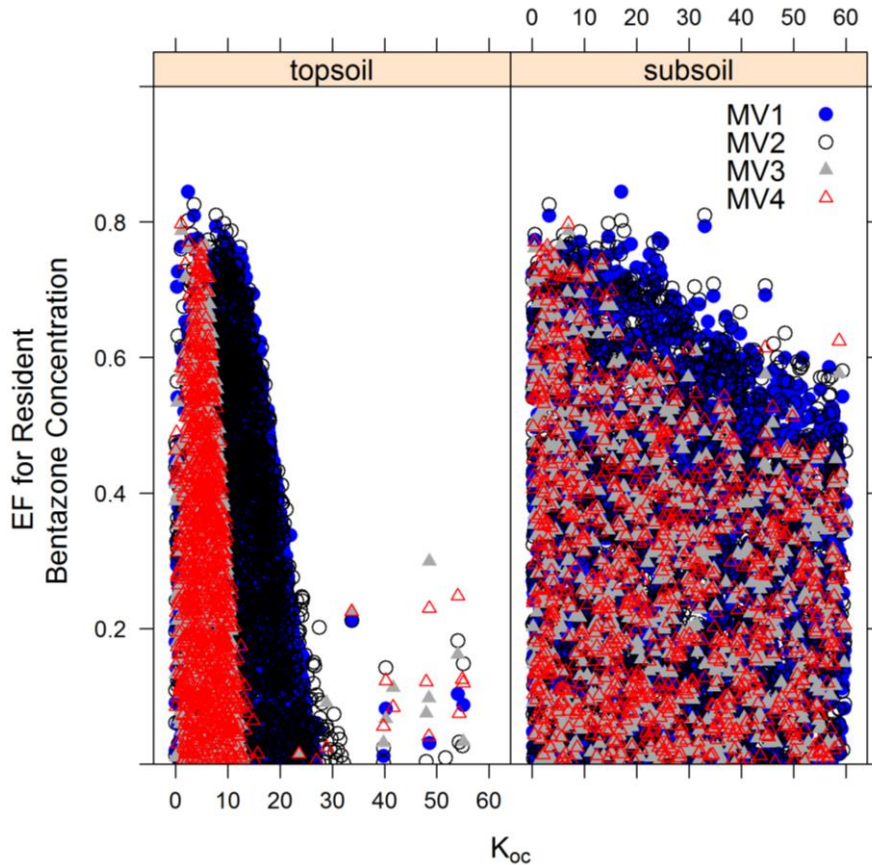


Figure 10. Field observations (black dots) at Lanna, *Västra Götaland*, between October 1994 and December 1995 compared to model simulations (small grey dots) for (A) drainflow, (B) concentration of the herbicide bentazone in drainflow and (C) concentration of the non-reactive tracer Bromide in drainflow. Simulations with all 56 acceptable parameter combinations for paper II are displayed.

In paper I, a clear reduction in the posterior distributions was observed compared to the prior distributions for several parameters (paper I, Table 5). This is exemplified in *Figure 11* for  $K_{oc}$ , especially in the topsoil, while a greater degree of equifinality was found for the subsoil. Apart from a significant reduction in the posterior parameter ranges in the topsoil, a clear distinction between the optimum ranges for models that account for temperature dependent sorption (MV3, MV4) and those that do not account for it (MV1, MV2) was observed with smaller optimal  $K_{oc}$  values in the former case (*Figure 11*).

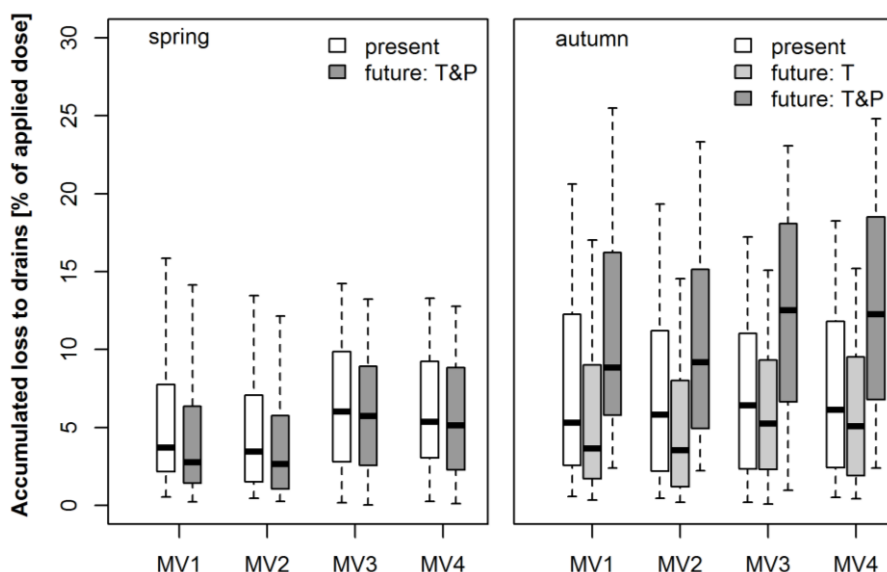


*Figure 11.* Performance of the parameter values for the sorption coefficient  $K_{oc}$  for each of the four model versions (MV; see *Figure 6*) analysed in paper I. The modelling efficiency (EF) was obtained based on comparisons between simulations with the particular parameter values in the topsoil and subsoil and measurements of bentazone resident concentration in the soil. The range of values on the x-axis represents the prior parameter range.

### 5.1.2 Pesticide Losses under Climate Change

Losses of pesticides to drains decreased with increasing sorption strength of the compounds and losses after spring application were generally lower than losses after autumn application for present and future climate (cf. *Figure 12*). This was observed independent of model structural version (paper I) or climate scenario (paper II).

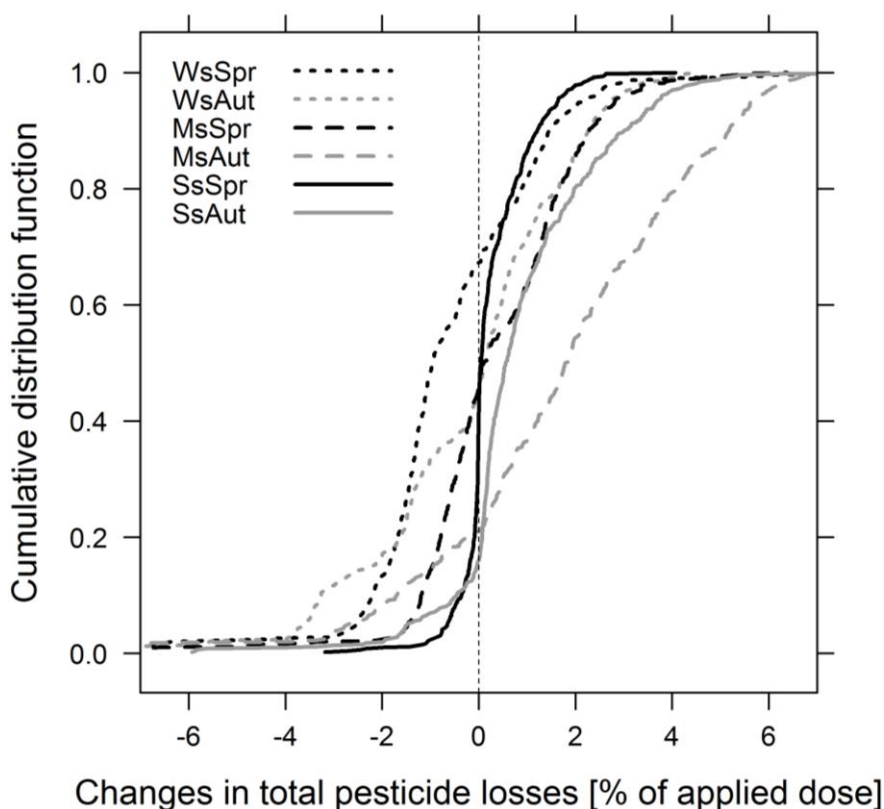
In paper I, losses of pesticide to drains after spring application decreased from the present to the future climate for all model versions and pesticide compounds with the exception of the SsSpr-scenario with the models accounting for temperature dependent sorption (MV3, MV4). In these cases, the changes were negligible and not consistent between parameter combinations (paper I, Table 7), since the effect of temperature on sorption counteracted the effect on degradation. Leaching after autumn applications increased in the future climate in all cases. This was mainly triggered by increases in winter precipitation, since losses were reduced when only changes in temperature were considered (*Figure 12*).



*Figure 12.* Accumulated loss to tile-drains of the moderately sorbed pesticide after spring and autumn application for all model versions (MVs; *Figure 6*). The boxes mark the inter-quartile range, the black bar the median and the whiskers the 5<sup>th</sup> and 95<sup>th</sup> percentile of the results derived with the ensemble of acceptable parameter combinations. Results for present and future climates with changes in both temperature and precipitation (T&P) are presented. For autumn application, a future climate with only changes in temperature (T) is also shown.



In paper II, we showed that the direction and magnitude of change depended on the choice of the climate scenario for all PAS's (paper II, Figs. 4 and 5). An ensemble of parameter sets and climate scenarios was used to make a probabilistic assessment of the direction of change of pesticide leaching in a future climate (*Figure 13*). The ensemble estimated a 70% chance that the losses of a weakly sorbed compound applied in spring would decrease in a future climate. For moderately and strongly sorbed compounds applied in spring, the likelihood of reduced or increased future losses was similar (50%). For autumn applications, the probability of an increase in leaching losses ranged from 50% for the weakly sorbed compound to 80% for the moderately and strongly sorbed compounds.



*Figure 13.* Cumulative distribution function of the ensemble mean generated from all parameter sets and climate scenarios for changes from present to future for all pesticide application scenarios (PAS; as in Table 2): *Ws* denotes the weakly sorbed, *Ms* the moderately sorbed and *Ss* the strongly sorbed compound, while *Spr* stands for spring applications and *Aut* for autumn application.

### 5.1.3 Model Structural Differences vs. Parameter Uncertainty

In Paper I, a statistical analysis using the Kolmogorov-Smirnov test showed that the effects of model structural differences could be distinguished despite large parameter uncertainty. It indicated that the dominant factor for moderately and strongly sorbed compounds was temperature dependent sorption, while temperature dependent diffusion was more important for weakly sorbed compounds. This demonstrated that the effect of temperature on sorption is higher for compounds with higher sorption strength.

For the weakly sorbed compound, losses were smaller when temperature dependent sorption was accounted for (see paper I, Fig.10) as the typical daily average temperatures in Sweden are less than the reference temperature of 20°C. However, for moderately and strongly sorbed compounds, the losses increased with the model accounting for temperature dependent sorption (cf. *Figure 12*). The most likely explanation for this is that stronger sorption of these compounds means that they stay close to the soil surface for longer, which increases the likelihood of losses via macropore flow (McGrath *et al.*, 2010; Larsson & Jarvis, 1999).

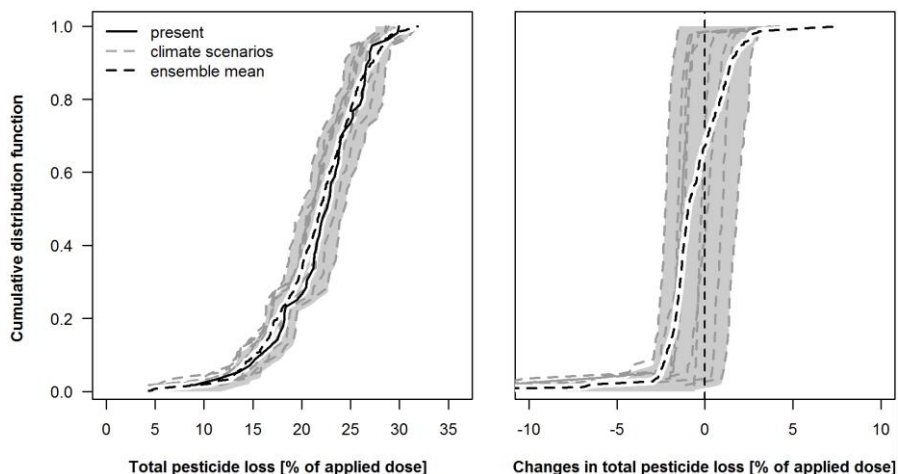
As noted above, the direction of change of losses from present to future climate conditions was consistent among parameter sets and the same direction was predicted by all model versions for a given PAS with the exception of the SsSpr-scenario. The magnitude of change, however, was affected by the choice of model structure. Including temperature dependent sorption led to a relative increase of losses for all compounds (*Figure 12*), due to a reduction in sorption strength at higher temperatures (*Figure 5*).

### 5.1.4 Climate Input Uncertainty vs. Parameter Uncertainty

In paper II, the effects of parameter uncertainty in MACRO were compared with the effects of uncertainty in the model driving data derived from the climate model projections. The relative importance of these two sources of uncertainty was found to depend on whether absolute pesticide losses or changes in these losses between present and future climates are of interest. This is in accordance to findings by Kong *et al.* (2013) regarding the modelling of the fate of PCBs in the environment. *Figure 14* demonstrates this difference for the weakly sorbed compound applied in spring. The effect of parameter uncertainty is demonstrated by the spread in the outputs for a given climate input data set (i.e. present or any climate scenario). The effect of climate input uncertainty is reflected by the spread between the nine climate scenarios, which is illustrated by the underlying grey area. The parameter uncertainty in this approach lumps all uncertainties related to the model (i.e. model structure, boundary conditions, parameters, etc.) and, thus, overestimates the pure parameter uncertainty

(Vrugt *et al.*, 2009). The contribution of parameter uncertainty to the overall variation in predictions decreased from 92% to 55% when focusing at predicted changes compared with absolute losses, while the effect of climate uncertainty increased from 8% to 45%. This effect was most pronounced in the case of a weakly sorbed pesticide applied in autumn, where the uncertainty due to climate input data increased from 12% to 64%, and least pronounced for the strongly sorbed compound applied in autumn (3% to 30%). See paper II for details.

A non-parametric analysis of variance (Kruskal-Wallis test) showed that the ensemble mean prediction for the changes in pesticide losses between present and future climate did not differ significantly between the individual parameterizations of MACRO for the spring applied compounds and the weakly sorbed compound in autumn (paper II, Table 3 & Fig. 7). This suggests that using only one MACRO-parameterization per soil type together with an ensemble of climate scenarios could be a reasonable strategy to adopt for large scale studies. However, for moderately and strongly sorbed compounds applied in autumn, this simplification might lead to biased results. Nevertheless, probabilistic predictions of future pesticide losses or changes in losses, as illustrated in *Figure 13*, require ensembles of both MACRO-parameterizations and climate scenarios.



*Figure 14.* Cumulative distribution functions of simulated pesticide losses (left) and predicted changes in pesticide losses (right) for the weakly sorbed pesticide applied in spring (WsSpr). The changes are calculated as future minus present, i.e. values larger than zero represent an increase in the future, and values smaller than zero a reduction.

## 5.2 Regional Scale

### 5.2.1 Model Evaluation against Monitoring Data

Table 5 shows that 29 out of 33 herbicides were correctly classified by MACRO-SE as either *leachable* or *non-leachable* in the comparison with groundwater monitoring data. This gives some confidence in the simulation results, even if a quantitative evaluation remains to be performed. Table 6 presents the fraction of the area for which simulated concentrations exceeded the LOD. Of the 12 herbicides that were simulated as *leachable* (see Table 6), only flurtamone and propoxycarbazone-sodium were never detected in any groundwater sample, probably because they are rather new (first registered in 2002 and 2005) and may not have had sufficient time yet to leach to the groundwater (see also Åkesson *et al.*, 2014). Point sources are possible explanations for the compounds that were detected but not simulated with concentrations above LOD. For further discussions on the comparison between simulations and monitoring results, see paper III.

Table 5. Comparison of the modelling results with regional groundwater monitoring results. Each cell of this “confusion matrix” shows the number of true positives, false positives, true negatives and false negatives, respectively. This is based on simulated concentrations above or below the limit of detections (LOD) of  $0.01 \mu\text{g l}^{-1}$  (“true” and “false”) compared to detects or non-detects in groundwater monitoring (“positives” and “negatives”). Four of the 37 simulated herbicides were not analysed in any of the monitoring studies and therefore excluded here.

Simulations Monitoring	Simulated concentrations > LOD	Simulated concentrations < LOD	SUM
Detected	10	2	12
Not detected	2	19	21
SUM	12	21	33

Table 6. Area-averaged relative contribution of different herbicides to the total herbicide concentration in leachate [%] and the fraction of the arable area for which modelled herbicide concentrations exceeded the limit of detection (LOD) of  $0.01 \mu\text{g l}^{-1}$ . Only those herbicides and their physicochemical properties are listed, for which simulated concentrations exceeded the LOD at least in some part of the area.

Herbicide	$K_{\text{foc}}$ [ml g <sup>-1</sup> ]	DT <sub>50</sub> [days]	n <sub>f</sub> [-]	Contribution to total herbicide concentration [%]	Fraction of the area which exceeded the LOD of $\mu\text{g l}^{-1}$ .
clopyralid	5.0	34	1.00	42.9	1.000
bentazone	55.3	45	1.00	26.9	0.990
metazachlor	79.6	16	0.99	10.0	0.830
metamitron	86.4	19	0.81	8.4	0.860
propoxycarbazone-Na	28.8	61	1.00	4.5	0.920
ethofumesate	187.3	97	0.88	1.6	0.330
MCPA	74.0	24	0.68	1.3	0.120
quinmerac	86.0	17	0.88	1.0	0.038
flurtamone	329.0	130	0.90	0.8	0.037
chloridazon	199.0	43	0.84	0.8	0.018
fluroxypyr	68.0	13	0.93	0.6	0.004
metribuzin	37.9	12	1.08	0.4	0.025

### 5.2.2 Simulated Field-Scale Leachate Concentrations

Figure 15 gives an overview of the field-scale herbicide concentrations simulated for each PAS and soil type included in paper III. It suggests that herbicide properties have a stronger influence on the overall *leachability* than soil properties (texture class, organic matter content) and hydrological class. The indicated changes (+/-) refer to the direct effects of climate change. The simulated concentrations decreased in the future for compounds that leached at the highest concentrations under present conditions (bentazone, clopyralid, propoxycarbazone-Na), whereas they increased for most other compounds. Predicted concentrations increased for a few compounds that did not leach under present conditions (the *non-leachable* ones), but for most of them no change was simulated. These field-scale concentrations do not include landscape or regional scale features such as soil surface, fractional crop coverage, or fraction of the crop area sprayed with the herbicide. However, these results are valuable for the interpretation of aggregated landscape or regional scale results and necessary to disentangle key-factors. Discussions on the specific responses of individual herbicides to climatic or soil-related factors are, however, outside the scope of this thesis.

**Figure 15.** Matrix of simulated field-scale herbicide concentrations in leachate for all pesticide application scenarios (see abbreviation list, *Table 6* and *Table S2* in paper II) and FOOTPRINT-soil types (see *4.3.2*) under present climate conditions. Colour coding ranges from white ( $0 \mu\text{g l}^{-1}$ ) to black ( $>5 \mu\text{g l}^{-1}$ ). Average changes in the future of more than  $0.001\mu\text{g l}^{-1}$  are indicated by “+” for increases and “-” for decreases (results for the scenario that only considered the direct effects).

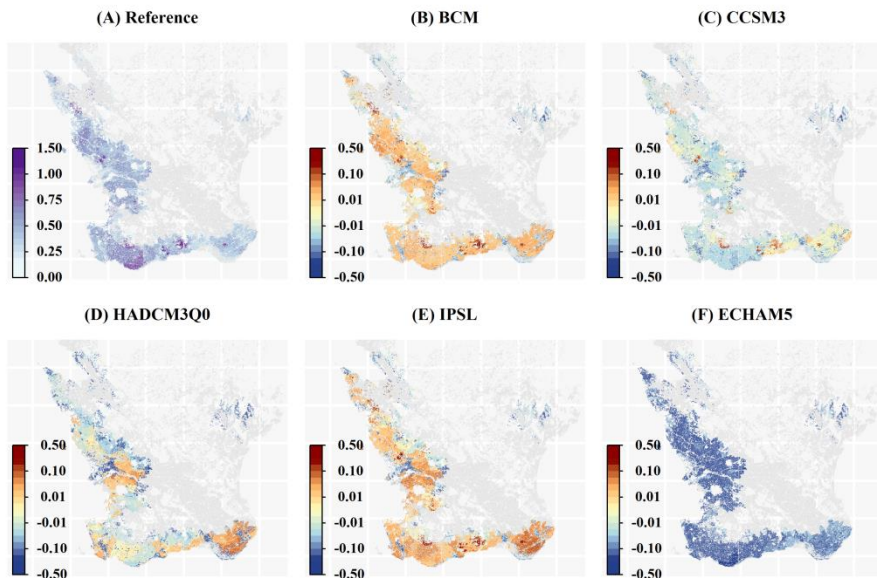


Figure 16. Herbicide concentration in leachate [ $\mu\text{g l}^{-1}$ ] under present climatic conditions (A) and under future climate conditions (B-F) when only the direct effects of climate change were considered as projected based on the five climate scenarios (see Table 3).

### 5.2.3 Aggregated Herbicide Concentrations in Leachate

Aggregated herbicide concentrations in leachate under present conditions varied spatially between zero and  $1.4 \mu\text{g l}^{-1}$  (Figure 16A). Regions with high concentrations correspond to areas with soils of larger clay content (see Figure 15 and paper III, Figs. 3 & S8), because the PTFs in MACRO-SE predict macropore flow to be stronger in these soils (Moeys *et al.*, 2012). In clayey till soils, typical for southern Sweden, preferential flow extends well below the root zone due to the presence of fissures (Stenemo *et al.*, 2005; Jørgensen *et al.*, 1998). Areas with higher clay contents can, therefore, be at risk of groundwater pollution (Stenemo *et al.*, 2005).

Figure 17 shows the change in these simulated concentrations in relation to topsoil properties and changes in climate variables. Topsoil clay content had the strongest impact on the relative change in concentration in a future climate compared to present conditions (Figure 17A). Thus, areas most at risk today as a result of pronounced leaching in macropores are projected to become even more at risk in the future. This agrees with the experimental findings reported by Beulke *et al.* (2002). Changes in annual precipitation seemed more influential than changes in temperature (Figure 17C, D). A simple correlation analysis confirmed these visual impressions (see paper III).

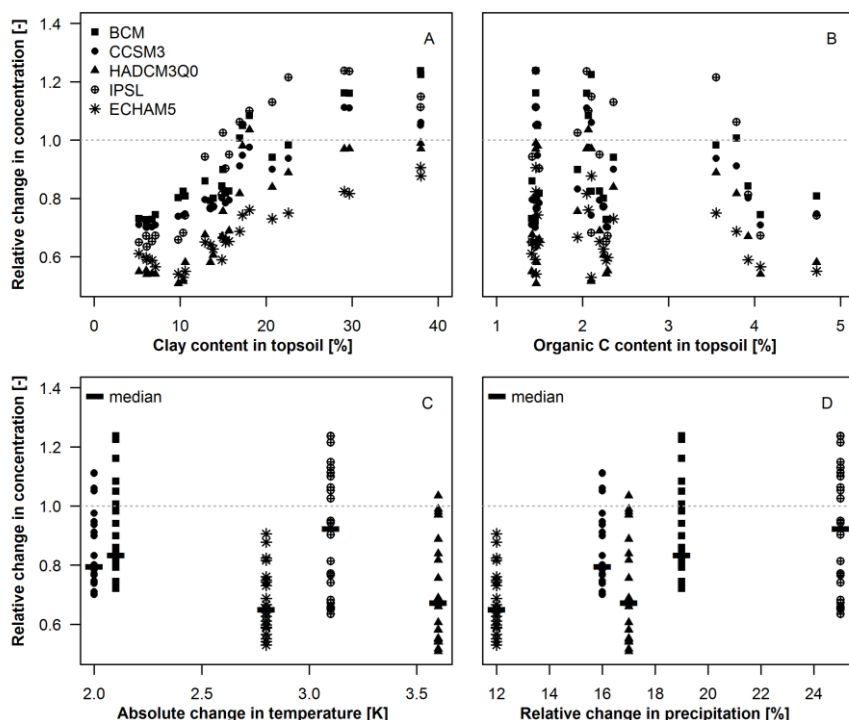


Figure 17. Relative change in herbicide leachate concentration from present to future in relation to topsoil properties (A: clay content; B: organic carbon content) and climatic variables (C: change in annual temperature; D: relative change in annual precipitation) for the future herbicide use scenario (A) with only direct effects of climate change. For each climate scenario (see legend), each dot represent one of the 24 soils that were simulated.

The changes in predicted herbicide concentrations depended on the climate scenario (Figure 16). Simulated changes for scenario (A), which only considered direct effects of climate change, ranged from strong reductions (Figure 16 (F) ECHAM5) to small or moderate increases over the entire region (Figure 16 (B) BCM, (C) IPSL). This reflects the correlation with the projected precipitation amounts (Figure 17D) as ECHAM5 is the climate scenario that projected smallest increases in precipitation amounts, while IPSL and BCM projected largest increases in annual rainfall (see paper III, Table 1).

Only a few herbicides contributed to the overall concentrations in leachate to groundwater (Table 6; Figure 15). The contribution of the different crops to the total leaching (see Table 7) is not only influenced by the herbicides used on those crops, but also depends on how widely the crop is grown and how much of the crop is sprayed with that herbicide. Spring cereals, peas and winter rape were the main contributors to overall simulated concentrations, followed by sugar beets and winter cereals.



Table 7. Area-averaged relative contributions (%) of the different crops to the overall herbicide concentrations in leachate to groundwater for present and future conditions.

Crop	Present	Future climate conditions		
		Scenario (A)	Scenario (B)	Scenario (C)
Winter cereals	7.80	3.80	5.30	3.90
Spring cereals	29.30	23.80	7.90	6.40
Winter rape	24.50	28.50	37.40	36.80
Sugar beets	10.80	19.20	16.50	20.40
Peas	25.50	22.60	19.20	16.30
Potatoes	0.50	0.60	0.50	0.40
Maize	1.40	1.40	13.20	15.80
Spring rape	0.04	0.06	0.00	0.00

The contribution of the crops differed between present and future climate conditions and also changed with the future scenarios for herbicide use (Table 7) as a result of the projected changes in cropping patterns and the effects of climate on the leaching of specific compounds (cf. Figure 15). The contribution of peas decreased, while the contribution of sugar beets increased markedly under future climate conditions, although the area of both crops was unchanged. This direct effect of climate change suggests that the herbicides used on sugar beets are rather susceptible to macropore flow.

The contribution of winter cereals decreased in a future climate, although the cropped area and the estimated future use of herbicides increased. In this case, the direct effects of climate change outweighed the indirect effects. Many of the herbicides used on winter cereals are either strongly sorbed and not leachable or low-dose mobile compounds, which are less susceptible to macropore flow. Before performing this study, the expectation was that an increased cultivation of winter cereals would have negative impacts on future pesticide leaching, because of the higher losses from autumn applied pesticides compared to those applied in spring (paper I, II, Lewan *et al.*, 2009). This regional scale study stressed, however, the importance of considering real compounds at their actual recommended doses rather than hypothetical ones. Comparing a compound applied in spring and autumn on winter cereals gave equivalent results to what was found in paper I and II (see e.g. flurtamon, Figure 15). Applications of a compound to spring cereals gave similar or higher concentrations than if the same compound was applied on winter cereals in spring, even if the application rate was lower (e.g. MCPA). This is because applications on spring cereals usually occur later (see paper III, Table S2) on less developed crop canopies, so the interception of pesticides is less than in winter cereals.

Contrary to winter cereals, winter rape is a larger contributor partly because leachable compounds such as metazachlor and quinmerac (see *Figure 15* and *Table 6*) are applied in autumn, and in the case of metazachlor even at high application rates. Additionally, 70% of the applications occur in autumn compared to less than 50% in the case of winter cereals. Thus, based on this, efforts should be put into reducing leaching risks from sugar beet and winter rape, as their contribution is projected to increase even when only direct effects of climate change are accounted for, which are likely to occur, even if the extent is uncertain.

Spatial aggregation of the results showed that under present conditions, simulated concentrations in leachate to groundwater were likely to exceed the EU drinking water guideline value of  $0.5 \mu\text{g l}^{-1}$  on 35% of the arable land in the study area (*Figure 18*). Accounting only for the direct effects of climate change (scenario A), this area was projected to decrease to 31%, as estimated by the ensemble mean. The variation among the five climate models ranged from a decrease of the area at risk to 5% to an increase to 47%. Accounting for indirect effects of climate change, the area with simulated concentrations exceeding the guideline value increased to 50% (19-70%) in the case of scenario (B) (i.e. only considering changes in cropping patterns) and to 70% (50-80%), when a likely increase in herbicide use was also considered (scenario C). This suggests a doubling of the area at risk of groundwater contamination in the future compared to present-day climatic conditions.

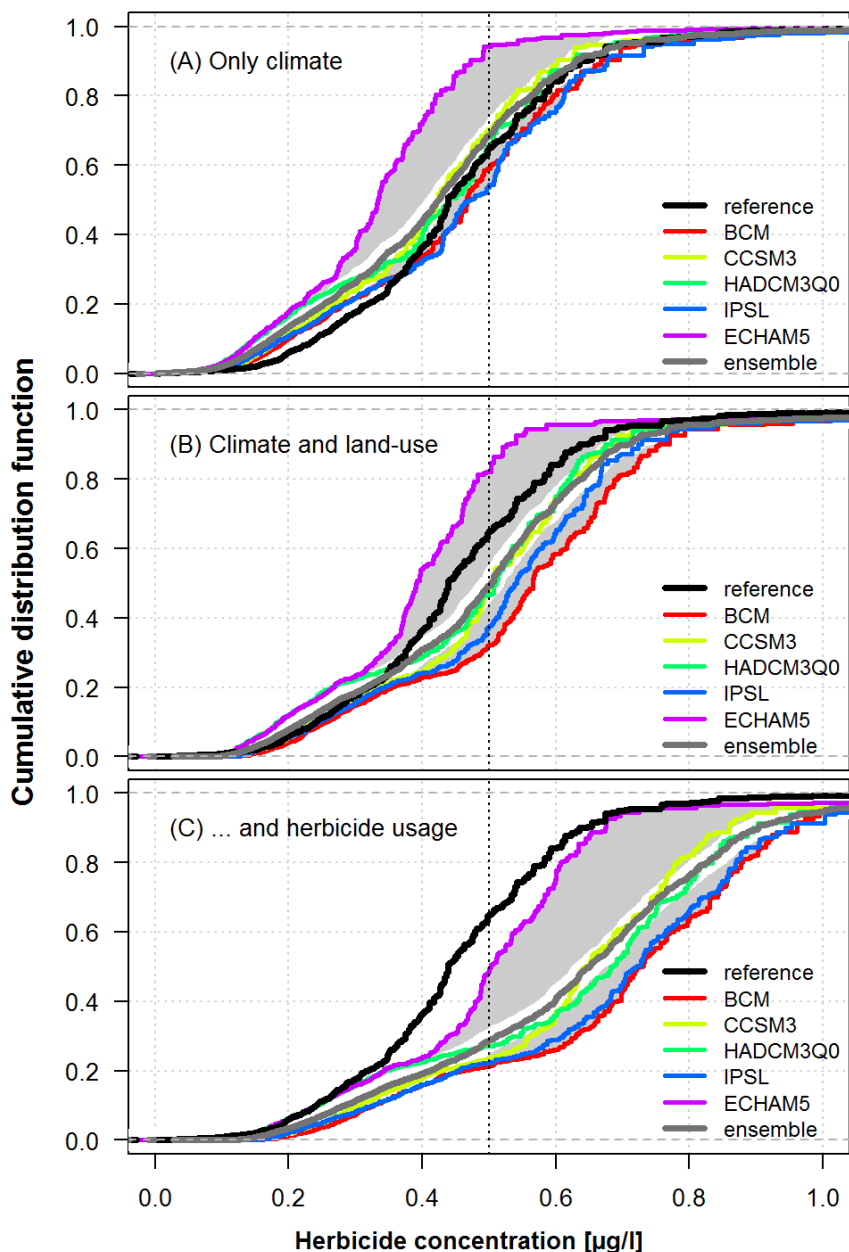


Figure 18. Spatial aggregation of the herbicide concentration in leachate for the entire simulated region (aggregated over each pixel) for the three future herbicide use scenarios analysed in paper III. Each curve represents the fraction of the arable land for which the herbicide leachate concentration is predicted not to exceed a certain threshold value (e.g. the EU drinking water guideline value of  $0.5 \mu\text{g l}^{-1}$ ). The area for which the concentrations might exceed that value can be calculated as  $1 - \text{“y-value”}$ . The ensemble prediction is calculated from the results obtained with the five future climate scenarios (see Table 3).

## 5.3 Uncertainties

### 5.3.1 Different Sources of Uncertainty

This thesis tried to disentangle the effects of some of the uncertainties inherent to modelling pesticide fate under climate change and to evaluate their relative importance. Papers I and II demonstrated that the level of uncertainty depended on the pesticide application scenario and on whether absolute losses were considered as output or predicted changes. For absolute pesticide losses, the effect of parameter uncertainty was large. Nevertheless, effects of model structural differences could still be identified. For predicted changes, the climate input uncertainty dominated, while parameter uncertainty was less important. This is also implied by the results of paper I, as the different structural model versions indicated the same direction of change for most of the PAS, even if the magnitude of change was clearly affected by the model version.

To assess the part of the *cascade of uncertainty* related to the generation of the climate scenarios, a limited analysis was performed based on the data used in paper II. It showed that the uncertainty arising from the choice of GCMs had a larger impact than the variation in emission scenarios or the natural variability represented by the variation in initial states of the GCM. Whether this was only due to the larger number of realisations (5 different GCMs, compared to 3 different GHG emission scenarios and 3 different initial states; see *Table 3*), was not further analysed. Nevertheless, it is in line with findings of studies in various fields of research (e.g. Dobler *et al.*, 2012; Kjellström *et al.*, 2011; Graham *et al.*, 2007b). Although the uncertainties due to the choice of the RCMs or the downscaling method can be high (e.g. Chen *et al.*, 2011), they were not analysed in this thesis. Those uncertainties are likely to add to the climate uncertainty, which would further strengthen the conclusion of paper II that the climate uncertainty is very important.

### 5.3.2 Uncertainties in Regional Scale Assessments

In the regional scale study, only climate input uncertainty was included, which showed the same patterns as in the field scale analysis (paper II): the direction and magnitude of change was strongly influenced by the climate models (*Figure 16*). The strength of the effect depended on soil type and for some areas in the region concentrations were always lower in the future for any climate scenario and any future herbicide use scenario.

Parameter uncertainty was not accounted for at the regional scale, although it must have an impact on the simulations. Accounting for uncertainty was shown to increase predicted concentrations, especially for high-percentile

concentrations of spatially aggregated data (Van den Berg *et al.*, 2012; Heuvelink *et al.*, 2010). Coquet *et al.* (2005) furthermore showed that simulations with average values for pesticide properties ( $K_{oc}$ ,  $DT_{50}$ ) taken from a database underestimated risks compared to regional scale simulations based on site-specific estimates of the pesticide properties. How different site-specific values for  $K_{oc}$  and  $DT_{50}$  can be compared to database values is illustrated for bentazone in *Figure 9*, where the values estimated as good predictors for the field site (weakly sorbed compound) are marked together with the bentazone parameterization used in the regional scale study. Nevertheless, experience from the field studies reported in Papers I and II suggests that predicted changes in pesticide leaching are more robust in the face of parameter uncertainty and should depend mainly on the climate scenario.

The contribution of uncertainty in  $DT_{50}$  values has been found to be larger than the contribution of  $K_{oc}$  or uncertainty in organic matter content, soil texture or hydraulic conductivity for regional scale uncertainty assessments with GeoPEARL (Heuvelink *et al.*, 2010). For MACRO-SE, this might be different, as macropore flow is considered, which may increase the relative importance of sorption strength, as discussed earlier (chapter 5.1.3), and of the parameters governing the exchange between matrix and macropores. PTFs describing the spatial variability in degradation and sorption developed by e.g. Ghafoor *et al.* (2013; 2011), Fenner *et al.* (2007) or Von Götz & Richter (1999) could be implemented in future studies.

Uncertainty and variability in the fractional coverage of crops also affects the spatial estimates of leaching risk (Balderacchi *et al.*, 2008). *Figure 19* illustrates the effect of accounting for detailed (catchment-scale) statistics on the spatial distribution of crops compared to applying average statistics for the entire region: the spatial variability increases, hot-spots are more frequent and the predicted risks are higher, when higher resolution input data is available. The average herbicide concentration in leachate increased from  $0.43 \mu\text{g l}^{-1}$  with average crop statistics (*Figure 19B*) to  $0.45 \mu\text{g l}^{-1}$  with detailed statistics (*Figure 19A* or *Figure 16A*). For higher percentiles of spatially aggregated values, the changes might be larger than for the mean or median values.

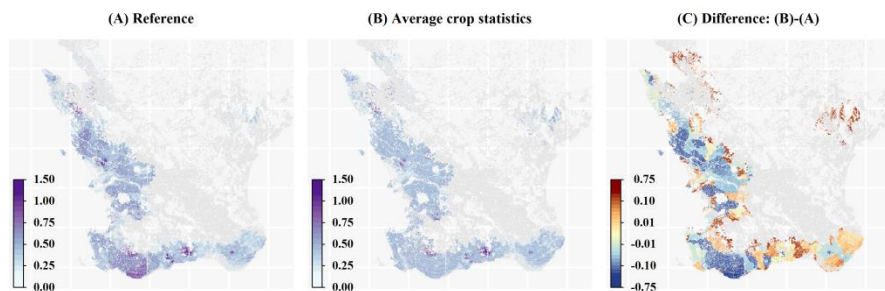


Figure 19. Effect of accounting for detailed catchment-scale crop statistics (A) in regional scale analysis as opposed to the use of average (more easily available) crop statistics (B) under present climatic conditions.

Uncertainty in pesticide usage will have large impacts in catchment or regional scale studies (Åkesson *et al.*, 2013; Kreuger & Törnqvist, 1998). The two catchments used in paper III to parameterize pesticide usage were rather representative for the entire GSS-region at least regarding the cropped area sprayed with herbicides and the fractional coverage of crops. To overcome constraints on the availability of input data for large scale assessments in the future, Miraglia *et al.* (2009) suggested exploring methodologies to derive actual pesticide usage information at the EU level and similarly, some Swedish authorities are discussing the possibility of collecting such information from the farmers (Moeys, J., pers. comm.). Detailed use information at a regional scale would certainly increase the reliability of predictive modelling exercises and reduce this type of epistemic uncertainty (Refsgaard *et al.*, 2013).

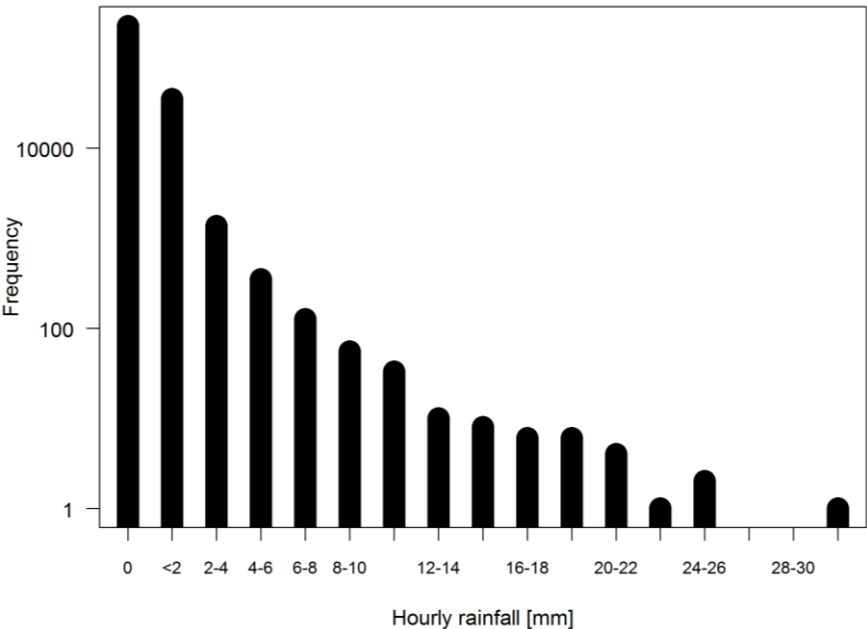
Uncertainties related to the scenarios chosen to represent future herbicide use are more difficult to analyse. It seems that the average increase in herbicide use (45%) was higher than the estimated 16 to 28% increase in pesticide use in the US (Koleva & Schneider, 2009), but within the range of estimates from Kattwinkel *et al.* (2011) on insecticide application rates in Europe (22% to 23-fold the current level). Although insecticide use might increase relatively more than herbicide use in Sweden, the estimated increases seem realistic considering that the changes in weed pressure will be higher at higher latitudes. Further uncertainties arise from the many direct and indirect effects that were not included in this thesis, which are difficult to quantify.

## 5.4 Other Potential Direct & Indirect Effects of Climate Change

The range of climate change effects that could be included in this thesis was limited due to computational and other technical constraints. In the following, I discuss a few additional aspects and factors that were not accounted for in the published papers and briefly discuss their implications.

### 5.4.1 Intensity and Frequency of Rainfall Events

Intensive rainfall events are very likely to become more frequent in a future climate (IPCC, 2012; Nikulin *et al.*, 2011; Christensen & Christensen, 2003). The delta-change approach used to generate future climate scenarios accounts for average changes in the monthly precipitation totals and changes the precipitation intensities accordingly. *Figure 20* presents a histogram of hourly rainfall for the reference climate of *Västra Götaland* (papers I and II) and *Table 8* gives the relative change in the frequency of hourly rainfall above a certain threshold for the different climate scenarios of paper II. Up to a threshold of 15 mm, the frequency of rainfall events increased by up to 97% depending on the climate scenario. The change in the frequency of rainfall events >20 mm was more uncertain, due to the small number of events, and ranged from -12% to +100% depending on the climate scenario.



*Figure 20.* Frequency distribution of hourly rainfall events under present climate conditions in *Västra Götaland* (reference time series in paper I and II).

Table 8. Relative change in the frequency of occurrence of hourly rainfall amounts above a certain threshold for all climate scenarios of paper II.

Climate Scenario	> 2 mm	>10 mm	>15 mm	>20 mm
CS1 (BCM)	+10%	+65%	+12%	+50%
CS2 (CCSM3)	+13%	+75%	+17%	-12%
CS3 (HADCM3)	+19%	+83%	+33%	+88%
CS4 (IPSL)	+22%	+97%	+33%	+100%
CS5 (ECHAM5-A1B-r1)	+17%	+75%	+12%	+50%
CS6 (ECHAM5-A1B-r2)	+21%	+95%	+33%	+25%
CS7 (ECHAM5-A1B-r3)	+12%	+83%	+21%	+62%
CS5 (ECHAM5-B1)	+ 9%	+49%	+ 4%	+/-0%
CS5 (ECHAM5-A2)	+18%	+87%	+21%	+25%

The method, however, did not change the number of days with rainfall and thus, did not account for changes in the length of wet and dry spells. For Swedish conditions, the likelihood of extended dry spells is rather low (Kjellström *et al.*, 2014) and, thus, this might not be overly important. Nevertheless, if the delta-change method overestimates the total number of rain days and/or underestimates potential drought periods, it is likely that pesticide losses will be underestimated because degradation rates would be reduced in drier soils and the days with rain would have relatively more intense rainstorms, which might trigger more macropore flow.

Another aspect is that the delta-change method cannot account for a change in the frequency distribution of rainfall events, which could mean a relatively larger increase in heavy rainfall events compared to the average increase in precipitation. According to recent projections with RCMs run at very high spatial resolution (1-3 km), high-intensity short-term rainfall event (convective rain showers) may increase even more in their intensity in a future warmer climate than previously projected (Kendon *et al.*, 2014). This would have most impact if these events occur close to the day of application.

The effect of randomly choosing another application date within the given 2-week application window, still applying pesticides on the same date under present and future conditions was tested as mentioned in paper II (see *Figure 21 WsSpr*). For the ensemble prediction of changes in pesticide losses from present to future, the effect seemed negligible. This should be the case for all compounds as weakly sorbed compounds are most strongly influenced by rainfall patterns shortly after pesticide application (McGrath *et al.*, 2010). An additional small test was performed, in which the application date for the different climate scenarios was varied. The effects of choosing the same date for present and future simulations or choosing different dates for different



climate scenarios were small for most pesticide application scenarios (Figure 21). Only for the weakly sorbed compound applied in spring, the uncertainty was higher, as expected from earlier studies (McGrath *et al.*, 2010). However, the general tendency towards a reduction in pesticide losses still held. This gives some indication of potential results obtained from simulations that account for changes in rainfall patterns around the date of application, which previous studies have shown to be important (e.g. Brown & van Beinum, 2009; Lewan *et al.*, 2009; Nolan *et al.*, 2008). Nevertheless, a more thorough investigation of the effect of changes in rainfall patterns would be valuable. This is especially important if the focus is on the risk of surface water contamination via runoff or sub-surface drains, especially for predictions of the maximum concentrations that are important for ecotoxicological effects, rather than average concentrations in the leachate.

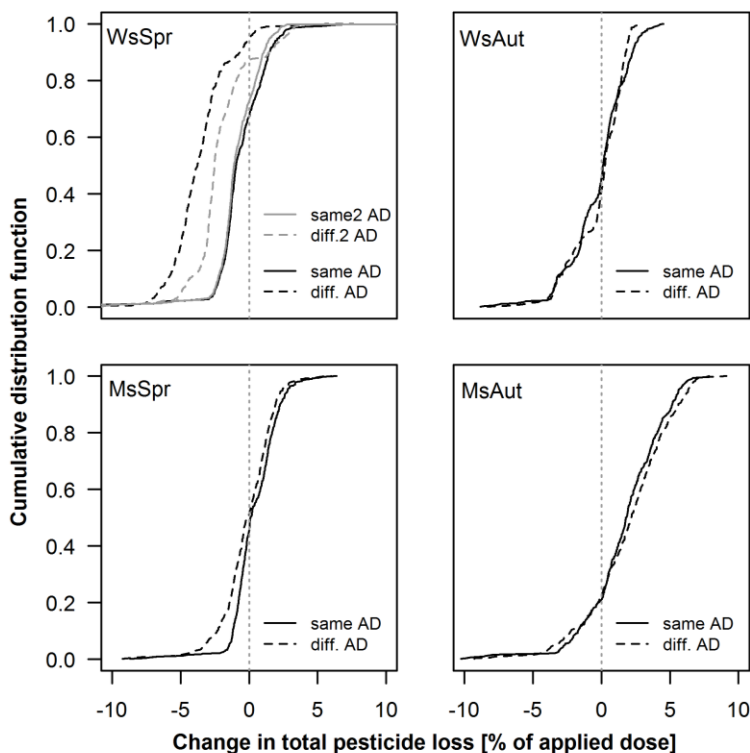


Figure 21. Effect of rainfall patterns around the day of application for the PAS of the weakly and the moderately sorbed compounds applied in spring and autumn (see Table 2). “same AD” denotes that the application date (AD) was the same for present and all nine climate scenarios. “diff. AD” denotes that the AD differed between the climate scenarios and the reference conditions. For the PAS of WsSpr, a second set of both, the case of identical AD as well as different AD was tested, which are shown in grey and marked as “same2” and “diff.2”.

### 5.4.2 Soil properties

The organic carbon content of the soil acts as a major sorbent for pesticides and thus reduces leaching (see also *Figure 15*). Changes in climate variables will have effects on the soil organic carbon content (see *Table 1*), which could be assessed using carbon turnover models (Lugato *et al.*, 2014; Jones *et al.*, 2005). Organic carbon content might decrease in a warmer climate due to increased turn-over of the organic matter, but this could be counteracted by a higher biomass production, which would lead to higher carbon inputs to the soil (Davidson & Janssens, 2006). A preliminary sensitivity test showed that the slight change (3%) in organic carbon content (predicted by Lugato *et al.*, 2014) had little effect on the predictions. Not surprisingly, more drastic changes in soil organic carbon content (-40%) would lead to significant changes in predicted leaching (+30%) as demonstrated by a comparison of similar FSTs, which mainly differ in their organic carbon coding<sup>4</sup>. Drastic changes in soil organic matter content are rather unlikely to occur purely as a result of the direct effects of climate change, but could possibly occur due to changes in land management practices (i.e. land-use, fertilization, drainage) that affect the soil organic carbon stocks, as shown by Karlsson *et al.* (2003) from long-term monitoring data in Sweden.

Changes in soil structure resulting from altered frequencies of freeze-thaw cycles and extended drought periods may also affect pesticide leaching in a changing climate (*Table 1*). This would have consequences for rapid leaching via macropores as shown experimentally by Beulke *et al.* (2002).

### 5.4.3 Land-use

A change in the area of land used for agriculture is another aspect which could have been included in this thesis (Kattwinkel *et al.*, 2011; Beulke *et al.*, 2007). In Sweden, the trend in the recent past has been a reduction in the area of arable land by 28% since the 1950s and by 10% since the 1980s, mainly due to afforestation and urbanization (SCB, 2013a). However, these trends are likely to slow down, at least in major agricultural areas such as Scania (Länsstyrelsen, 2015). Kattwinkel *et al.* (2011) assumed that the area of cultivated arable land in Scandinavia would increase in the future and identified this as a major factor for the projected increase in aquatic exposure to insecticides in Scandinavia in a future climate. Similar results could be expected for aggregated herbicide concentrations.

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<sup>4</sup> Average herbicide concentration for Y22n (0.4 µg l<sup>-1</sup>) compared to Y22u (0.53 µg l<sup>-1</sup>).

#### 5.4.4 Crop development

Changes in crop development were not accounted for in our study, despite strong evidence of significantly prolonged growing seasons (e.g. Trnka *et al.*, 2011), which would imply shifts in sowing and pesticide application dates (Olesen *et al.*, 2012; 2011). It is difficult to judge the importance of these factors, as climate change affects not only crop development and application timings, but also application amounts (Henriksen *et al.*, 2013; Beulke *et al.*, 2007).

Nevertheless, Beulke *et al.* (2007) identified a four-fold increase in the application rate as the major driver of increased maximum daily concentrations predicted for the herbicide mecoprop, despite 5 weeks earlier application in spring and 10 days earlier spraying in autumn. This gives support to the conclusions drawn from a limited preliminary sensitivity analysis to the work carried out in Paper III that changes in application rate are more important than changes in crop development or application timing. Furthermore, changes in application date would probably be small in relation to the uncertainty and spread in application dates at the catchment scale (up to 8 weeks for many crop-herbicide combinations), which reflects inter-annual climate variation, differences between soil types and the workload of farmers and sprayers (paper III, Fig. S5).

However, as the aggregated results were dominated by a few compounds and crops, shifts in application dates for compounds used on these crops could have a significant impact on the overall results. The direction of such changes would generally be towards increased losses, when pesticides are applied later in autumn (Lewan *et al.*, 2009). If pesticides are applied earlier in spring, the time for degradation is longer, which would reduce leaching losses. Nevertheless, as discussed earlier, losses are more sensitive to changes in the precipitation patterns around the date of application, which can lead to high losses and thus outweigh this effect, as demonstrated by Lewan *et al.* (2009).

#### 5.4.5 Pesticide compounds

It is rather likely that there will be new compounds available by the end of the century (e.g. Beulke *et al.*, 2007) as suggested by the history of chemical plant protection from the beginning of the 19<sup>th</sup> century until today (Delaplane, 1996). The future developments are very difficult to predict, but social and political pressures are unlikely to allow the registration of new compounds that have worse environmental impact than today's compounds. In this respect, the regional scale study can be considered a worst-case business-as-usual scenario analysis for herbicide concentrations in leachate. The current trend in many

parts of Europe is towards farming with fewer pesticides as a result of EU-legislation (Hillocks, 2012).

The introduction of low-dose compounds in the 1980s/1990s resulted in reduced amounts of pesticides used in agriculture (see also SCB, 2013b). However, the total sold amounts of pesticides relative to the arable land in Sweden have slightly increased since the early 1990s partly due to an increase in area cultivated with cereals at the expenses of fallow land (SCB, 2013b). A limited analysis of the temporal trends of the median doses for different herbicides in the two monitoring catchments used in paper III showed that the changes were not very large for most compounds during the last 20 years. However, for a few compounds, the median dose did actually decrease during this period (e.g. florasulam used on spring cereals, ethofumesate and chloridazone used on sugar beets), which might suggest that the overall trend is towards applications with lower doses. In the case of sugar beets, it might be correlated to an increase in the spraying frequency, but this was not further analysed.

## 5.5 How Representative are these Results?

The field study was a rather extreme worst-case scenario with 8.5% of the applied herbicide lost to drains, which is considerably higher than typical losses to tile drains (<1%; Brown & van Beinum, 2009). Earlier studies showed that high leaching losses can occasionally occur (up to 10.6%; Brown & van Beinum, 2009) and can certainly be expected from such soils with no-till practice (e.g. Gish *et al.*, 1991).

The conclusions that can be drawn from the field scale studies on the effect of temperature dependent sorption depend on the studied compound and their thermodynamic behaviour as well as the soil type. As most pesticides sorb to soils with exothermic reactions (e.g. ten Hulscher & Cornelissen, 1996), these results are probably rather representative for most pesticides. The sorption enthalpy, for which suitable values from the range given in Spurlock (1995) were used, determined the magnitude of the effect of temperature on sorption and with a less negative value, a smaller effect would have been observed. As the binding mechanisms are very complex in reality and probably vary over time, it would be necessary to conduct specific experiments to obtain more specific parameters, which is not feasible for a general study such as this. Nevertheless, these results should give some indications of trends for a wide range of pesticide-soil combinations, which can be useful to discuss uncertainty in the modelling of pesticide leaching under climate change.

The results in this thesis are specific to pesticide leaching to surface water via tile drains and to groundwater and might not hold for other transport pathways (e.g. surface runoff), as other factors might dominate the losses than those analysed here. For paper III, the aggregated results (predicting total herbicide concentrations) are specific to the climate and climate change signals, the distribution of soil types, crops and the herbicides included in the study and are thus not easily transferable to other regions. Including all the soils of the GSS region in the study would have probably only affected the results to a minor extent. The soils that were excluded were mainly fine-textured (*Figure 8*) and would, therefore, be likely to contribute to leaching, but they contributed less than 3% of the total area, which might have overshadowed their overall impact at a regional scale. However, the field-scale-results presented in *Figure 15* may indicate general trends and could be transferred to other regions to guide mitigation measures, even if they have different climate conditions, soils, cropping and application patterns. For regions in Sweden with a larger proportion of heavy clay soils, the risk might even increase without any changes in land-use or pesticide usage, although these soils mostly pose a risk to surface waters via drainage, with the field site in Papers I and II being one example.



## 6 Conclusions

- Accounting for different sources of uncertainty reduces the risk of drawing overconfident conclusions (e.g. regarding the direction of change in pesticide losses in a future) and makes the assessment more robust.
- The relative importance of different sources of uncertainty depends on pesticide properties, application season and whether the focus is on absolute values or predicted changes. For changes in pesticide losses in the future compared to present conditions, the uncertainty in climate input dominated, which emphasized the need for ensemble modelling.
- The indirect effects of climate change need to be considered alongside the direct effects, as the predictions can be significantly affected: The area at risk of groundwater contamination in southern Sweden was only slightly affected by direct effects of climate change, but was projected to double due to changes in land-use and pesticide use (indirect effects) in a future climate.
- Currently vulnerable areas with medium to high clay contents might become even more vulnerable in the future as relative changes in leachate concentration were positively correlated with soil clay content.
- The key factors determining pesticide losses under climate change may differ between the field scale and larger scales.
- Implementation of strict regulations and improved mitigation measures will be required to protect current and future drinking water resources in a changing climate.





## 7 Implications and Future Research

This thesis has demonstrated what would happen if the likely increase in weed and pest pressures under future climate conditions in Sweden were mainly controlled by an increased use of pesticides: the area at risk of groundwater contamination would strongly increase. Despite the myriad uncertainties inherent in the modelling of pesticide leaching under climate change, there is enough evidence to claim that mitigation strategies to reduce risks of groundwater and surface water contamination are necessary to protect current and future drinking water resources.

### 7.1 Mitigation Measures to Reduce Pesticide Leaching Risks

Mitigation strategies for surface water contamination include measures that reduce spray drift, the implementation of surface runoff and erosion controls (Holvoet *et al.*, 2007) and the use of constructed (artificial) wetlands (Vymazal & Březinová, 2015; Gregoire *et al.*, 2009) to remove pesticides from agricultural drainage and runoff. Feasible mitigation measures for drainage and leaching pathways are reductions in pesticide application rates, product substitutions (see also Miraglia *et al.*, 2009) and changes in the timing of pesticide applications (Reichenberger *et al.*, 2007). Paper III suggests that product substitution may be highly effective, as the simulated total concentration in leachate was dominated by only a few substances. The low contribution of winter cereals to overall herbicide leaching risks could be an indicator that reductions in application dose can have significant effects on regional scale herbicides leaching risks, too.

Several management strategies that protect the crops but reduce pesticide use could be adopted: Adaptation in the farming system such as improved crop rotations (Balderacchi *et al.*, 2008) or inter-cropping; improvements of biological and mechanical plant protection methods in line with recent EU-directives on integrated pest management practices; crop breeding and bio-

technological methods, which produce crops that are resistant to pests (Phipps & Park, 2002); precision farming techniques or guided and targeted pest control with the help of (electronic) warning systems for farmers (Holvoet *et al.*, 2007). At regional scales, such measures could be most efficient if they are applied to the crops that were identified as major contributors to pesticide leaching risks, such as sugar beets and winter rape in the case of southern Sweden in a climate change perspective.

Regional scale modelling, as reported in this thesis, can be used to identify vulnerable areas, which could be used by regulatory authorities to restrict or permit the use of particular pesticides in certain areas (Balderacchi *et al.*, 2008) aiming at a reduction in the overall pesticide use in a region. It can further be used to guide monitoring and might help to distinguish point-sources from non-point sources (Balderacchi *et al.*, 2008) and thereby improve the targeted measures.

## 7.2 Future Research Topics

Many additional questions could be further developed and analysed in the field of climate change impacts on pesticide leaching. Here, I summarize some ideas including some of those that have already been discussed in this thesis.

### *Changes in precipitation patterns*

One essential aspect is to analyse the effect of changes in precipitation patterns, i.e. changes in rainfall frequency and in extremes. As several authors have pointed out, the timing of precipitation events in relation to the application timing is an important factor for losses to surface water via tile-drains or surface runoff (McGrath *et al.*, 2010; Lewan *et al.*, 2009; Nolan *et al.*, 2008). Furthermore, climate studies suggest that the frequency of heavy rainfall events is increasing, especially of short-term heavy rainfall events (Kendon *et al.*, 2014); probably beyond what can be handled with the delta-change method applied in this thesis (Teutschbein & Seibert, 2013; Nikulin *et al.*, 2011). This would require identifying a suitable downscaling or bias correction method that accounts for such changes (e.g. Olsson *et al.*, 2012). As the uncertainty due to GCMs often overshadows the uncertainty related to, for instance, the downscaling methods (e.g. Dobler *et al.*, 2012), an ensemble of GCMs should be included in the analysis rather than testing different downscaling methods.

### *Field scale analysis with MACRO*

With respect to paper I, it would be interesting to analyse the impact of accounting for temperature dependent sorption (and diffusion) on other soil

types. This would help to evaluate the importance of these processes at larger scales.

Furthermore in order to perform a complete uncertainty analysis at the field scale, a longer experiment with equally comprehensive measurements would be required. A minimum of two to three years of continuous measurements (or several periods with at least one year of continuous measurements) would be needed for a split-sample analysis (as e.g. discussed in Jarvis & Larsbo, 2012) for which one part of the measurements (at least one year) is used to calibrate the model (as in paper I & II) and the remaining measurements are used to validate the model.

#### *Regional scale risk assessments (MACRO-SE)*

MACRO-SE could be used for several interesting additional studies. One idea would be to do a similar study but for surface water contamination. This requires the implementation and testing of a surface runoff and erosion routine. This kind of study would also greatly benefit from suitably downscaled rainfall time series that account for changes in rainfall frequency and intensity as runoff is often generated in heavy rainfall events (Holvoet et al., 2007; Wauchope, 1978). An extension to such a study would be to combine the exposure assessment with ecotoxicological models or indicators (such as toxic units; see Bundschuh et al., 2014) to evaluate the ecological impacts of changes in climate (Kattwinkel et al., 2011; Noyes et al., 2009).

The risk of pesticide losses at any location depends on soil type, pesticide properties and pesticide use, but also on the climate. Thus, risk assessment can be improved by using high-resolution spatially-variable climate data, especially rainfall data. For projections into the future, the climate scenarios should account for the spatial correlations between climate variables.

A complete uncertainty analysis with MACRO-SE that includes the effects of the uncertainty in soil and pesticide properties (similar to Van den Berg et al., 2012) or due to PTFs (similar to Stenemo & Jarvis, 2007) would be interesting, but incredibly demanding of computer resources. An assessment of the effects of spatial variability of sorption and degradation processes (e.g. Ghafoor et al., 2013; 2011) would also be valuable. It could also be worthwhile to perform a more comprehensive sensitivity analysis that disentangles effects of climate change that were not considered here, such as changes in organic carbon content and crop development/application timing and evaluates further scenarios that account for mitigation strategies (e.g. substance substitution or halving of pesticide use).



## 8 Sammanfattning (Swedish Summary)

Klimatförändringar kommer sannolikt att medföra ökad temperatur och nederbörd i Sverige. Ett varmare och blötare klimat kommer att öka trycket av ogräs och skadegörare, vilket i sin tur kan innebära en ökad användning av kemiska bekämpningsmedel. Syftet med denna avhandling var att belysa hur klimatförändringar kan komma att påverka bekämpningsmedelsläckaget från svensk åkermark baserat på dagens (1970-1999) och framtidens (2070-2099) klimat. För att beräkna pesticidläckage via dräneringsvatten på fältskala användes en dynamisk simuleringmodell (MACRO) som beskriver nedbrytning och transport av pesticider i mark som funktion av klimat-data. Betydelsen av olika osäkerhetskällor i beräkningskedjan för simulerade pesticidkoncentrationer och förändringar i pesticidutlakning analyserades. För att även belysa betydelsen av indirekta effekter av klimatförändringar, dvs ändringar i areell fördelning av olika grödor och i pesticidanvändning, på herbicidläckaget till grundvatten, användes en regionaliserad modellversion (MACRO-SE).

Resultat från studierna på fältskala visade att valet av modellstruktur påverkade simulerade pesticidförluster, trots att parameterosäkerheten var stor. Parameterosäkerheten hade större betydelse för beräknade absolutvärden (pesticidförluster) än för beräknade relativa förändringar. Effekten av osäkerheter i klimatdata hade däremot större betydelse för beräknade förändringar i pesticidförluster (i dagens klimat jämfört med framtida klimat). Riktning och storlek i simulerade förändringar i pesticidförluster berodde på ett komplext samspel mellan pesticidegenskaper, tidpunkt för bekämpning och val av klimatscenario. På regional skala var emellertid de direkta effekterna av förändringar i klimatet marginell, medan de indirekta effekterna hade stor betydelse för beräknade pesticidförluster till grundvattnet. Förväntade klimatrelaterade förändringar i grödor och pesticidanvändning resulterade i en fördubbling av den areal inom vilken risken för kontaminering av grundvattnet överskred EU:s gränsvärd för dricksvatten.

Slutsatser från denna studie är att (1) den relativa betydelsen av olika osäkerhetskällor beror både på pesticidegenskaper, spridningstidpunkt och om fokus ligger på absoluta pesticidförluster eller relativa förändringar av förlusterna, (2) osäkerheten i klimatscenario-data bör beaktas för att kunna göra robusta bedömningar (t ex genom s.k. "ensemble modelling") och (3) indirekta effekter av klimatförändringar bör beaktas i kombination med de direkta effekterna för att resultaten inte ska bli missvisande. Oavsett de stora osäkerheter som är en naturlig del av beräkningar baserat på olika typer av scenarier, understryker resultaten i denna avhandling behovet av effektiva åtgärder och strategier för att minimera risken för grund- och ytvattenkontaminering i en förändrad klimatsituation.

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