



Modelling of pesticide emissions for Life Cycle Inventory analysis: Model development, applications and implications

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Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Dijkman, T. J., Birkved, M., & Hauschild, M. Z. (2013). Modelling of pesticide emissions for Life Cycle Inventory analysis: Model development, applications and implications. Department of Management Engineering, Technical University of Denmark.

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Modelling of pesticide emissions for Life Cycle Inventory analysis: model development, applications and implications

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PhD Thesis
October 2013

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PREFACE

This PhD thesis presents the work conducted in the project ‘Modelling of pesticide emissions for Life Cycle Inventory analysis: model development, applications and implications’ at the Division for Quantitative Sustainability Assessment of the Department of Management Engineering, at the Technical University of Denmark. Supervision was provided by associate professor Morten Birkved and professor Michael Zwicky Hauschild.

The PhD project was conducted from September 2010 to October 2013 and included a stay at the New Zealand Plant and Food Research Ltd. in Hamilton (New Zealand), under supervision of dr. Karin Müller.

The main part of this thesis is based on four scientific articles, one of which has been published. The three others are manuscripts that will be submitted in the next months. These papers are included as appendices to this thesis. Throughout the thesis these papers are referred to by the numbers given below.

1. Dijkman, T.J., Birkved, M., Hauschild, M.Z. (2012) PestLCI 2.0: A second generation model for estimating emissions of pesticides from arable land in LCA, *International Journal of Life Cycle Assessment* 17(8): 973-986.
2. Birkved, M., Dijkman, T.J., Hauschild, M.Z. (2013) Modelling of pesticide emissions from fields in LCA: An inventory or an impact assessment task? *Manuscript*.
3. Dijkman, T.J., Müller, K., Green, S.R., Birkved, M. (2013) Spatial variations in pesticide emissions from kiwifruit orchards in New Zealand, *Manuscript*.
4. Dijkman, T.J., Birkved, M., Saxe, H., Wenzel, H., Hauschild, M.Z. (2013) Comparative attributional LCA of barley cultivation in Denmark under current and future climatic conditions, *Manuscript*.

This PhD project is part of the research program ‘Development of genetically modified cereals adapted to the increased CO₂ levels of the future’, funded by FødevarerErhverv.

ACKNOWLEDGEMENTS

When I started my PhD in September 2010, I knew little about Life Cycle Assessment other than its general principles (cradle to grave - holistic - functional unit) and the classic comparison of paper, plastic and ceramic coffee containers. In the last three years I have gained a lot of insight in the methodology and application of LCA, as well as in its strengths and weaknesses. I would like to say thanks to everyone from whom I learnt during my PhD studies...

I would like to thank my supervisors Morten Birkved and Michael Hauschild for their help, ideas and feedback over the course of the last three years. Also thank you to my supervisor in New Zealand, Karin Müller, for her help with defining and carrying out the kiwifruit project, and for showing me around in NZ.

I would like to thank all of my past and current colleagues at QSA, for the nice working environment, the movie and game nights with bad pizza and trips here and there that quickly made me feel at home in Denmark, and for the interesting discussions about LCA and sustainability in general.

Some of the best experiences during my PhD time may be more indirectly related to LCA, but are nevertheless things that I find worth to mention here. I'd like to say thanks to Joe Lane for the invitation to come to the pesticide flow modelling workshop in Brisbane and taking me to Mt Coot Tha and Lone Pine Koala Sanctuary; to Steve Green for taking me on a trip to dig down fluxmeters in kiwifruit orchards (after ending up at an apple growers' scientific conference) including a stop on SH5 for the most breathtaking view on the night sky I've ever had; and to Peter Fantke for the invitation to come to Stuttgart and discuss the integration of our models, a meeting from which I learnt a lot.

Finally, I'd like to thank Maj-Britt for listening, putting things in perspective and for being the wonderful person you are.

SUMMARY

The work presented in this thesis deals with quantification of pesticide emissions in the Life Cycle Inventory (LCI) analysis phase of Life Cycle Assessment (LCA). The motivation to model pesticide emissions is that reliable LCA results not only depend on accurate impact assessment models, but also good emission inventories. Recent LCA studies of agricultural products that take toxicity impacts into account show that pesticide emissions considerably contribute to toxicity impacts. At the same time, such conclusions are derived using a simplified approach to quantify pesticide emissions.

The research presented in this thesis centers around PestLCI 2.0, a model to calculate pesticide emissions to air, surface water and groundwater for use in LCI. PestLCI2.0 is an updated and expanded version of the PestLCI model, released in 2006. The boundaries between ecosphere and technosphere in the model are defined by a 'technosphere box', which includes the arable land where the pesticide is applied, the field soil up to 1 meter of depth and the air column above the field up to 100 meter. When a pesticide leaves this box, it is considered an emission. The model works with a primary distribution, where the pesticide is deposited on the crop, on soil or emitted due to wind drift, followed by secondary processes that determine the pesticides' fate.

In PestLCI 2.0, most fate process modelling has been updated, most notably the modelling of pesticide volatilization from leaves and pesticide runoff. The model was expanded by the inclusion of macropore flow, which leads to pesticide emissions to groundwater. Moreover, PestLCI 2.0s databases with active ingredients, climates and soils were updated, broadening the applicability of the model to European circumstances. A case study showed that emissions vary with variations in the climates and soils present in Europe.

Emissions of pesticides to surface water and groundwater calculated by PestLCI 2.0 were compared with models used for risk assessment. Compared to the MACRO module in SWASH 3.1 model, which calculates surface water emissions by runoff and drainage, pesticide emissions to surface water calculated by PestLCI 2.0 were generally higher, which was attributed to differences in the modelling approach between the two models. The model comparison for emissions to groundwater showed that PestLCI 2.0 calculated higher emissions than

FOCUSPEARL 4.4.4 (modelling chromatographic flow of water through the soil), which was attributed to the omission of emissions via macropore flow in the latter model. The comparison was complicated by the fact that the scenarios used were not fully identical.

In order to quantify the implications of using PestLCI 2.0, human toxicity and freshwater ecotoxicity impacts obtained with two inventory approaches were compared. The first approach was PestLCI 2.0, the second is the currently prevalent approach (the Ecoinvent approach), which assumes that 100% of the applied mass is emitted to agricultural soil.

For both impact categories it was found that the PestLCI approach results in impacts that on average are three orders of magnitude lower. This conclusion was found to be valid for characterization of the impacts with both USEtox and US-ES-LCA 2.0 characterization factors.

The difference observed between these approaches will have implications for the comparison of toxicity impacts between conventional and organic agriculture. However, the difference in pesticide use and the corresponding environmental impacts is only one of the many aspects that are relevant to assess when discussing sustainability of both types of agriculture. A second implication from these findings is that the contribution of pesticide emissions to the overall toxicity impacts of agricultural products may be lower than what is currently found in LCA studies.

Since the PestLCI and Ecoinvent approaches differ in both their ecosphere-technosphere boundary setting and in the modelling of fate processes within the technosphere, a hybrid approach was also used to calculate toxicological impacts. This approach combined the fate modelling of the PestLCI approach with the technosphere boundaries of the Ecoinvent approach. The toxicological impacts of this approach showed that it is the technosphere boundaries, rather than the in- or exclusion of fate processes, that determines the differences observed between the PestLCI and Ecoinvent approaches. This technosphere-ecosphere boundary is impossible to define objectively in the case of LCAs of agricultural products: it depends on the practitioners' values what is environment and what is man-made production system. Therefore it is advisable to discuss what LCA should aim to protect, instead of where the boundary should be located.

The first of the two applications of PestLCI 2.0 presented in this thesis is the case of pesticide emissions in conventional kiwifruit cultivation in the Western Bay of Plenty district in New Zealand. For nine scenarios, based on different combinations of local soils and climates, pesticide emissions were calculated with PestLCI 2.0 and subsequently characterized with characterization factors obtained using USEtox. The emissions to air showed little variation between the nine assessed scenarios. Emissions to surface water and groundwater showed larger variations. Despite this, the differences in the freshwater ecotoxicity and human toxicity for the nine scenarios were small. In an LCA context, when considering uncertainties in emission modelling and impact assessment, these differences probably are not relevant. For all nine scenarios, it was found that emissions of cyanamide dominated the toxicological impacts.

A second application of PestLCI 2.0 was in the comparison of the environmental impacts of barley cultivation in Denmark under current (2010) and future (2050) climatic circumstances. The functional unit of this study was 1 kg of barley at the farm gate. Using an attributional approach, impacts of co-products were handled by economic allocation. Impact assessment was done with ReCiPe (hierarchist perspective), except for toxicity impacts, which were characterized using USEtox. The differences between four scenarios, based on combinations of wet and dry climates, and sandy and sandy loam soils, for barley cultivation under current climatic conditions were found to be small. Differences in impacts between cultivation in current and future climatic conditions were concluded to be mainly driven by differences in grain yield. The use of economic allocation was found to be a key issue, since the price levels of 2050 can't be predicted with any reasonable certainty.

Although PestLCI has been updated and expanded, further improvements are still possible. A number of improvements and suggestions to increase the model's applicability are discussed. These suggestions focus on both the fate modelling (for example wind drift, degradation and volatilization from leaves) and the boundary setting of the model.

RESUMÉ

Arbejdet præsenteret i denne afhandling omhandler kvantificering af pesticid-emissioner i Life Cycle Inventory (LCI) analysefasen af en livscyklusvurdering (LCA).

Motivationen for at modellere pesticidmissioner er at pålidelige LCA resultater ikke kun afhænger af præcise modeller for miljøeffekter fra emissioner men også gode emissionsopgørelser (inventories).

Nylige LCA studier af landbrugsprodukter der medregner betydningen af toksicitet viser at pesticidmissioner bidrager betydeligt til den samlede toksiske miljøeffekt. Disse konklusioner er dog fremkommet ved brug af en simplificeret tilgang til kvantificering af pesticidmissioner.

Forskningen præsenteret i denne afhandling er centreret om PestLCI 2.0. PestLCI 2.0 er en model til at beregne pesticidmissioner til luft, overfladevand og grundvand til brug i LCI.

PestLCI 2.0 er en opdateret og udvidet version af PestLCI modellen, der blev lanceret i 2006. Grænserne mellem økosfære og teknosfære i modellen er defineret ved en ”teknosfæreboks”, som inkluderer landbrugsarealet hvortil der tilføres pesticider, landbrugsjorden ned til en meters dybde og kolonnen af luft over jordoverfladen op til 100 meter. Når et pesticid forlader denne boks betragtes det som en emission. Modellen arbejder med en primær distribution, hvor pesticidet deponeres på afgrøden eller jorden eller emitteres via luftstrømme. Den primære distribution efterfølges af sekundære processer, som bestemmer pesticidets endelige skæbne.

I den nye udgave af PestLCI 2.0 er modelleringen af de fleste skæbneprocesser opdateret, særligt modelleringen af pesticidfordampning fra blade og pesticidudvaskning. Modellen er blevet udvidet ved inkludering af makroporestrømning som fører til pesticidudvaskning til grundvand. Desuden er databasen med aktivstoffer, klimatyper og jordprofiler opdateret i PestLCI 2.0, hvilket øger anvendeligheden af modellen til europæiske forhold. Et case studie på PestLCI 2.0 viste at emissionerne fra et aktivstof varierer med de klima og jordtyper der findes i Europa.

Emissioner af pesticider til overflade- og grundvand beregnet med PestLCI 2.0 blev sammenlignet med modeller, der anvendes til risikovurdering. Sammenlig-

net med MACRO modulen i SWASH 3.1 modellen, var emissionerne til overfladevand beregnet med PestLCI 2.0 generelt lavere, hvilket kan forklares ved forskelle i modelleringsmetoden. Sammenligningen mellem modeller for emissioner til grundvand viste at beregninger med PestLCI 2.0 giver højere emissioner end FOCUSPEARL 4.4.4, hvilket blev forklaret ved udeladelsen af emissioner via makropore strømninger i sidstnævnte model. For begge sammenligninger gælder dog at de ikke er optimale da scenarierne der blev anvendt ikke var identiske.

For at kvantificere konsekvensen af at bruge PestLCI 2.0 til at beregne pesticid-emissioner fremfor den nuværende gængse tilgang (Ecoinvent tilgangen), som antager at 100 % af den påførte masse afgives til landbrugsjorden, blev resultaterne for human toksicitet og ferskvands økotoksicitet sammenlignet. For begge påvirkningskategorier blev det fundet at PestLCI tilgangens resultater i gennemsnit er tre størrelsesordener lavere end Ecoinvent tilgangens resultater. Denne konklusion var gældende for karakteriseringen af mikljøeffekter for såvel USEtox som USES-LCA 2.0 karakteriseringsfaktorer.

Den observerede forskel mellem disse tilgange har betydning for sammenligningen af toksiske miljøeffekter fra konventionelt og økologisk landbrug. Dog er forskellen i pesticidforbrug og den tilsvarende miljøpåvirkning kun en af flere aspekter der er relevante at undersøge i diskussionen af bæredygtigheden af begge typer landbrug. En anden betydning af resultaterne er bidraget af pesticid-emissioner til de overordnede toksiske miljøeffekter af landbrugsprodukter kan være lavere end hvad der på nuværende tidspunkt er fundet i LCA studier.

Da PestLCI og Ecoinvent tilgangene adskiller sig i både grænserne mellem økosfære og teknosfære og i modelleringen af skæbneprocesser indenfor teknosfæren, blev en hybridmetode også udviklet til at beregne de toksikologiske effekter. Denne hybridmetode kombinerede skæbnemodellering fra PestLCI tilgangen med teknosfæregrensene fra Ecoinvent tilgangen. De toksikologiske effekter af denne tilgang viste at det er teknosfæregrensene snarere end in- eller eksklusio- nen af skæbneprocesser der er afgørende for de observerede forskelle mellem PestLCI og Ecoinvent. Der er ikke muligt at definere teknosfæregrensene i LCA af landbrugsprodukter da det kommer an på hvad LCA brugere definerer som miljø og produktionssystem. Derfor anbefales det at diskutere hvad en LCA skal designes til at beskytte fremfor hvor grænsen skal sættes.

Den første af de to anvendelser af PestLCI 2.0, der er præsenteret i denne afhandling, omhandler pesticidemissioner fra konventionel kiwi dyrkning i Western Bay of Plenty distriktet i New Zealand. For ni scenarier baseret på forskellige kombinationer af lokale jordprofiler og klimatyper, blev pesticidemissioner beregnet med PestLCI 2.0 og efterfølgende karakteriseret med karakteriseringsfaktorer udledt ved brug af USEtox. Emissionerne til luft viste lav variation mellem de ni undersøgte scenarier. Emissionerne til overfladevand og grundvand viste større variationer. På trods af dette, var forskellene på ferskvands-økotoksicitet og human toksicitet små for de ni scenarier. Når usikkerheder i emissionsmodellering og effektmodellering betragtes i LCA kontekst er disse forskelle sikkert ikke af betydning. For alle ni scenarier blev det fundet at emissionen af cyanamid dominerede de toksiske effekter.

En anden anvendelse af PestLCI 2.0 var en sammenligning af miljøpåvirkningen af bygdyrkning i Danmark under nuværende (2010) og fremtidige (2050) klimabetingelser. Den funktionelle enhed i dette studie var 1 kg byg ved gårdporten (farm gate). Ved anvendelse af en attributional tilgang, blev biprodukter håndteret ved økonomisk allokering. Vurderingen af miljøeffekter blev udført med ReCiPe (hierarkisk perspektiv) med undtagelse af toksiske effekter som blev karakteriseret ved brug af USEtox. Forskellene mellem fire scenarier baseret på kombinationer af våde og tørre klimaer samt sand og sandet lerjord for byg dyrkning under nuværende klimabetingelser var små. Forskellene i effekter mellem dyrkning under nuværende og fremtidige klimabetingelser blev konkluderet at være drevet primært af forskelle i kornudbytte. Anvendelsen af økonomisk allokering blev fundet problematisk da prisniveauerne for 2050 ikke kan forudsiges med rimelig sikkerhed.

Selvom PestLCI er blevet opdateret og udvidet er det stadig muligt at lave yderligere forbedringer. Et antal forbedringer og forslag til at øge modellens anvendelighed er diskuteret. Disse forslag fokuserer både på skæbnemodellering (fx. emissioner via luftstrømme, nedbrydning og fordampning fra blade) og definitionen af modellens grænser.

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LIST OF ABBREVIATIONS

aLCA	Attributional Life Cycle Assessment
CF	Characterization factor
ERA	Environmental Risk Assessment
GMO	Genetically Modified Organism
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory analysis
LCIA	Life Cycle Impact Assessment
WBOP	Western Bay of Plenty region (New Zealand)

1 INTRODUCTION

1.1 CONTEXT AND OBJECTIVES OF THE PHD PROJECT

Life Cycle Assessment (LCA) is a holistic, comprehensive tool to analyze the environmental impacts of products and systems. One of its intended applications is decision support (International Standard Organization, 2006a). It was exactly for this application that the work presented in this thesis was funded, as a part of the larger project 'Development of genetically modified cereals adapted to the increased CO₂ levels of the future'. This research project aimed at developing a barley crop specially well adapted for the higher atmospheric CO₂ concentrations of the future with higher zinc and protein content through investigating zinc uptake into the grain, studying nitrogen use efficiency and mapping the availability of barley varieties with elevated protein content. As a part of the project, LCA as well as other environmental assessment methodologies was intended to be applied to explore the sustainability aspects of the introduction of a genetically modified crop (hereafter referred to as GMO) by comparing the environmental impacts of the GMO with the impacts of a conventional barley crop.

In order to compare the sustainability aspects of the different barley crops, my research was originally planned to consist of two parts. The first part is the expansion, update and validation of the PestLCI model, a model to calculate emissions of pesticide to air, surface water and groundwater. The model is to be used in the Life Cycle Inventory (LCI) phase of an LCA, in which all inputs from, and outputs to the environment from a product's life cycle are compiled. Improvements of the model would allow for accurate calculation of pesticide emissions from an agricultural field, for example a field on which barley is cultivated: the second part of the project. In this second part an LCA of barley cultivation in Denmark under current and future climatic conditions would be carried out for two crop variants: conventional barley and GMO barley. This part of the project was intended to contribute to a balanced picture of the advantages and disadvantages of the introduction of GMO crops in Danish agriculture. Practice did not follow planning, so this second part of my project took another shape as was foreseen in September 2010. An opportunity arose to test PestLCI under New Zealand circumstances. At the same time the development of the GMO barley turned out to take more time than foreseen, so my research set-up for the barley LCA had to be more or less completely reworked. In addition to these changes,

there was some time to reflect on the PestLCI framework and boundary settings applied in LCA practice.

Looking back at the past three years of research, the work done in the context of this PhD project has focused on a number of objectives, all in various degrees related to the assessment of pesticide emissions in agricultural LCA:

- to develop an LCI model, PestLCI 2.0, in order to calculate of pesticide emissions to the environment, to be applicable under European circumstances (paper 1).
- to validate the pesticide emission model by comparing it to other (risk assessment) models (paper 1, 3).
- to apply the PestLCI 2.0 model to estimate pesticide emissions in kiwifruit cultivation in New Zealand, thereby helping to develop a ‘toxicity footprint’ of kiwifruit growing (paper 3).
- to apply PestLCI 2.0 in the case of barley cultivation in Denmark, under both current and future climatic circumstances (paper 4).
- to discuss the technosphere-ecosphere boundary setting used in LCA, with a focus on the case of pesticide emission modelling in agricultural LCA (paper 2).

As can be seen from this list of objectives, the results of the research are communicated to the scientific community through four scientific, peer-reviewed papers.

1.2 CONTENT AND STRUCTURE OF THE PHD THESIS

The contents of this thesis are mainly based on the papers that have been written during the course of the PhD project, though without necessarily repeating all contents from these papers. In addition some of the contents draw upon presentations given at conferences and workshops. In some chapters, new results are presented.

This thesis tries to summarize the work done in the course of the PhD project, applying the PestLCI 2.0 model as a red thread. The thesis is built up as follows. Chapter 2 starts with a description of PestLCI 2.0. The motivation and context for the development of the model is discussed, as well as the boundary setting and framework of the model. The improvements done to the model and its validation are subsequently discussed. The second chapter closes with suggestions

for further improvements of the model. This second chapter covers the model development, which can be seen as the foundation upon which the following parts of the project were built. Before building on this foundation, I will in chapter 3 take a step back and subject the foundation to a closer inspection: does the choice of boundary between product system and environment, upon which the model is based, actually make sense? And what happens if we choose the boundaries differently? The next two chapters are based on results obtained using PestLCI 2.0. Chapter 4 describes the application of the model in the calculation of pesticide emissions in kiwifruit cultivation in New Zealand. In a similar fashion, chapter 5 describes a second application of PestLCI 2.0: in an attributional LCA of barley cultivation under current and future climatic circumstances. This thesis then finishes with an overall conclusion and outlook. The journal papers upon which the chapters in this thesis are based, are found in the appendices.

2 MODEL DEVELOPMENT: CURRENT APPROACHES IN PESTICIDE LCI AND THE PESTLCI APPROACH

2.1 CONTEXT: PESTICIDE EMISSIONS MODELLING IN LCA

2.1.1 WHY MODEL PESTICIDE EMISSIONS?

A considerable number of the agricultural LCA case study articles published in the *International Journal of Life Cycle Assessment* in the period from 2010 to late August 2013, did not consider toxicity impacts arising from pesticides (e.g. Bessou *et al.*, 2013; Dressler, Loewen & Nelles, 2012; Muñoz, Milà i Canals & Fernández-Alba, 2010; Torellas *et al.*, 2012). Bessou *et al.* (2013) state that the toxicity of pesticides is not assessed because there is a lack of knowledge about how pesticides are distributed over environmental compartments: one good reason to model the fate of pesticides.

Other publications that consider toxicity impacts, do unfortunately not always discuss the origins of these impacts (Amores *et al.*, 2013), whilst Schmidt (2010) mentions pesticides as one of the main contributors to toxicity impacts. The same conclusion is drawn by Nemecek *et al.* (2011), based on the assumption that all of the applied pesticide is emitted to soil: a second reason to model pesticide emissions. After all, only an accurate overview of how much pesticides end up in which environmental compartment will allow drawing such a conclusion.

A final argument for modelling pesticide emissions is that reliable LCA results depend on both accurate Life Cycle Inventories (LCI) and accurate Life Cycle Impact Assessment (LCIA). Recent LCIA methods such as USES-LCA 2.0 (Van Zelm, Huijbregts & Van de Meent, 2009) and USEtox (Rosenbaum *et al.*, 2008) already provide characterization factors for a selection of pesticides. It is therefore important that reliable LCI data, describing the processes that occur before emission of the pesticide, are available as well.

2.1.2 CURRENT MODELLING OF PESTICIDE INVENTORIES

Since most LCA practitioners use databases to provide LCI data, it is worth considering how three commonly used databases deal with pesticide inventories.

Starting with the Ecoinvent database (Ecoinvent centre, 2007), it is assumed that the complete mass of pesticides applied is emitted to agricultural soil (Nemecek & Kägi, 2007). No reason is given for this assumption. This approach leaves the modelling of the pesticide fate inside and outside the field after emission to agricultural soil to fate modelling in impact assessment, and thus limits the development of spatially differentiated pesticide emission inventories. In the US LCI database (NREL, 2003) emissions are normally split between air and surface water. Emissions to air typically account for 96% of the emissions, though for some pesticides in some processes this percentage may be a few percent points more or less. As was the case in the Ecoinvent approach, the summed mass of emissions in the US LCI database equals the mass of pesticide applied. Ecoinvent and the US LCI database differ in the emission compartments: in the first approach, the fate of a pesticide once emitted to the field depends on the characterization model, whilst in the US LCI database 100% of the mass of applied pesticide is assumed to leave the field. Finally, in the Danish LCI Food database (Nielsen *et al.*, 2003) pesticides are not considered.

Obviously, these approaches are simplifications to which a number of objections can be raised. One of such objections is that processes that occur between pesticide release from the spray equipment and deposition on soil (Ecoinvent) or release to water and air (US LCI database) are not considered. In the time between release and emission a pesticide may undergo fate processes such as degradation or volatilization. In the space between spray nozzle and emission compartment air and plants are present, where other fate processes may occur. Moreover, these fate processes depend on local circumstances (Kroner *et al.*, 2004), as well as on pesticide characteristics (Jensen, Spliid & Svensmark, 2007). By assuming a fixed emission factor to a certain environmental compartment, spatial and chemical differences are ignored. In order to avoid this, it is necessary to model pesticide fate before emission to the environment.

2.1.3 THE PESTLCI APPROACH

The first version of PestLCI, hereafter called PestLCI 1, was published in 2006 (Birkved & Hauschild, 2006). This model calculated emissions to air, surface water and groundwater and was based on a boundary between technosphere and ecosphere defined by a so-called technosphere box, or field box. This box contained the field where the pesticide was applied, the soil down to 1 meter below this field, and the air column above the field up to 100 meter height. These dimensions were chosen because degradation of pesticides in soil was assumed not

to occur at depths below 1 meter, so that a pesticide reaching that depth would (at some point in time) reach the groundwater. An air column of 100 meter was included to make sure that aerial application of pesticides would be a process occurring in the technosphere.

From this technosphere description it follows that the crop which was to be protected, as well as other plants growing in the field and the field soil were considered part of the technosphere. In other words, the agricultural field is considered a biological production system, with a man-made nature. This boundary setting can be discussed, which will be done in chapter 3.

The technosphere setting also dictates the emission compartments that are included in the model: the only pathways available for a pesticide to move out of the technosphere box are through air, or via surface water or groundwater. Emissions to soil are not possible, for there is no pathway directly leading from air, soil, or water within the technosphere to soil outside the technosphere. This does not mean that pesticides will not end up in soil in the ecosphere, but these pathways have to be considered in LCIA modelling.

PestLCI 1 had a number of limitations, which led to the development of PestLCI 2. First of all, the model was limited to Danish circumstances. PestLCI 1 used a Danish climate profile, had included a Danish soil profile and the pesticide database consisted of pesticides that were approved for use in Denmark. Since in LCA most product systems are international, often global, this Danish scope was too narrow and limiting the use of the model outside Denmark. In addition it also did not allow for comparison of pesticide emissions on different locations, which may be relevant when moving towards more site-specificity in LCA. Second, the model did not cover macropore flow, which can quickly transport pesticides to deeper soil layers (Kördel, Egli & Klein, 2008) and these pores may therefore result in larger emission of pesticide to surface water or groundwater. Third, due to programming in Microsoft Excel, the model was not very transparent for the user. To overcome these limitations, PestLCI 2.0 was developed. The details of this model version are given in paper 1. Here the main updates will be described.

2.2 METHOD

This section describes the updates of PestLCI, the methods used for model validation as well as a case study about spatial variability of pesticide emissions.

2.2.1 PESTLCI 2.0: FRAMEWORK AND UPDATES

PestLCI 2.0 is based on the technosphere-ecosphere boundary setting described above, which is unchanged from PestLCI 1.

The model works with primary and secondary fate processes. Primary processes are the processes that occur directly after pesticide application. These processes determine how much pesticide is deposited on the crop and on topsoil, as well as how large a fraction is emitted to air due to wind drift. Secondary processes are the fate processes that occur on the crop surface and on the topsoil, here defined as the first 1 cm of soil. These processes determine the fate of the pesticide. An overview of these secondary processes is given in Figure 2.1.

On leaves, three fate processes are considered: degradation, uptake into leaves, and volatilization which results in an emission to air. In the topsoil, degradation and volatilization are considered as well. At the moment of the first rainfall after pesticide application, the pesticide residues on the crop are assumed to wash off to the topsoil. Together with the pesticide remaining on topsoil this mass is subject to runoff and macropore flow. The mass of pesticide then remaining is assumed to start leaching downward through the subsoil. In the subsoil, degradation takes places. In case a drainage system is applied, a fraction of the pesticide

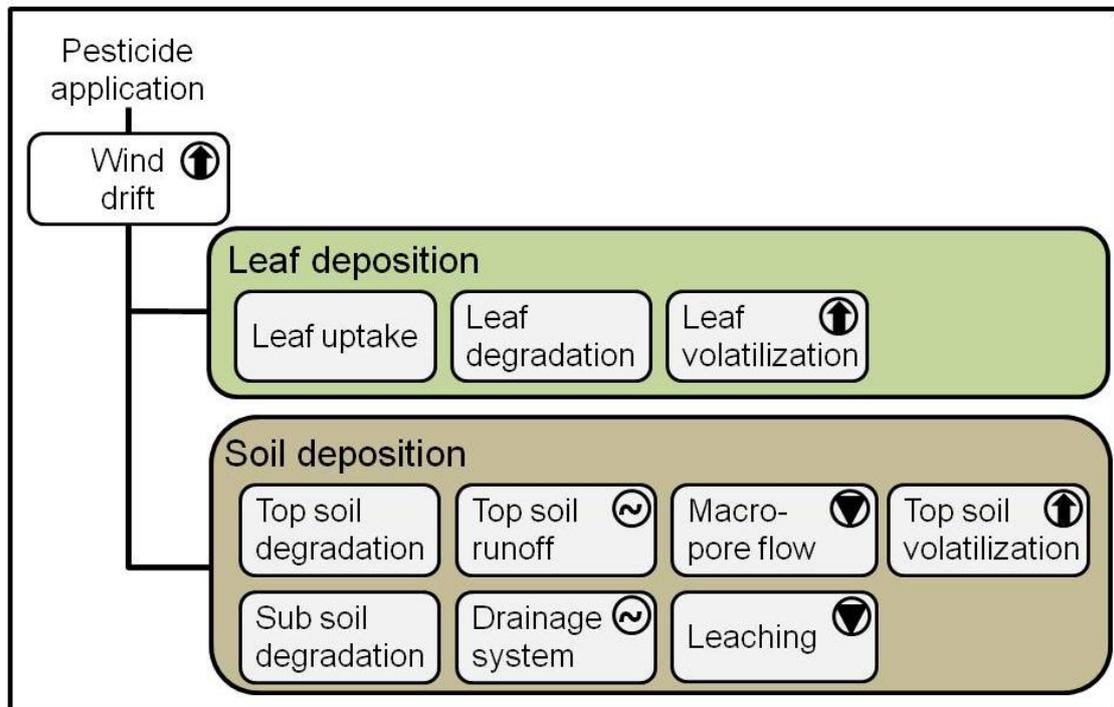


Figure 2.1: Overview of the PestLCI model framework. Emissions to air are indicated with an upward arrow, emissions to surface water with a tilde and emission to groundwater with a triangle. Other processes remove the pesticide from the system.

is intercepted by the drainage, leading to an additional emission to surface water. Once a pesticide reaches a depth of 1 meter in the soil, it is assumed to be emitted to groundwater.

In the development of PestLCI 2, several of the fate processes were updated. Starting with wind drift, additional wind drift curves were introduced, based on the IMAG drift calculator (Holterman & Van de Zande, 2003). These curves did not replace, but supplement the curves included in PestLCI 1. The reason for introducing these additional curves was that they covered a broader range of crops than the ones included in the first version of the model.

Regarding the secondary processes taking place on the leaves, mainly small modifications were done: new regressions were made for the degradation and uptake data used in PestLCI 1. A new approach for volatilization from the leaves was introduced. In the PestLCI 1 approach a pesticide was assigned a volatilization rate constant based on its air-water distribution coefficient K_{aw} . In total three rates of volatilizations were present, each covering a given range of K_{aw} s. The new approach was based on a regression of volatilization rates against vapour pressures by Van Wesenbeeck, Driver and Ross (2008). The advantage of this approach is that it provides a continuous relation between vapour pressure and volatilization. The new approach better reflects the differences between chemicals. Application of the model showed however, that this approach overestimated volatilization of volatile (vapour pressure $>10^{-3}$ Pa) chemicals. Therefore, in paper 3 another approach to calculate the volatilization from leaves was introduced, based on a regression of volatilization data reported by Guth *et al.* (2004). Here a fixed volatilization rate was assumed for pesticides with a vapour pressure below 10^{-6} Pa. The volatilization rate then increases with increasing vapour pressure up to a maximum so that no more than 80% of an applied dose is volatilized within 24 hours.

The modelling of fate processes occurring in soil has been changed to various degrees. The calculation of biodegradation was modified only slightly: a new equation was introduced for calculation of the biodegradation rate's dependence on the temperature, and the topsoil temperature was no longer assumed to be the same as the air temperature. The calculation of volatilization from soil was adapted to a higher degree. It was simplified compared to the PestLCI 1 approach by means of using a fugacity level 3 model, based on the Surface soil model by Mackay (2001). This simplification can be justified by the fact that volatilization

from soil typically makes up only a very small part of the total emissions to air. Another update was that the partitioning of ionic pesticides in soils was made pH-dependent in PestLCI 2.0, reflecting that the degree of dissociation of these pesticides depends on the acidity of the topsoil.

For runoff, a new equation was introduced so that runoff can now be calculated for all rainfall intensities. In PestLCI 1, this was only possible when the precipitation was more than 17 mm per precipitation event.

Finally, the concept of pesticide leaching via macropores was introduced to the model. Macropores are structures that are mainly formed in structured soils such as silt and clay soils. When such a structured soil dries or when organisms, for example rain worms, are active, pores with a relatively large diameter are formed. These pores form a 'bypass' for dissolved pesticides, making them reach the groundwater considerably faster than what would be expected when flow through the soil matrix was the only path available (Kördel, Egli & Klein, 2008). Because macropore flow may be an important contributor to groundwater emissions, it is relevant to include it in PestLCI. Macropore flow was modelled using a 'tipping bucket'-approach in which the soil is split in four domains. The first three domains are formed by the pores in the soil matrix. In the first of these soil matrix domains the water does not flow, and these parts therefore have little relevance for pesticide emissions. In the other two domains the water moves through the pores, but at different rates. The final domains are made up by the macropores. In the applied approach, it is assumed that the rain water will first fill up the pores in the domain where the water can not flow. Afterwards the pores where water slowly flows are filled. Only when the water holding capacity of these domains is exceeded, will rain water enter the macropores. Based on the amount of rainfall and the intensity of rainfall, an average fraction of rainfall is assumed to enter macropores. In this water, an amount of pesticide is dissolved, potentially leading to a direct emission to groundwater. In the first version of PestLCI 2.0, presented in paper 1, it was assumed that all pesticides that engaged in macropore flow would be emitted to groundwater. In later versions of the model (from version 2.0.6), used in the other papers on which this thesis is based, it was assumed that only a fraction of the macropores directly results in emissions to groundwater. This fraction was fitted to 0.1. Moreover these versions of the model assumed a fixed macroporosity for soils (3% of the soil volume).

Since the tillage method has an effect on macropore formation, the model users are given different options regarding tillage.

The PestLCI 1 modules used for the other processes occurring in the soil (i.e. degradation, fresh water emissions by drainage, and pesticide leaching towards groundwater), were not changed for inclusion in PestLCI 2.0.

Finally, some of the databases of PestLCI were expanded in order to broaden the model scope from Denmark to Europe. The coverage of chemicals was increased with 20 active ingredients to approximately 90. The added active ingredients were selected on basis of their appearance in a ranking of most widely sold pesticides in Europe in the period 1999-2003 (Eurostat, 2007), which were the most recent data available at the time the database was updated. The Danish climate profile included in PestLCI 1 was replaced with 25 profiles covering the 16 European climate zones distinguished in the FOOTPRINT project (Centofanti *et al.*, 2008) with up to three sets of climate data per climate zone. The soil database was expanded with seven European soil profiles with different compositions. These were selected from the Spade Database (European Communities, 2010) on basis of varying clay, silt and sand contents, in order to cover a wide range of likely soil compositions.

2.2.2 VALIDATION OF PESTLCI 2.0

MCPA emissions calculated by PestLCI 2.0 were compared with 2 models used in Environmental Risk Assessment (ERA). Surface water emissions were compared with the MACRO module contained in SWASH 3.1 (Alterra, 2009). Groundwater emissions calculated by PestLCI 2.0 were compared with FOCUSPEARL 4.4.4 (RIVM, PBL and Alterra, 2011). MCPA is a phenoxy herbicide that was selected for this case study because it is among the most sold pesticides (measured in kg active ingredient) in Danish agriculture (Miljøstyrelsen, 2012).

The properties of MCPA inserted to all models were the same, though some models needed data not required for other models. However, soil and climate data present in the risk assessment models were, apart from a single exception, not included in PestLCI and vice versa. Therefore the most similar soil and climate profiles were chosen.

2.2.3 CASE STUDY: SPATIAL AND TEMPORAL VARIABILITY OF PESTICIDE EMISSIONS

In order to illustrate the spatial variability in pesticide emissions, a total of nine MCPA emission scenarios were run, combining three climate sets and three soil

profiles. The exact description of these scenarios can be found in paper 1. In short, the compared climate data correspond to Temperate Maritime, Continental 2 and Mediterranean 1 climates in the FOOTPRINT terminology. These climates will be referred to as DK, HU and GR, respectively, since the data used in PestLCI 2.0 are taken from weather stations in Denmark, Hungary and Greece. The three soils used in the case study are the ones with a relatively high sand content, a high clay content and an ‘average’ soil, the composition of which is close to the average sand, silt and clay contents found in the SPADE database. In order to obtain a fair comparison, all other parameters were kept the same.

2.3 RESULTS AND DISCUSSION

Here, the results of the validation of PestLCI 2.0 and the case study will be described. Moreover, suggestions for further improvements of the model are discussed.

2.3.1 COMPARISON WITH RISK ASSESSMENT MODELS

Table 2.1 presents a summary of the results from the comparisons of MCPA emissions between PestLCI 2.0 and the respective risk assessment models. The results have been taken from paper 1. More details on the results can be found in this paper.

These results show that the results found by PestLCI for surface water emissions are generally lower than those found by SWASH. The reason for this is twofold. Firstly, SWASH is a model developed for ERA. In contrast to LCA, which aims at modelling ‘average’ situations, ERA aims at modelling realistic worst-case scenarios. Secondly, not all input parameters to the models, especially the soil data, were identical for both soil types. As a consequence, the outcomes should not be expected to be identical. So whilst the first reason suggests why the surface water emissions calculated by PestLCI are generally lower, the second indicates that the results should not be expected to match each other exactly. On the other hand, comparing the results may give an indication of how accurate PestLCI is.

Table 2.1: Comparison of pesticide emissions to surface water and groundwater, calculated by PestLCI 2.0 and the indicated ERA models

Surface water			
Scenario	SWASH 3.1	PestLCI 2.0	Ratio SWASH:PestLCI 2.0
1	$3.06 \cdot 10^{-2}$	$2.20 \cdot 10^{-4}$	139
2	$2.74 \cdot 10^{-3}$	$1.60 \cdot 10^{-4}$	17
3	$1.03 \cdot 10^{-3}$	$9.30 \cdot 10^{-5}$	11
4	$1.00 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$	0.50
Groundwater			
Scenario	PEARL 4.4	PestLCI 2.0	Ratio PEARL:PestLCI 2.0
1	$2.08 \cdot 10^{-3}$	$2.10 \cdot 10^{-3}$	0.99
2	$2.72 \cdot 10^{-3}$	$3.80 \cdot 10^{-3}$	0.72
3	$1.53 \cdot 10^{-3}$	$6.10 \cdot 10^{-3}$	0.25
4	$5.80 \cdot 10^{-4}$	$6.10 \cdot 10^{-3}$	0.095
5	$2.47 \cdot 10^{-4}$	$4.40 \cdot 10^{-3}$	0.056
6	$4.35 \cdot 10^{-5}$	$3.90 \cdot 10^{-3}$	0.011

Since the inputs to PEARL and PestLCI also were not completely identical, no identical results should be expected here, but still the results can be taken as an indication of the validity of the model. From Table 2.1 it can be seen that the surface water results calculated by PestLCI are typically higher than those found by PEARL. This is explained by the fact that the scenarios used in the PEARL simulations did not consider macropore flow. In addition, the macropore flow observed in PestLCI seems to be in the higher end of measured emission to groundwater due to macropores (Kördel, Egli & Klein, 2008). Therefore, emissions via macropores may therefore be overestimated in the model version used in paper 1.

A limitation of this comparison of models is that it is done for a single compound, MCPA. Running the models for a number of pesticides might have resulted in a better ground for concluding on the validity of PestLCI 2.0. A second limitation was that there are no models available to cover emissions to surface water and groundwater at the same time, let alone a model that includes all the three emission pathways included in PestLCI.

Despite the differences observed between PestLCI 2.0 on the one hand, and the ERA models on the other hand, it was concluded that the match between the models was acceptable. The differences between the ERA models and PestLCI typically were up to one order of magnitude. If this is considered as the uncertainty of the results, then these are similar or lower than those observed in characterization factors such as those calculated by USEtox (Rosenbaum *et al.*, 2008).

2.3.2 CASE STUDY: SPATIAL AND TEMPORAL VARIABILITY OF PESTICIDE EMISSIONS

The results for the comparison of emissions to air, surface water and groundwater for different European climates and soils are presented in Table 2.2.

Table 2.2 shows that the difference between the lowest and highest emissions to air is a factor 1.1. For surface water emissions, the difference is larger: the highest emission is 67 times the lowest emission. For emissions to groundwater, the difference lies in between the values found for air and surface water. The highest emission to surface water is 7.8 times the lowest emission. Hence the variation in emissions to air and groundwater for MCPA is less than 1 order of magnitude. The same conclusion can be drawn for the majority of surface water emissions.

Table 2.2: Overview of MCPA emissions to air (f_{air}), surface water (f_{sw}) and groundwater (f_{gw})

climate		DK	
Soil	sand	average	clay
f_{air}	$1.89 \cdot 10^{-2}$	$1.89 \cdot 10^{-2}$	$1.89 \cdot 10^{-2}$
f_{sw}	$1.39 \cdot 10^{-5}$	$3.43 \cdot 10^{-4}$	$4.04 \cdot 10^{-4}$
f_{gw}	$1.22 \cdot 10^{-3}$	$1.64 \cdot 10^{-3}$	$4.10 \cdot 10^{-3}$
climate		HU	
Soil	sand	average	clay
f_{air}	$1.97 \cdot 10^{-2}$	$1.97 \cdot 10^{-2}$	$1.98 \cdot 10^{-2}$
f_{sw}	$2.22 \cdot 10^{-4}$	$7.88 \cdot 10^{-4}$	$9.45 \cdot 10^{-4}$
f_{gw}	$2.86 \cdot 10^{-3}$	$3.79 \cdot 10^{-3}$	$9.48 \cdot 10^{-3}$
climate		GR	
Soil	sand	average	clay
f_{air}	$2.06 \cdot 10^{-2}$	$2.06 \cdot 10^{-2}$	$2.07 \cdot 10^{-2}$
f_{sw}	$1.97 \cdot 10^{-4}$	$7.15 \cdot 10^{-4}$	$8.58 \cdot 10^{-4}$
f_{gw}	$2.59 \cdot 10^{-3}$	$3.44 \cdot 10^{-3}$	$8.60 \cdot 10^{-3}$

It was concluded that emissions to air are mainly related to the air temperature, which affects the rate of volatilization. This explains why the air emissions are lowest in the DK scenario and highest in the GR scenario. Wind drift losses are not dependent on temperature. During application the active ingredient is formulated, so that droplets are spread. The main factor determining the emissions is in this case not the pesticide properties, but rather the characteristics of the spray equipment (Carlsen, Spliid & Svensmark, 2008). Surface water emissions in turn were found to depend on both climatic and soil factors, with the soil parameters explaining most of the variation. Relevant climatic parameters are precipitation amount and precipitation frequency. The important soil parameters are the soil type and the pH. The parameters that were found to be relevant for surface water emissions were also determining the emission to ground water. These conclusions were supported by a sensitivity analysis of the model.

The results here show that the spatial variation of pesticide emissions typically is less than one order of magnitude. For paper 1, the results were calculated for only one pesticide (MCPA). The sensitivity analysis of paper 2 however showed that also for other pesticides the emissions typically are within one order of magnitude. However, emissions of active ingredients with different properties to the environmental compartments can differ with a few orders of magnitude.

2.3.3 SUGGESTIONS FOR FURTHER IMPROVEMENTS

The fact that PestLCI 2.0 has been published, does not mean that there are no more improvement possibilities for the model. In this section some suggestions for further improvement will be discussed, starting with a number of suggestions for improvement of the modelling of the pesticide fate processes, followed by three suggestions to make the model wider applicable.

Focusing more on the fate process modelling done in PestLCI 2, there are a few options for further development of the model. Starting with wind drift, the wind drift curves currently used in the model are equations designed to calculate which fraction of applied active ingredient, usually in drops of the formulated pesticide, is deposited on off-field soil. In PestLCI, these curves are used to calculate emissions to air. Looking at the technosphere box defined in PestLCI, this is correct: when drifting away from the field, the active ingredient crosses the field border while being airborne. However, considering that most of this pesticide will be deposited shortly afterwards, and that this process is specific to pesticides and therefore (currently) not covered by LCIA methods, it might be recommendable to consider the fraction of pesticide that is subject to wind drift as an emission to soil. This means that the technosphere borders of PestLCI have to be modified, or that a temporal aspect has to be introduced. When modelling volatilization from leaves, the regression used has proved to result in very high volatilization results for compounds with a high ($>10^{-2}$ Pa) vapour pressure. It may be that the regression is not adequate for these high vapour pressure cases. Although the new approach introduced in paper 3 resulted in lower volatilization of chemicals with these high volatilization rates, the modelling of this fate process is something that has to be looked into. Perhaps an approach that is based on the physics of the volatilization process instead of on a regression of experimental data is a way forward. Another conclusion from paper 3 was that PestLCI 2.0 overestimates the degradation rate on leaves. Since degradation is a reaction that takes place at the same time as volatilization to air and uptake into leaves, these reactions are competing. If one reaction rate is overestimated, then the others will as a conse-

quence be underestimated. Therefore, the overestimation of degradation will result in underestimation of emissions to air due to volatilization. This observation was also made in paper 3, when comparing emissions to air calculated by PestLCI 2.0 to emissions calculated by The Soil-Plant-AtmoSphere MOdel (SPAS-MO) developed for modelling water, nutrient and agrochemical flows under New Zealand circumstances. Therefore, the modelling of degradation on leaves may be reconsidered. One option here would be to start the modelling from foliar half lives instead of the photodegradation-based approach currently used. Finally, the current pesticide database covers less than 100 compounds even though many more compounds are approved for use in Europe. Therefore, substance coverage can be improved.

One improvement to increase the appeal of the model may be to develop a version which allows for running more than one scenario at a time. At the moment, each scenario needs to be run individually, which makes calculating a large number of scenarios a time-consuming task. A second improvement would be to couple the model to a geographic information system (GIS). For example, if climate and soil input data could be taken from GIS instead of using the predefined data in the PestLCI databases, more spatially differentiated emission patterns could be generated. Thirdly, the current and previous versions have the boundaries between technosphere and ecosphere set as discussed in section 2.3. In contrast to these boundary settings, some impact assessment methods, such as for example ReCiPe (Wegener Sleeswijk *et al.*, 2008), consider agricultural soil as an environmental compartment, and pesticides emitted to agricultural soils contribute to terrestrial ecotoxicity. In order to increase the compatibility of PestLCI with different LCIA methods, it may therefore be desirable to develop a model version which allows for a user-defined technosphere boundary setting. This allows the user to choose the boundary setting required for the LCIA method he is working with, or to set the boundaries in a way that reflect what he thinks is part of the environment, instead of being limited by the technosphere - ecosphere boundary set by the model. Choosing system boundaries and the consequences of such choices in terms of the implications on the magnitude of environmental impacts will be discussed further in chapter 3.

In conclusion: even though PestLCI 2.0 is an improvement compared to the first version, there is still plenty of room for improvement and expansion.

2.4 CONCLUSION

The development of PestLCI 2.0 resulted in a model which calculates emissions to air, surface water and groundwater. The updates of the model compared to the first version of PestLCI comprised of reworked modelling of a number of fate processes, the addition of pesticide leaching to groundwater via macropores, expansion of the model's pesticide, climate, and soil databases as well as a shift to another modelling platform. The model was compared to models used in risk assessment. In addition, it was shown that pesticide emissions to air, surface water and groundwater depend on the location where the pesticide is used. A number of improvements and expansions of PestLCI 2.0 are suggested.

3 IMPLICATIONS: COMPARISON OF THE PESTLCI FRAMEWORK WITH OTHER PESTICIDE EMISSION INVENTORY APPROACHES

3.1 INTRODUCTION

In the previous chapter a number of Life Cycle Inventory (LCI) approaches were mentioned. In comparison to the PestLCI approach, the Ecoinvent and the US LCI database approaches are relatively simple in the sense that they assume that pesticide properties or local circumstances do not influence the fate of a pesticide in the field, as well as ignoring processes occurring before the pesticide is emitted to the environment. This latter assumption leads to pesticide emissions that amount to 100% of the mass of applied pesticides.

After presenting PestLCI 2.0 in chapter 2, an obvious question is whether the additional modelling of pesticide fate as done for PestLCI is actually relevant for Life Cycle Assessment (LCA) practice. In other words: how much do toxicological impacts actually change when calculating these impacts using PestLCI 2.0, instead of using, for example, Ecoinvent?

The most straightforward way to answer this question was to simply calculate toxicological impacts. The results of the calculations were presented in paper 2, with additional work presented at the SETAC Europe 23rd Annual Meeting (Glasgow, May 2012). Whilst in paper 2 results for both human toxicity and freshwater ecotoxicity were presented, this chapter focuses on the freshwater ecotoxicity solely. The reason for this is twofold: the results for both toxicity categories were similar and this thesis does not aim at repeating the papers it was based upon.

3.2 METHOD

In order to determine the importance of the choice of LCI approach on environmental toxicity impacts, three LCI approaches were compared.

The first approach is the one used in the widely used LCI database Ecoinvent (Ecoinvent centre, 2007). It is here used as the approach to which the other two approaches presented here are compared. This approach is based on an eco-sphere-technosphere boundary which seems to be located at a location between the nozzles of the spray equipment and the agricultural field soil. No fate processes are considered prior to emission to environment. In this approach it is assumed that 100% of the applied mass of pesticide is emitted to the environment. In the rest of this chapter, this approach will be called ‘Ecoinvent approach’.

The PestLCI approach applies PestLCI 2.0 (paper 1) to calculate emissions to various environmental compartments. As described in chapter 2, the ecosphere-technosphere boundary setting is based on the ‘technosphere box’ containing the agricultural field with the crop, the soil up to a depth of 1 meter and the air column above it up to 100 meter height. Inside this technosphere box the pesticide fate processes occurring from release from the sprayer to emission or removal via degradation and uptake are modelled, yielding emission fractions to air, surface water and groundwater. This approach will be referred to as ‘PestLCI approach’ throughout this chapter.

The third approach, hereafter called ‘hybrid approach’, is a hybrid between the Ecoinvent and PestLCI approaches. Its technosphere-ecosphere boundary setting is based on the PestLCI technosphere box concept, but with removal of the soil from the technosphere. Instead the soil is considered part of the ecosphere, as in the Ecoinvent approach. Within the technosphere fate processes are considered. As a consequence of the technosphere boundary settings, the emission compartments differ from both the Ecoinvent and the PestLCI approach. Compared to the PestLCI approach, soil has been moved from the technosphere to the ecosphere, and has now become an emission compartment, substituting surface water and groundwater: a pesticide molecule can’t be emitted to surface water or groundwater without first entering the soil inside the technosphere. Air remains an emission compartments since wind drift and volatilization emissions are taken into account. Table 3.1 summarizes the approaches considered.

Table 3.1: Overview of LCI approaches for pesticide emissions applied in this chapter

Approach	Ecoinvent	PestLCI	Hybrid
Consideration of technosphere fate processes?	No	Yes	Yes
Emission compartments	Soil	Air Surface water Groundwater	Air Soil

In order to go from pesticide emission inventories to toxicological impacts, characterization factors (CF) for the relevant emission compartments were used. In paper 2, impacts were calculated using two Life Cycle Impact Assessment (LCIA) approaches. In one approach CFs calculated with USEtox (Rosenbaum *et al.*, 2008) were used, in the other CFs were obtained from USES-LCA 2.0 (Van Zelm, Huijbregts & Van de Meent, 2009). Since neither of these LCIA methods provides characterization factors for groundwater, emissions to this environmental compartment could not be quantified. Given that the results for both LCIA models showed the same trend, only the results obtained using USEtox CFs are discussed here.

This study was done using 23 active ingredients. These were selected on basis of three criteria: the active ingredients must be present in the PestLCI 2.0 database, CFs must be available in both USEtox and USES-LCA 2.0, and the pesticide must be approved for use in Denmark in 2010 (DEPA, 2011). The pesticides used are listed in Table 3.2.

Table 3.2: Overview of pesticides used for the comparison of LCI approaches

Fungicides	Metsulfuron-methyl
Fosetyl-Al	Pendimethalin
Mancozeb	Phenmedipham
Propamocarb	Thifensulfuron-methyl
Propiconazole	Tribenuron-methyl
Propyzamide	Insecticides
Tebuconazole	Alpha-cypermethrin
Herbicides	Cypermethrin
2,4-D	Pirimicarb
Asulam	Growth regulators
Bentazone	Etephon
Bromoxynyl	Maleic hydrazine
Glyphosate	Mepiquat chloride

For each of the 23 active ingredients, three pesticide application scenarios were modelled. In these scenarios the treated crop, time of application and therefore crop development stage and climatic circumstances, and application technique were varied. Scenario 1 was based on pesticide application in April on bare soil or cereals, scenario 2 on application in July on bare soil or rapeseed, and scenario 3 was calculated as the average of one application in each of the year's twelve months, applied on bare soil or rapeseed.

The summed sold mass of the pesticides included here accounts for 60% of the pesticides sold in Denmark in 2010. For all scenarios used here it was assumed that 1 kg/ha active ingredient was applied. Though this does not reflect agricultural practice, the intention of this study was not to model actual application amounts.

Using the comparison of the Ecoinvent and PestLCI inventory approaches as a starting point, a sensitivity analysis was done in which a number of input parameters to PestLCI was varied, in order to see how this would affect the results. The parameters varied are listed in Table 3.3. In total, this yielded sets of 45 alternative scenarios per active ingredient considered.

*Table 3.3: Overview of input parameters subjected to sensitivity analysis for the PestLCI approach. Parameters used in the base scenario are indicated with *.*

Climate ¹	Maritime temperate 1*, North Mediterranean, Mediterranean 2, Continental 1, Continental 2
Month	January, February, March, April*, May, June, July, August, September, October, November, December
Soil ²	Average*, low clay, high clay, low silt, high silt, low sand, high sand
Plant interception ³	0; 0.25; 0.5; 0.8*, 1
Spray equipment ⁴	IMAG conventional boom - cereals*; IMAG conventional boom - potato; PestLCI 1 - field crops; PestLCI 1 - tall crops
Field width (m)	100*, 250, 500
Field slope (%)	0.5; 1.5*; 2.5; 5; 10
Drainage fraction ⁵	0*; 0.5; 1
Drainage depth (m)	0.4; 0.66; 0.9
Irrigation (mm/year)	0*, 100, 250, 500
Tillage	Conventional*, reduced, none

1: Climate types based on FOOTPRINT project (Centofanti *et al.*, 2008), see chapter 2 for more details; 2: Soils based on SPADE database (European Communities, 2010), see chapter 2 for more details; 3: Fraction of applied pesticide intercepted by the plant leaves; 4: Spray equipment determines wind drift. IMAG wind drift curves are taken from Holterman & Van de

Zande (2003), PestLCI curves are the ones included in the first version of PestLCI (Birkved & Hauschild, 2006); 5: Fraction of the agricultural field where drainage tubes are installed

3.3 RESULTS

The results presented here are the freshwater ecotoxicity results, i.e. the LCIA results. The LCI (emission) results calculated with the various impact assessment models will not be presented in this thesis. Instead they can be found in paper 2.

3.3.1 COMPARISON OF ECOINVENT - PESTLCI APPROACHES

Figure 3.1 presents the freshwater ecotoxicity impacts calculated with the PestLCI approach plotted against the impacts calculated with the Ecoinvent approach. It can be seen that the impacts calculated with both approaches span 7 orders of magnitude. Had all data points been on the diagonal, then the impacts calculated with both LCI approaches would be similar.

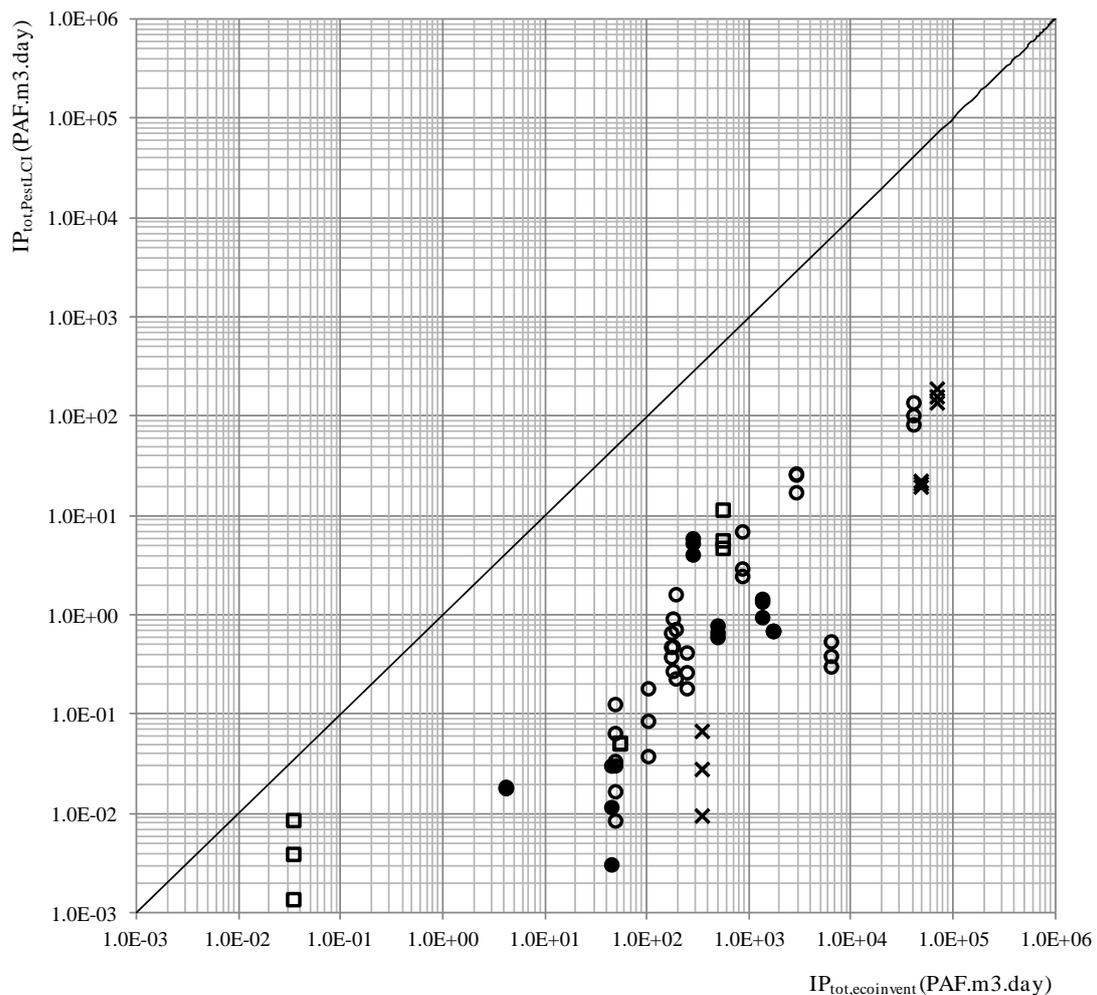


Figure 3.1: Comparison of freshwater ecotoxicity impacts calculated with the Ecoinvent and PestLCI approaches. Fungicides are indicated with ●, herbicides with ○, insecticides with ×, and growth regulators with □. Note that the scale is logarithmic.

However, as can be seen from the Figure 3.1, this is not the case. The impacts calculated with the PestLCI approach typically are a few orders of magnitude lower than those calculated with Ecoinvent: the average ratio $IP_{Ecoinvent}:IP_{PestLCI}$ is 2043, with a minimum of 2.9 and a maximum of 21491.

3.3.2 COMPARISON OF ECOINVENT - HYBRID APPROACHES

The comparison between the Ecoinvent (horizontal axis) and the hybrid (vertical axis) approaches is presented in Figure 3.2. It can be seen that by including the soil into the ecosphere the freshwater ecotoxicity impacts approach the diagonal, meaning that both approaches yield a similar impact.

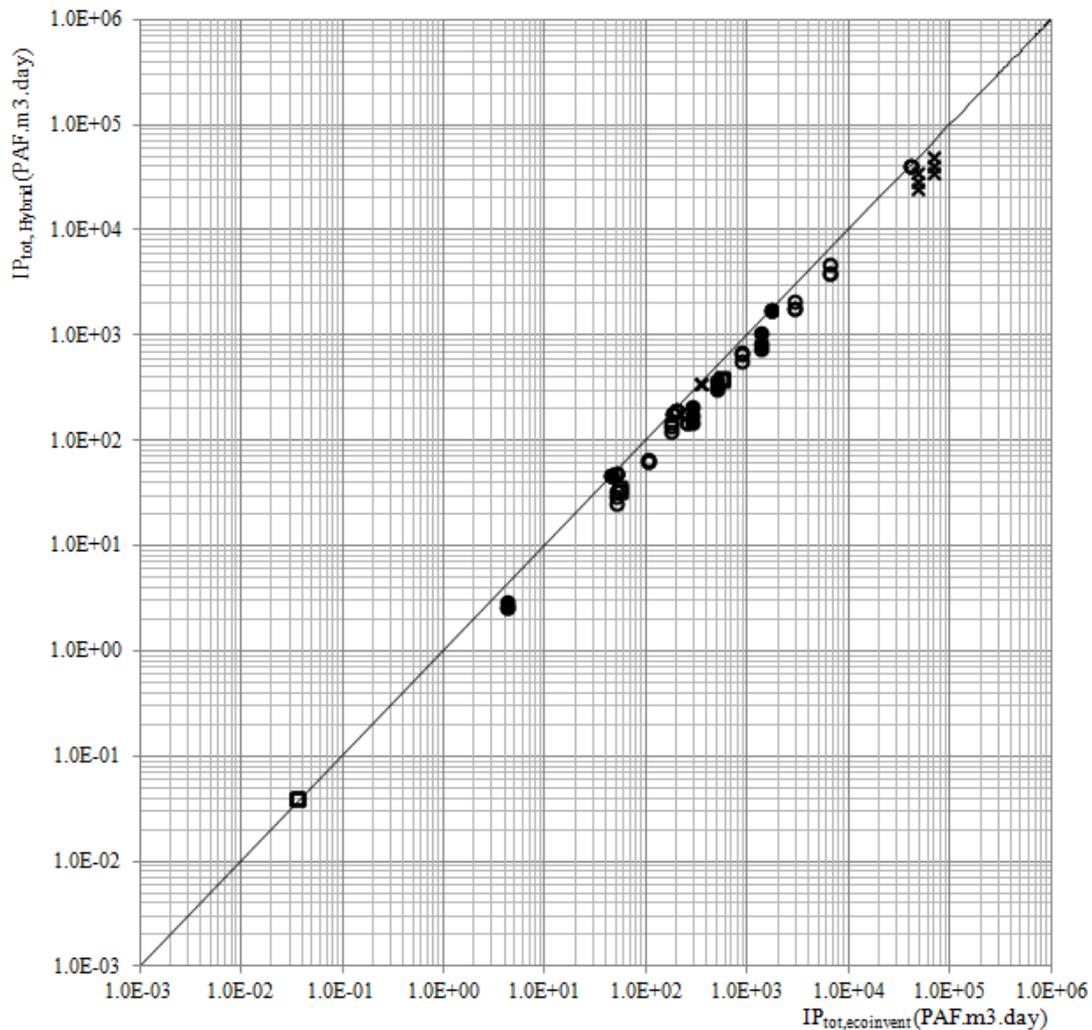


Figure 3.2: Comparison of freshwater ecotoxicity impacts calculated with the Ecoinvent and hybrid approaches as LCI methodology. In this figure fungicides are indicated with ●, herbicides with o, insecticides with ×, and growth regulators with □. Note that the scale is logarithmic.

The average ratio $IP_{\text{Ecoinvent}}:IP_{\text{PestLCI}}$ in this comparison is 1.4, meaning that the Ecoinvent approach results on average in impacts that are 1.4 times the impacts found with the hybrid inventory approach. The minimum ratio found is 0.88, the maximum is 2.0. These numbers are rather contrasting with the PestLCI - Ecoinvent comparison.

3.3.3 SENSITIVITY ANALYSIS

The results of the sensitivity analysis are presented in Figure 3.3. In this figure the impacts applying the Ecoinvent and PestLCI inventory approaches are compared. The most important observation from Figure 3.3 is that for virtually all pesticides the conclusion holds that the Ecoinvent inventory approach results in higher freshwater ecotoxicological impacts than the PestLCI approach. The exception here is alpha-cypermethin, where the PestLCI inventory approach in some cases (6 out of 45 tested) results in higher impacts.

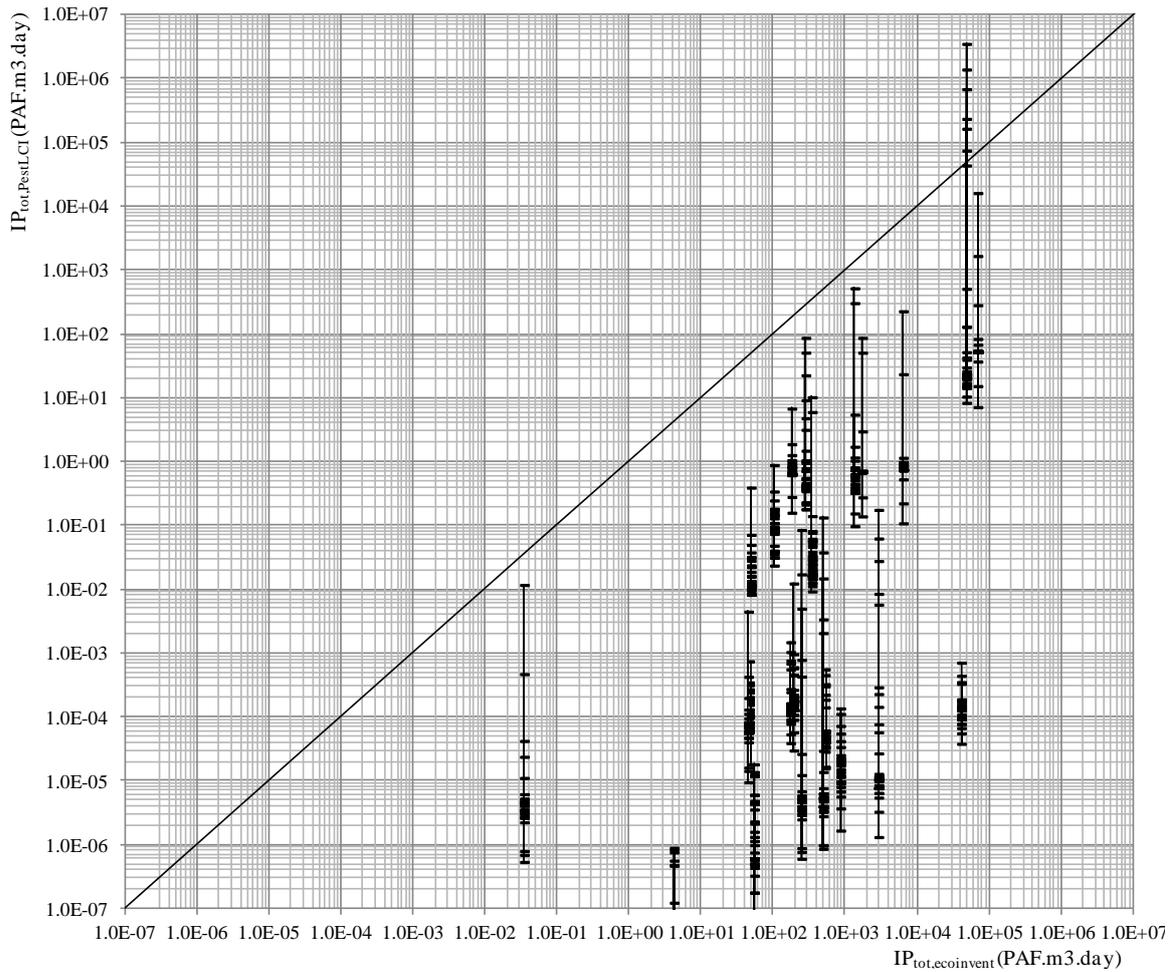


Figure 3.3: Sensitivity analysis comparing the freshwater ecotoxicity impacts for 23 pesticides, scenario 1.

From Figure 3.3 it can furthermore be concluded that the impact potentials obtained for one pesticide can vary up to 7 orders of magnitude according to the PestLCI approach. These differences are attributed to variations in emissions to the different environmental compartments, as calculated with PestLCI 2.0. Despite this observation, the impacts resulting from most of the 45 scenarios for each pesticide are typically close to each other: on average across the 23 pesticides considered, the impacts for 34 out of 45 scenarios were within a factor 2 from the base scenario value. Factors affecting air emissions from the field, most notably pesticide application method and field width, were the input parameters that explained most of the variation in the results.

3.4 DISCUSSION

This discussion is split into three parts: one dealing with the results presented in the previous sections, one with the implication of the results, and one discussing technosphere-ecosphere boundaries on a more general level.

3.4.1 RESULTS

From the results it can be seen that when comparing the Ecoinvent and PestLCI inventory approaches for pesticide emissions, which was the focus of paper 2, Ecoinvent almost consistently results in higher toxicological impacts. This was confirmed by the sensitivity analysis, where only 1 pesticide in some cases showed higher impacts when using PestLCI 2.0 to calculate emissions.

This difference has two reasons. Firstly, the total emissions are higher in the Ecoinvent approach. In this approach, it is assumed that 100% of the applied pesticide is emitted whilst in the PestLCI approach a considerable fraction of the pesticide is degraded or taken up into the crop (i.e. degraded or absorbed in the technosphere). Secondly, the emission compartments are different, and the CFs for these compartments are not the same. The CFs for emissions to freshwater are typically highest, the CFs for emissions to air typically are the lowest. Consequently the CF for emissions to soil typically is in between these two. The higher emissions in the Ecoinvent approach are therefore partially offset by the lower CF for soil emissions, compared to the CFs for air emissions. This trend is yet again counterbalanced by the higher CF for surface water emissions compared to soil emission CFs.

Of the three emission compartments considered in the PestLCI approach, only two were taken into account in the impact assessment, because CFs for groundwater emissions are not yet included into USEtox. This does not mean that it can be concluded that the difference between the two LCI approaches is smaller than shown in Figure 3.1: for emissions to soil, groundwater is not considered in the fate modelling either.

The comparison between Ecoinvent and PestLCI is a double one: not only are different approaches to considering fate processes in the field compared, the comparison is also between two technosphere definitions. For this reason the hybrid scenario was defined. Based on the PestLCI approach, the technosphere borders were changed in order to resemble those used in Ecoinvent. This gives some

insight into which of the two factors compared is more determining for the observed difference in potential environmental impacts.

Figure 3.2 shows that when adapting similar technosphere system boundary settings, but including fate process modelling in the technosphere, the resulting impacts look very similar to those obtained with the Ecoinvent approach. From this it can be concluded that the system boundary definition is the more important factor influencing the impacts. This could have been expected, considering that when including the soil in the technosphere only a fraction of the pesticide is emitted (namely via run-off or leaching to the groundwater). If in contrast the soil is defined as an emission compartment, then obviously the fraction of emitted pesticides will become larger.

In conclusion, it appears that in- or exclusion of the agricultural soil is an important driver for pesticide toxicity impacts. The question following from this is whether this soil compartment should be considered as part of the technosphere, as in PestLCI, or as ecosphere, as in Ecoinvent. This question will be discussed in section 3.4.3.

3.4.2 IMPLICATIONS FOR LCA PRACTICE

If we assume that PestLCI 2.0 is the right inventory path to follow for calculation of pesticide emissions, then this may have considerable consequences for outcomes of LCAs, at least when it comes to toxicological impact categories. Two of these consequences will be discussed here.

The first implication is the environmental footprint of organic agriculture. This type of agriculture aims at an agricultural practice which “sustains the health of soils, ecosystems and people” (IFOAM, 2013). In practical terms, the main difference from conventional agriculture is in avoidance of synthetic-chemical pesticides and fertilizers, and the use of manure and compost as the main source of fertilization (Badgley *et al.*, 2007). Nemecek *et al.* (2011) did a LCA comparing crop production in conventional/integrated agriculture with organic production. When comparing both forms of agriculture on basis of an identical mass of product, the impacts for some impact categories (global warming impacts, resource and energy consumption) were clearly favouring the organic farming practice, whilst land use was higher in the case of organic farming. For other categories, such as ozone formation, acidification and eutrophication no clear conclusions

could be drawn. In all toxicity impact categories, organic farming had a clearly lower impact: in aquatic and terrestrial ecotoxicity the impacts of organic farming were 16% of those in conventional farming, whilst human toxicity was at 40-45% of conventional farming impact. The authors attribute this large difference to the greatly reduced use of pesticides in organic production. The observation that both forms of agriculture have advantages and disadvantages also appears from other LCA studies. For example, Cederberg & Mattsson, 2000; De Backer *et al.*, 2009) show that organic farming is not by definition more sustainable than conventional production when the functional unit is mass-based. For some categories the impacts are somewhat lower, for others they are somewhat higher. De Backer *et al.* (2009) showed that the organic production of a kg of leek results in higher resource depletion, stratospheric ozone depletion, photochemical oxidant formation, and eutrophication impacts. Conventional leek production resulted in higher impacts for climate change, human and terrestrial toxicity, and acidification. Cederberg & Mattson (2000) found that for the production of a given mass of milk, conventional farming results in higher global warming and acidification impacts, whilst organic farming showed higher eutrophication and photochemical oxidant formation impacts, and required more land. In this study, pesticide use was discussed only quantitatively.

In an overview of available literature, Foster *et al.* (2006) concluded the same as the picture that arises from the limited number of LCA studies mentioned here: organic farming is not by definition more sustainable than conventional farming. Conventional farming has lower impacts for some impact categories and some crops, and the same can be said for organic agriculture.

In the studies mentioned above, the toxicity impacts of the pesticides that were accounted for, were considerably lower in the case of organic production (where the use of for example copper results in some toxicity impacts). If the pesticide emissions in these studies would be recalculated with PestLCI, the resulting toxicity impacts would be considerably lower than the ones reported in the studies mentioned above. As a consequence, the share of pesticides in toxicity impacts would be lowered, so that avoidance of synthetic pesticides in organic farming becomes less of a benefit when comparing the environmental impacts of this type of farming to conventional farming. Hence the results in one of the impact categories in which organic farming currently has a distinct environmental benefit compared to conventional production would become lower, resulting in (even)

less clear results for LCA-based comparisons of conventional and organic agriculture.

Even if the LCA results presented here can't be considered to favour either conventional or organic agriculture, they are still limited to a number of the sustainability aspects of both agricultural approaches. Looking only at the differences in toxicological impacts, inventory analysis and impact assessment do not cover the non-synthetic pesticides used in organic farming, such as the microbial pesticide *Bacillus thuringiensis*. Moreover, health impacts of pesticide residues in crops are not (yet) considered in LCA studies. Recent models such as DynamiCROP (Fantke *et al.*, 2011) may be helpful in doing so. Looking beyond toxicological impacts, some impact categories that are relevant to assess sustainability aspects of farming practices, are still not well developed or fully integrated into LCA practice. Examples of such impacts are (indirect) land use change and biodiversity. Finally, the discussion above only focuses on the environmental aspects of sustainability, whilst the social and economic aspects also need to be taken into consideration. So, whilst the application of PestLCI to calculate emissions of pesticides may have an effect on the way toxicological impact of these emissions are considered, the comparison of conventional and organic agriculture involves many more aspects.

Another, slightly ironic, implication of the fact that the PestLCI approach results in lower toxicity impacts than the Ecoinvent approach is the contribution of pesticide emissions to toxicity impacts in LCA. One of the reasons to develop PestLCI was described in chapter 2: the large contribution of pesticides to toxicity impacts in agricultural LCAs. However, when modelling pesticide emissions with PestLCI, the resulting impacts are a few orders of magnitude lower, as was shown in this chapter. As a consequence the contribution of pesticides to toxic impacts may no longer be so large. As an illustration, Herrmann *et al.* (2013) report an LCA done on rapeseed biodiesel production through various pathways. In this study pesticide emissions were calculated using PestLCI 1 (Birkved & Hauschild, 2006). It was found that though pesticides were the main contributor to freshwater ecotoxicity impacts, human toxicity impacts were dominated by the production of nitrogen, phosphorous and potassium chloride, as well as fuel consumed in the cultivation of rapeseed. Even though this is only one example and may not be representative for agricultural LCAs in general, it may be that the

problem that triggered the development of PestLCI turns out to be a relatively small problem when analyzing pesticide emissions with PestLCI.

3.4.3 SETTING THE TECHNOSPHERE - ECOSPHERE BOUNDARY

As concluded from the results of the hybrid approach, it is mainly the setting of the technosphere-ecosphere boundary that determines the difference between the toxicity impacts that were observed between the Ecoinvent and PestLCI pesticide emission inventory approaches. This raises the question how the boundary between ecosphere and technosphere should be set, if at least there exists something like a correct boundary setting.

Before answering these questions, a clear definition is needed of what exactly the ‘technosphere’ and ‘ecosphere’ are. Though these terms will have an implicit meaning for most LCA practitioners, neither the ISO standard describing the LCA framework (ISO 14040) nor the standard describing the requirements and guidelines (ISO 14044) explicitly defines them (International Standards Organization 2006a, 2006b). However, ISO 14040 does define an elementary flow as “material or energy entering the system being studied that has been drawn from the environment without previous human transformation, or material or energy leaving the system being studied that is released into the environment without subsequent human transformation” (International Standards Organization, 2006a). From this definition the technosphere can be interpreted as the sphere in which humans manipulate materials or energy for one reason or another. This technosphere is sometimes defined as the socio-economic system (Werner & Scholz, 2002). At the same time, the ecosphere is defined as ‘the environment’, which in itself does not clarify matters much. From the previous it follows that the boundary between ecosphere and technosphere is set correctly when it lies there where the human-made systems end and the environment starts.

The next question is if such a setting can be found in the case of agricultural LCAs. Agriculture seems to be on the edge of technosphere and ecosphere: agricultural production is a human activity created in order to produce crops for food, feed or other purposes such as production of fuels, and to generate an income for the people involved. At the same time, these systems depend on processes that are (usually) not controlled by human action, such as rainfall or photosynthesis. In my opinion it is therefore *not* possible to objectively determine where the border between ecosphere and technosphere, i.e. between environment and production system, is located since there are different opinions about what the environ-

ment is. As an example, I will consider the boundaries chosen in PestLCI, for which valid arguments both in favour and reasoning against the chosen boundaries can be defined.

In the PestLCI approach the soil on which the crop is grown as well as some of the air above it are basically considered a production facility manipulated by man, producing biological products. The field is considered part of the technosphere for three reasons. To start with, agricultural land is converted by humans from an original, one can say 'natural' state, to a managed state in which it functions to provide an economic function or service. As a consequence of obtaining an economic function, the field becomes part of the socio-economic system. Therefore, it is in accordance with the ISO definition presented above part of the technosphere.

Secondly, when in use as agricultural land, a crop and the field in which it is cultivated is continuously manipulated by human actions: the soil is disturbed by for example ploughing, agricultural chemicals are distributed and sometimes drainage tubes are dug down into the soil. Thirdly, agricultural soils are protected by different legislations than natural areas. For example, all Danish nature areas are protected by the Nature Protection Law (Naturbeskyttelsesloven, Danish Ministry of the Environment, 2013) while arable land is protected the Law on Management of Arable Land (Lov om drift af landbrugsjorder). Similarly, in e.g. the Netherlands arable land is also distinguished from natural areas (Dutch Ministry of Economic Affairs, 2013). From the ongoing nature of human intervention of soil on arable land and from the different legal status arable land has compared to natural land, it is reasoned that agricultural fields is not part of the environment.

However, reasons to consider agricultural land as part of the environment can also be put forward. Firstly, despite the human manipulation of the soil and the human efforts to keep unwanted species away from the field, the system still is a system that can't be fully controlled by human activity. Though the biodiversity is lower than in natural areas (Reidsma *et al.*, 2006), the field still is part of a biological system that is not fully controlled by humans, at least not in current agricultural practice, so that the field can be considered part of the environment. Following a more formal reasoning based on how an LCA should be carried out, the ISO definition of a elementary flow can be used to argue that after a pesticide is released from the sprayer, 'human transformation afterwards' will not occur.

Once out in the field the chemical is subject to a number of processes (most notably degradation) that transform the active ingredient into another chemical. Such processes are not driven by human activities. Some processes, such as the interception of water-dissolved pesticide by drainage systems or applying irrigation may have effects on pesticide emissions to surface water or groundwater, are human-driven. Although these processes were not designed for the purpose, they do affect the fate of the pesticide but do in itself not transform the chemical. Considering the field and its soil as a (human affected) part of a broader ecosystem, and considering that human exert little, if any, influence on the further transformations of the pesticide after application, it can be argued that agricultural land is best considered as part of the environment.

An argument which does not necessarily imply that the soil should be considered part of either the technosphere or the ecosphere is that an application of a pesticide leads not only to the suppression of a pest, but often also to damage to off-target organisms present in the field. One can argue that these unwanted effects also need to be accounted for, in one way or another.

Even though the arguments listed here are probably only a selection of the reasons that can be given to include or exclude the agricultural field from the technosphere, they illustrate that in the case of agricultural LCA (at least when dealing with pesticide application) the boundary between the technosphere and the ecosphere can not be defined in a way which all LCA practitioners can agree upon. LCA practitioners have different ideas about what the ecosphere and technosphere are. This conclusion that practitioners can have different opinions about what the environment is, is also presented by Hofstetter, Baumgartner and Scholz (2002). These authors therefore go on to propose the creation of an additional sphere in LCA practice, which they defined as valuesphere. This valuesphere contains both ecosphere and technosphere. Inclusion of this sphere into LCA should allow for the incorporation of the decision makers' views on what constitutes the ecosphere, and on what an adverse effect of the environment means. This concept has been operationalized using Cultural Theory in the impact assessment method Eco-Indicator '99 (Goedkoop *et al.*, 1998) and its successor ReCiPe (Goedkoop *et al.*, 2009).

An option to avoid making a hard cut between ecosphere and technosphere not yet considered in the discussion here is, to make the inclusion of the field into the

technosphere time-dependent, as for example proposed by Van Zelm, Larrey-Lassalle and Roux (2012). In the case of pesticide application, this time-dependency would mean that for a short time after the application, the field is considered part of the technosphere after which it is considered part of the ecosphere again. On the one hand, it can be said that this approach accurately reflects the placement of the field on the border of the technosphere and ecosphere, and considers that off-target impacts may occur in the field. On the other hand, it introduces another point of discussion: for how long should the field be considered part of the technosphere? Moreover, no matter what time frame is set, this approach would always result in including too much impacts, or cutting off a part of the impacts, depending on the practitioners' opinion on whether impacts on organisms in the field should be included or not. On a more practical side, compared to PestLCI, this solution does not immediately appear to be a major improvement in terms of data requirement. These three reasons seem to make a time-dependent technosphere boundary not a solution for the problem what to consider as an emission and hence what impacts should be accounted for. It rather shifts the problem from spatial borders to temporal borders.

Perhaps it would be better to accept that it is impossible in some cases to define a clear border between ecosphere and technosphere. One might ask whether it is always necessary to draw such a line in the first place.

This discussion showed that in systems where the boundary definition between ecosphere and technosphere is open for discussion, the in- or exclusion of the soil in the ecosphere can importantly change the freshwater toxicological impact results of an LCA. Also in other areas a strict definition of ecosphere and technosphere can lead to odd consequences. For example, when carrying out an LCA according to the ICLD handbook, the human health impacts caused by indoor exposure to chemicals, consumption of food and drinks, use of personal care products, and (workplace) accidents should be reported separately from the LCI, and the impacts assessed separately, since the flows causing such impacts all occur within the technosphere (European Commission, 2010). In principle this approach could also be followed to account for on-field, off-target impacts of pesticide application, though this may not be the most practical approach.

In both examples the need to draw boundaries between ecosphere and technosphere seems to be an obstacle for what LCA should, in my opinion, intend to do: assessing impacts on natural environment, human health and resources, inde-

pendent of where the effects that we consider adverse take place, and independent of the pathway between emission and impacts. Therefore, the question where to put the boundary between ecosphere and technosphere should not be the main discussion point. Instead, a better question would be: what do we actually want to protect, and how do we best model the impacts of human actions on what we want to protect? After that, a more pragmatic approach can be taken to where and when in the different phases of LCA pesticide fate should be considered.

In Life Cycle Sustainability Analysis (LCSA), the boundaries between LCI and LCIA modelling are fading, exactly because the technosphere and ecosphere have been found to be difficult to distinguish from each other. Instead both phases are increasingly merged into one modelling procedure (Guinee *et al.*, 2011). Perhaps this may also turn out to be the way forward for agricultural LCA. There are several options to operationalize such an idea. One suggestion is the development of a single model that models the full fate of pesticides after application, potentially combined with exposure and effect modelling. In such a case, the LCI mainly serves as an administrative tool to account for the amount of pesticides applied. A second suggestion is the development of matching inventory and impact assessment models tailored for pesticide emissions, sharing the same technosphere-ecosphere boundary settings.

3.5 CONCLUSION

It was shown that when comparing Ecoinvent (100% of applied pesticide emitted to agricultural soil, no consideration of fate processes) and PestLCI (a temporally variable fraction of applied pesticide emitted to air, surface water and groundwater, fate processes are considered) as Life Cycle Inventory approach for pesticide emissions, the resulting freshwater toxicity emissions are consistently lower in the PestLCI approach. The difference between both approaches is typically a few orders of magnitude.

Since the comparison between both approaches was a comparison between different considerations of fate processes and technosphere-ecosphere boundaries, ecotoxicity impacts were also calculated for an approach which considers fate processes but with a technosphere definition resembling Ecoinvent. Results of this hybrid approach showed that the definition of technosphere boundaries most likely is the main cause for the differences observed in the comparison between the Ecoinvent and PestLCI inventory approaches. Choosing the PestLCI ap-

proach over the Ecoinvent approach may have implications for the way organic farming performs in LCA relative to other farming practices such as conventional farming, as well as for the overall contribution of pesticides to toxicity impacts of agricultural products.

The discussion about the relevance of ecosphere-technosphere boundaries concluded that it is not possible to define a correct boundary setting, since the definition of what part of the world that belongs to the environment is a subjective decision heavily influenced by LCA practitioners' political, moral and ethical value set. Consequently, the way forward may be to define what should be protected in LCA, and calculate the impacts through one model, putting less weight on the current distinction between LCI and LCIA.

4 APPLICATIONS: PESTICIDE EMISSIONS IN KIWIFRUIT GROWING

4.1 CONTEXT

In 2010 the production of kiwifruit in New Zealand accounted for more than a quarter of the global kiwifruit production (FAOstat, 2013). Some sustainability aspects of kiwifruit growing have been addressed by previous research, such as a carbon footprint calculated by Mithraratne *et al.* (2010). Water footprints were calculated following a number of footprinting approaches (Deurer *et al.*, 2011). Work on toxicological impacts of kiwifruit growing was carried out by Müller *et al.* (2011), who calculated the emissions of four pesticides to soil, surface water and groundwater.

In the research presented in this chapter, which is based on paper 3, additional work is done for the development of a pesticide toxicity footprint. PestLCI 2.0 is used to model emissions of the synthetic agricultural chemicals used in conventional kiwifruit growing in the Western Bay of Plenty (WBOP) region. This region, with an area of approximately 2000 km² is located on the east coast of the North Island. Most of the kiwifruit produced in New Zealand, namely 85%, is grown in this region. Characterizing the calculated emissions resulted in toxicity impacts for both human toxicity and freshwater ecotoxicity. Moreover, since regional differences in terms of climates and soils within the WBOP were identified, the research also allowed a study of the regional differences in pesticide emissions and the resulting toxicity impacts occurring in kiwifruit growing. This chapter will thus focus on the calculation of kiwifruit toxicity footprints, and the regional variation in toxicity impacts. The chapter will not go into great detail to describe the methods applied, nor will the results be discussed extensively here, since this is already done in paper 3.

4.2 METHODS

This section presents the scenarios used to model kiwifruit growing, the pesticide emission modelling and the impact assessment approach.

4.2.1 SCENARIOS

From the pesticide spray diaries of 20 kiwifruit growers in the WBOP the pesticides used in the production of conventional kiwifruit were identified. These 20 spray diaries were considered representative for kiwifruit production in the WBOP (Müller, 2013). The selected pesticides covered the majority of pesticide applications that were recorded in the diaries, as can be seen from Table 4.1. This table presents an overview of the selected pesticides, their month of application and the application rate. The application rates mentioned in the table were based on the product label instructions/recommended application rate.

Pesticides that are applied in conventional kiwifruit production that have been excluded here are copper hydroxide which is used as fungicide, as well as the insecticides bacillus thuringiensis, and mineral and petroleum oils (both are distillates). The first two were excluded due to their non-synthetic chemical natures, whilst the mineral and petroleum oils were not included because these are mixtures of chemicals.

Table 4.1: Overview of active ingredients used in kiwifruit growing that were included in the study, their share in total applications per class, time of application and dosage. Percentages are rounded, therefore individual contributions may not sum up to the percentage per functional class.

Active ingredient	Applications covered (%)	Month of application	Application rate (kg/ha)
Fungicides	95		
Iprodione	35	November	0.75
Trifloxystrobin	59	October	0.15
Growth regulator	100		
Cyanamide	100	August	15
Herbicides	100		
Glyphosate (early application)	50	October	0.66
Glyphosate (late application)	50	January	0.66
Insecticides	69		
Chlorpyrifos	6	September	0.50
Emamectin benzoate	24	December	0.002
Methoxyfenozide	10	December	0.10
Spirotetramat	18	November	0.096
Thiacloprid	9	October	0.19
Thiamethoxam	2	September	0.10

Table 4.2: Overview of the nine scenarios for which pesticide emissions were modelled.

Scenario	Location (climate)	Soil	Soil Type, current NZ soil classification scheme (Hewitt, 1998)
1	Waihi	Katikati sandy loam	Typic orthic allophanic soil
2	Katikati	Katikati sandy loam	idem
3	Tauranga	Katikati sandy loam	idem
4	Tauranga	Ohinepanea loamy sand	Typic orthic pumice soil
5	Tauranga	Oropi coarse sandy loam	idem
6	Tauranga	Paengaroa sandy loam	Buried-allophanic orthic pumice soil
7	Te Puke	Ohinepanea loamy sand	Typic orthic pumice soil
8	Te Puke	Oropi coarse sandy loam	idem
9	Te Puke	Paengaroa sandy loam	Buried-allophanic orthic pumice soil

Within the WBOP region four climate archetypes were identified. Based on soil samples taken from kiwifruit orchards, four soil types were identified to represent kiwifruit cultivation in the WBOP. Combining the localization of these soils with the climatic circumstances prevailing within the region, a total of nine scenarios with combinations of climate and soil were defined. The scenarios are presented in Table 4.2.

4.2.2 CALCULATION OF PESTICIDE EMISSIONS

The pesticide emissions were calculated with an updated version of PestLCI 2.0. The model was adapted to the circumstances in the WBOP, both in terms of soils and climates. Soil data were based on New Zealand's National Soils Database (Wilde, 2003), climate data were a 10-year average from New Zealand's Virtual Climate Station Network (National Institute of Water and Atmospheric Research, 2012). Moreover, a module was added to the model to represent shelterbelts, also called wind breaks. These are 5 to 10 meters high belts, usually of coniferous trees, surrounding kiwifruit orchards. The purpose of shelterbelts is to break the wind, in order to prevent damage to the plant and fruit and to create a microclimate for improved plant growth. Another benefit is that these belts intercept drifting pesticide droplets, resulting in reduction of pesticide emissions due to wind drift (Hewitt, 2001). The shelterbelt was considered part of the technosphere. Pesticides intercepted by the shelterbelt were modelled to undergo the same fate processes as pesticides landing on plants: volatilization, degradation, uptake, and wash off during rain events.

Moreover, the modelling of macroporous flows was adapted for this study, as well as the regression used for volatilization from leaves. These adaptations are

briefly described in chapter 2, and more extensively in paper 3 and will therefore not be repeated here.

4.2.3 CHARACTERIZATION OF PESTICIDE EMISSIONS

The pesticide emissions to air and surface water, calculated applying PestLCI, were subsequently characterized in order to determine the freshwater ecotoxicity and human toxicity impact potentials. Characterization factors (CF) for emissions to rural air and continental freshwater were obtained using USEtox (Rosenbaum *et al.*, 2008). CFs for iprodione were taken from the USEtox database, for the other pesticides new characterization factors were derived, also applying USEtox.

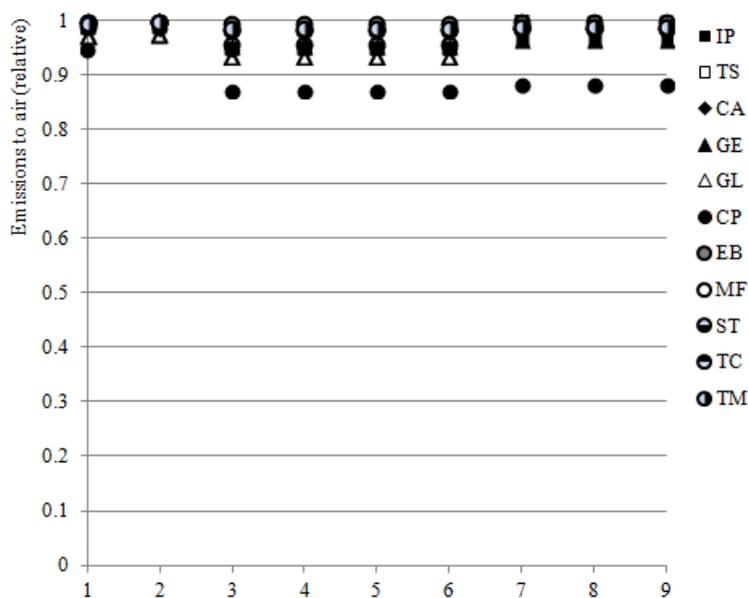
4.3 RESULTS AND DISCUSSION

The spatial variations observed in the pesticide emissions and the resulting toxicity impacts are presented and discussed in this chapter. The results of the pesticide toxicity footprint will be discussed in the second part of this section, as well as further steps that need to be taken in order to arrive at a toxicity footprint.

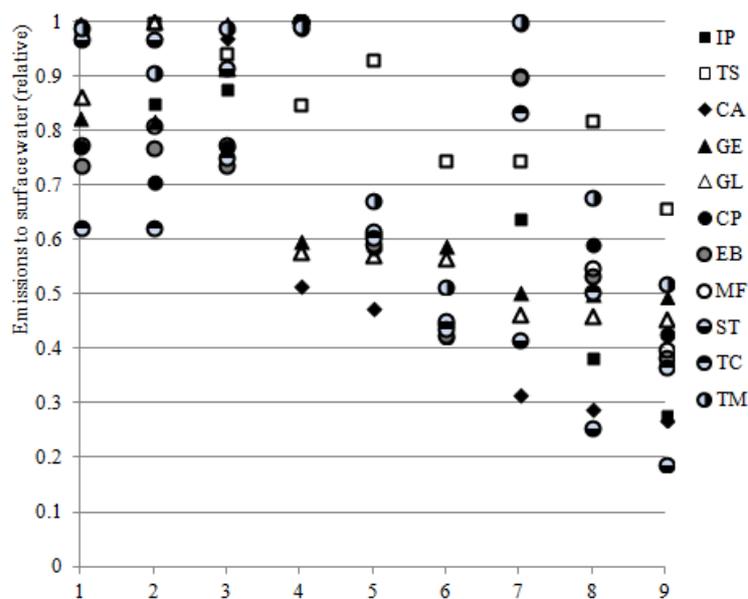
4.3.1 SPATIAL VARIATION IN PESTICIDE EMISSIONS AND TOXICITY IMPACTS

In Figure 4.1 the variation in emission fractions of pesticides to air, surface water and groundwater are shown for the nine scenarios given in Table 4.2. In this figure, the emissions for each pesticide are plotted relative to the scenario in which this pesticide was modelled to have the highest emissions. So, the emission of a given pesticide to a given environmental compartment is set to 1 for the scenario in which the emission is highest. The emission of that pesticide in other scenarios is expressed as a fraction of this highest impact ('relative emissions').

The emissions to air do in most cases not vary considerable among the various scenarios: the relative emissions in Figure 4.1a are close to 1 for most pesticides in most scenarios. This is because for most pesticides, the emissions to air are mainly determined by emissions during wind drift. In the modelling of wind drift, the type of spraying equipment and the distance to the field or orchard border are the parameters that determine pesticide emissions. This reflects the fact that the active ingredient is formulated during application, and therefore the properties of the pesticide are of minor importance for the wind drift emission (Carlsen *et al.*, 2006).

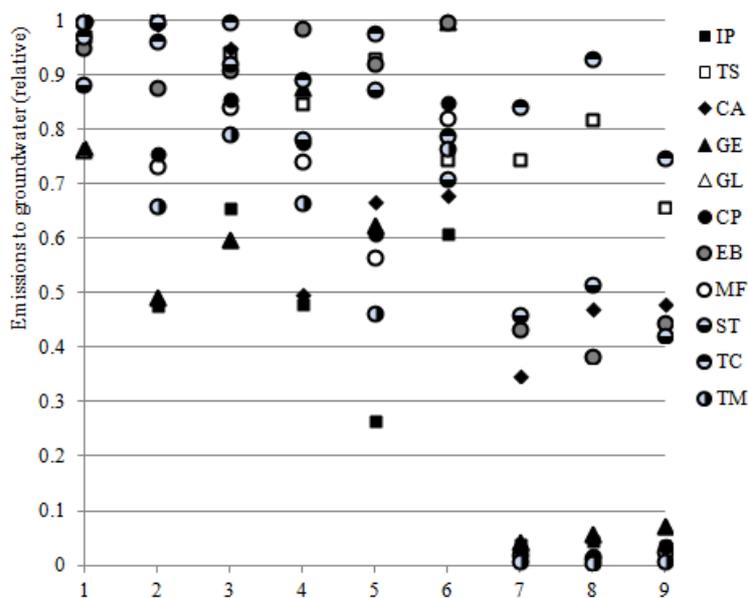


(a)



(b)

Figure 4.1: Spatial variation of emissions to (a) air, (b) surface water and (c) groundwater for the nine scenarios given in Table 4.2. For each pesticide, the scenario with the highest emissions is set to 1, the other emissions are expressed as a fraction of this emission. Since the emissions are expressed in a relative way in this figures, no units are given on the vertical axis. Abbreviations (alphabetically): CP: chlorpyrifos; CY: cyanamide; GE: glyphosate, early application; GL: glyphosate, late application; IP: iprodione; MF: methoxyfenozide; TC: thiacloprid; TM: thiamethoxam; TS: trifloxystrobin.



(c)

Figure 4.1(continued): Spatial variation of emissions to (a) air, (b) surface water and (c) groundwater for the nine scenarios given in Table 4.2. For each pesticide, the scenario with the highest emissions is set to 1, the other emissions are expressed as a fraction of this emission. Since the emissions are expressed in a relative way in this figures, no units are given on the vertical axis.

Abbreviations (alphabetically): CP: chlorpyrifos; CY: cyanamide; GE: glyphosate, early application; GL: glyphosate, late application; IP: iprodione; MF: methoxyfenozide; TC: thiacloprid; TM: thiamethoxam; TS: trifloxystrobin.

The variations with location that is observed in Figure 4.1(a), is attributed to the contribution of volatilization from leaves to emissions to air. Here, the effects of temperature on volatilization, as well as the residence time of the pesticide on the leaves, are visible.

Emissions to surface water in Figure 4.1(b) show more variation towards the nine assessed scenarios. Regarding the effect of soil type on surface water emissions, it was found for eight out of 11 pesticides in Tauranga that emissions decreased in the order Ohinepanea loamy sand > Katikati sandy loam > Oropi coarse sandy loam > Paengaroa sandy loam. This order reflects the increasing amounts of organic carbon present in these soil: the more organic carbon, the higher a fraction of pesticides that is bound. As a consequence, less pesticide is available for runoff. The exception in this case is the Katikati sandy loam soil, which has the

highest organic carbon content of the soils. Since this soil has a low sand content (38.6%) another algorithm is used to calculate the fraction of rain that runs off, as specified in paper 1. This results in more runoff. Therefore, the observed effect can be considered a combination of soil characteristics and the chosen modelling approach. There were no clear relations between surface water emissions and climate that could be observed.

Groundwater emissions, presented in Figure 4.1(c), varied a few orders of magnitude for some pesticides. For the nine scenarios, the pesticides could be split in two groups, depending on their half-lives in soil. For pesticides with short half-lives, such as cyanamide, spirotetramat, thiacloprid, and trifloxystrobin, emissions to groundwater are dominated by macropore flow. Emissions of the other compounds are dominated by soil matrix flow.

For macropore flow-dominated chemicals, clear conclusions could not be drawn about which climate or soil parameters influenced the emissions. However, it was observed that the emissions were highest on Katikati sandy loam soils, while the emissions in the Te Puke region were the lowest. The higher emissions on the Katikati sandy loam soil were due to the soil's low sand content, giving this soil a lower water holding capacity than the other soils modelled. Following the tipping bucket approach, macropore flow will therefore occur more often than on soils with higher sand contents. The lower pesticide emissions in the Te Puke case can be explained by lower and less frequent rainfall events in this region. As a consequence, macropore flow occurred less often, and less pesticide was left at the time of the first rainfall event after pesticide application. For the pesticides where matrix flow dominated the emissions, the groundwater emissions decreased in the order Waihi > Tauranga > Katikati > Te Puke. This observation can be attributed to the annual precipitation volume, which decreases in the same sequence as the groundwater emissions. Lower annual rainfall means, in the way the flow of pesticides through the soil matrix is modelled in PestLCI, that the pesticides move at a lower rate through the soil. As a consequence, less pesticide will reach a depth of 1 meter because more degradation will occur. No clear relationship could be distinguished between soil properties and groundwater emissions by matrix flow.

For the cases described above where no relationship between environmental parameters and emission could be distinguished, the observed emissions can most

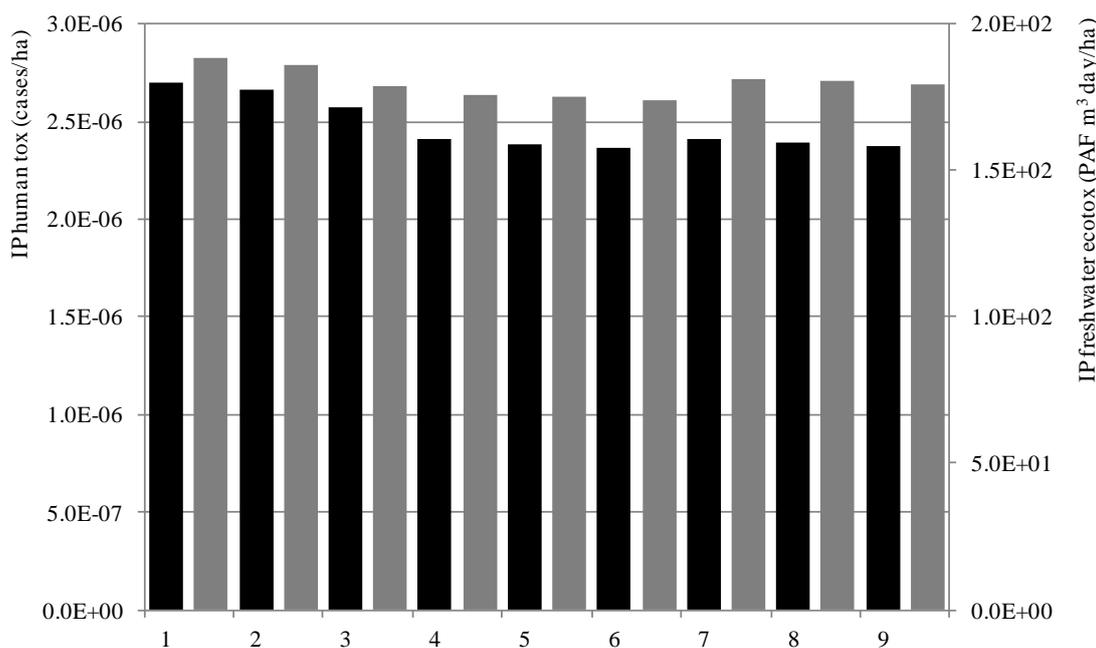


Figure 4.2: Human toxicological (in black, left vertical axis) and freshwater ecotoxicological (in grey, right vertical axis) impacts found for the nine emissions scenarios.

likely be explained by a number of climate and/or soil parameters, which together define the emissions, without one parameter being the determining one.

When going from the emissions in the nine scenarios to toxicity impacts (Figure 4.2), it was found that the impacts for both freshwater ecotoxicity and human toxicity were dominated by cyanamide. Emissions of this chemical to air were in turn contributing most to the overall toxicological impacts found for cyanamide: Depending on the scenario, human toxicological impacts were determined for ~99%, and freshwater ecotoxicological impacts for ~94%, by cyanamide emissions to air.

Figure 4.2 suggests that the variation in the toxicological impacts results observed for the nine emission scenarios are generally small. This can be explained by the modest size (approximately 2000 km²) of the WBOP region, so that the four climates included in the model only show small differences. In addition, all the four soils modelled are volcanic soils with similar properties.

At the same time, this small variation in results led to the conclusion that, at least for the case of kiwifruit growing in the WBOP, developing spatially dependent inventories at the level done in this study may not be needed, since the uncertain-

ties in the results probably (at least) match the calculated differences in impacts. This conclusion was based on the uncertainties in especially the impact assessment. The uncertainty of USEtox characterization factors is a factor 10-100 for freshwater ecotoxicity CFs, and in the order of 100-1000 for human toxicity CFs (Rosenbaum *et al.*, 2008). Although this uncertainty probably is reduced in the case studied here, because all scenarios involve the same chemicals (though in different amounts), it may very well be larger than the differences in impacts between the scenarios. Moreover, there is also a (not quantified) uncertainty associated with the pesticide emission modelling.

This does not mean that the results are not useful to research into soil- or climate-related differences in toxicological impacts caused by kiwifruit cultivation. The study presented in paper 3 focused on the WBOP only. Kiwifruit are also grown in other regions in New Zealand, as well as in other countries, where other chemicals may be used. For example, approximately 30% of the global annual kiwifruit production is grown in Italy (data for 2010, FAOstat, 2013) where use of cyanamide is no longer permitted (University of Hertfordshire, 2013). Therefore, the toxicological impacts associated with kiwifruit growing in other regions may be different from what was found for kiwifruit production in the WBOP.

4.3.2 TOWARDS THE DEVELOPMENT OF A TOXICITY FOOTPRINT FOR KI-WIFRUIT PRODUCTION

The work presented in paper 3 can be considered as the next step in the development of a toxicity footprint for kiwifruit cultivation. However, additional work needs to be done before such an approach is fully operational. First of all, the work presented in paper 3 is limited to conventional kiwifruit farming. The impacts of organic cultivation have not been quantified. Within the conventional kiwifruit production, paper 3 included ten active ingredients, all synthetic agricultural chemicals. The emissions and resulting impacts of several compounds that were excluded here, such as copper hydroxide and mineral oils, have to be included. Secondly, apart from including all pesticides, such a footprint will have to take a life cycle approach, not only looking at pesticide emissions, but at all potentially toxic emissions that occur during any life cycle stage, from the kiwifruit orchard, over pesticide production, consumption patterns, to consumer behavior and waste patterns.

The impacts assessment (LCIA) presented in paper 3 was done at characterization level using USEtox, resulting in separate impacts for freshwater ecotoxicity and human toxicity. Since USEtox is a recent model developed in a consensus process by the developers of several other toxicity LCIA models, it was selected to be used in this study. A disadvantage of this model is that it currently does not cover terrestrial ecotoxicity and marine toxicity, which are for example covered by USES-LCA 2.0 (Van Zelm *et al.*, 2009).

If the aim of a toxicity footprint is to express the impacts in a single number, parallel to the carbon footprint, the freshwater ecotoxicity and human toxicity categories used here have to be aggregated to one number. Here, normalization and weighting may be an option. Currently, USEtox normalization factors are available on continental level for Europe and North America (Laurent *et al.*, 2011), as well as on a global level (Cucurachi *et al.*, 2013; Laurent *et al.*, 2013). Normalization references will have to be developed for New Zealand. Afterwards, a meaningful weighting step will have to be developed.

4.4 CONCLUSION

The nine emission scenarios that were modelled showed little variation in emissions to air, whilst the emissions to surface water and groundwater varied more. For some emission pathways the variations in emissions could be explained in terms of climate or soil parameters, or modelling approach. In other cases it was not possible to identify one or more parameters to which differences in emissions could be attributed. Both freshwater ecotoxicity and human toxicity impacts were dominated by cyanamide, which contributed to more than 99% of the impacts in both categories. Small differences in impacts were observed between the nine modelled scenarios. Considering the large uncertainties of the characterization factors, and further considering that the emission inventories also have (unquantified) uncertainties, it can be concluded that the differences in impacts between the nine modelled scenarios probably are too small to allow for a meaningful way to regionally differentiate pesticide toxicity impacts in the WBOP. This work was only a small step on the way to a toxicity footprint for kiwifruit. On the inventory side, a life cycle approach needs to be taken, including chemicals excluded in paper 3, but also considering non-pesticide toxic impacts. On the impact assessment side, normalization and weighting may be needed.

5 APPLICATIONS: LIFE CYCLE ASSESSMENT OF BARLEY UNDER CURRENT AND FUTURE CLIMATIC CONDITIONS

5.1 CONTEXT

With the release of the IPCC's fifth assessment report (IPCC, 2013), it seems more certain than ever that the future climate will be different from the current, and that these changes are driven by human actions.

The perceived urgency of climate change and the political focus the issue has received can also be seen from the development of life cycle-based methodologies to assess greenhouse gas emissions of products, such as the Greenhouse Gas Protocol (World Business Council for Sustainable Development & World Resources Institute, 2004) or PAS 2050 (BSI, 2011). In the context of Life Cycle Assessment (LCA), climate change is considered in virtually all impact assessment methods (Hauschild *et al.*, 2013). Climate change is considered to affect two of the three areas of protection distinguishing in LCA: human health and natural environment (European Commission, 2010).

Therefore it can be concluded that when conducting LCAs or similar environmental assessments the impacts of products and services on climate change are well-considered. What is typically done in current LCA practice is that we model the time-integrated impacts that products currently being designed, produced, used or disposed of, exert on the environment. However, at the same time gradual changes in the climatic conditions may affect the way products and services are designed, produced or used, which in turn alters the environmental impacts of the product. In addition one can speculate that the demand for some products may change. Such feedback effects are not normally considered in LCA. From the literature it appears that little work has been done in this area.

The assessment of barley cultivation under current and future climatic aspects presented in paper 4 covered some of the above considerations. It was not attempted to cover all these aspects, since this is too ambitious a task to fit within the framework of this PhD study.

5.2 METHOD

The main aim of this work was to assess the environmental impacts that occur when barley is cultivated in Denmark, both under current and future climatic conditions. The focus was strictly on barley cultivation itself.

5.2.1 GOAL AND SCOPE

Imagine an agricultural field somewhere on a gently sloping hill in Denmark, where barley is ready for harvest when you pass by. Over the course of a few months, the farmer has prepared the soil, planted the seeds, applied fertilizers and sprayed a number of chemicals to keep various pests outside his field. All these actions have had an impact on the environment. Forty years from now, the climatic conditions will be different, but the farmer still grows barley on the same field. What are the environmental impacts in this case? This was the main question of this work. The idea of the study was not to assess what impacts occur when an additional kg of barley is produced in the future, but what the impacts of one kg of barley are when it is produced under the climatic conditions of 2050, instead of in the current climate. Whilst the preferred assessment method for production of an additional amount of barley in the future would be consequential LCA, attributional LCA (aLCA) is better suited for the purpose of this study. Furthermore, in order to allow for a focus on barley cultivation, a cradle-to-farm gate perspective was adopted in the study. Thirdly, possible developments in policy were excluded from the study since we were interested in the feedback of climate change onto barley cultivation, not in how policy changes might (or might not) modify environmental impacts.

The functional unit and reference flow chosen for the comparison of barley cultivation in Denmark under current and future climatic conditions is 1 kg of spring barley, at farm gate.

For both the 2010 and 2050 main scenario four sub scenarios were defined, based on the four possible combinations of two Danish soil types (sandy and sandy loam) and two Danish climates (wet and dry). The 4 sub-scenarios are specified in Table 5.1.

Table 5.1: The 4 sub-scenarios used for modelling barley cultivation

Main scenario	Subscenario							
	1		2		3		4	
	soil	climate	soil	climate	soil	climate	soil	climate
2010								
2050	sandy	wet	sandy	dry	sandy loam	wet	sandy loam	dry

The 2050 climate scenarios are different from the 2010 scenarios in various aspects. Starting with the atmospheric CO₂ concentration, an increase from ~400 ppm in 2010 to ~530 ppm in 2050 was assumed. This increase is in line with the IPCC A1B scenario (IPCC, 2000). This scenario, along with others describes different atmospheric CO₂ concentration development paths, have been used to model greenhouse gas emissions in the third and fourth IPCC climate change assessment report. In short, this A1B scenario is based on continuing globalization of both economies and cultures and a rapid economic growth. The global population is assumed to peak in the middle of the 21st century to decrease thereafter. Looking at greenhouse gas emissions, the A1B scenario is in the middle of the range of IPCC scenarios. Other aspects of the 2050 climate considered for Danish circumstances are higher temperatures and more precipitation in winter, and less in summer, compared to the 2010 scenario.

5.2.2 INVENTORY

The main features of the inventory are described in this section, the details are presented in paper 4 and will not be repeated here.

In the 2010 scenarios barley yields are 4250 kg and 4850 kg dry matter (DM)/ha on sandy and sandy loam soils, respectively, assuming the crop is grown with a catch crop (Hamelin *et al.*, 2012). Compared to 2010, higher atmospheric CO₂ concentrations increase the photosynthesis rate, which may increase yields up to 20% (Saxe, 2013). At the same time do higher temperatures result in a shorter grain filling time, which lowers grain yields compared to 2010 (Børgesen & Olesen, 2011). Based on model results from Doltra, Lægdsmand and Olesen (2012) a 10% decrease of yields was assumed: 3825 and 4365 kg DM/ha for sandy and sandy loam soils, respectively.

In terms of fertilization, nitrogen, phosphorous and potassium (N, P, K) were considered. The inputs of these elements were based on norm values from the Danish Ministry of Food, Agriculture and Fisheries (2009). It was assumed that

half the required N demand was provided with pig slurry. The mineral fertilizers, i.e. diammonium phosphate, calcium ammonium nitrate and potassium chloride, used in the modelling of the product system were based on the sales volumes of mineral fertilizers in Denmark (Nielsen *et al.*, 2011) as well as the availability of the fertilizers in the Ecoinvent database (Ecoinvent centre, 2007).

Emissions of nitrates to surface water were taken from Hamelin (2013b), whilst the emissions of nitrogen-containing gaseous conversion products of manure and mineral fertilizers were calculated using emission factors given in Hamelin (2013a). In accordance with the emission factors presented by this author, it was assumed that a 5 % of P surplus was emitted to surface water. In this case, a surplus is defined as the difference between P inputs and the P contained in grains and straw that is removed from the field upon harvest. Emissions of K to surface water were not taken into account, since these are not considered in the characterization models applied in this study.

For the 2050 scenarios, the emissions were calculated following the same methodology as for the 2010 scenarios, except for nitrate leaching. Nitrate leaching was determined by interpolation of modelled leaching results from Doltra, Lægdsmand and Olesen (2012). These results showed an increase in emissions of 2% and 60% in 2050 for sandy and sandy loam soils, respectively.

Pesticide use was based on Henriksen *et al.* (2013). Based on pesticides currently used in barley cultivation in Denmark, and considering the pests occurring in areas currently having a climate that is assumed representative for the climate that is forecasted for Denmark in 2050 (southern Germany and northern France), Henriksen *et al.* (2013) made a scenario for pesticide use in barley cultivation in Denmark in 2050. In short, pesticides currently applied will be applied 5 to 10 days earlier in the future, because the growing season will start earlier. In addition, an application of λ -cyhalotrin on sandy loam soils can be omitted in 2050, since the crop is assumed to be harvested before the target pest (aphids) appear.

Pesticide emissions were calculated using PestLCI 2.1, a modified version of PestLCI 2.0 presented in chapter 2. Apart from a modification of the macropore flow approach that was described in paper 3, were all modifications adaptations or expansions of the model databases: new soil profiles for sandy and sandy loam soils were included (Greve & Breuning-Madsen, 1999), as well as modified cli-

mate data. For the 2010 scenarios, the monthly precipitation amounts of a Danish climate profile already present in the model database were increased in order to arrive at 650 and 900 mm/year, which is considered representative for the dry and wet climate sub-scenarios. A climate data set, representative for the north of France (a temperate maritime climate) was modified so that the annual total amount of precipitation matches the wet and dry Danish climate scenarios, thus resulting in a climate profile that is considered representative for the expected climatic conditions in Denmark in 2050.

In addition to pesticide, fertilizer and manure application, agricultural processes considered are ploughing, harrowing, seedbed harrowing followed by rolling, as well as harvesting. The fuel consumptions in the Ecoinvent processes used to model these processes were adjusted to Danish circumstances (Dalgaard, Halberg & Porter, 2001). In addition, fuel consumption on sandy soils was assumed to be 90% of that on sandy loam soils.

In the aLCA approach chosen, co-products were dealt with using economic allocation. In the case of barley, where both grains and straw are produced, an allocation factor of 0.91 was used for the grains. Furthermore an allocation was done for the environmental impacts of manure, which was considered a co-product from pig farming. An allocation factor of 0.076 was calculated for manure.

5.2.3 IMPACT ASSESSMENT

Classification and characterization were done at midpoint level. The ReCiPe methodology (Goedkoop *et al.*, 2009) was used, applying the hierarchist perspective for the following impact categories: climate change, ozone depletion, terrestrial acidification, freshwater and marine eutrophication, ionizing radiation, particulate matter formation, photochemical oxidant formation, freshwater ecotoxicity, human toxicity, fossil depletion, metal depletion, water depletion, agricultural land occupation, natural land transformation, and urban land occupation. In addition, human and freshwater ecotoxicity impacts from pesticide emissions to air and freshwater were characterized using USEtox (Rosenbaum *et al.*, 2008).

5.2.4 SENSITIVITY ANALYSIS

Based on an analysis of the contributions of the different processes to the impacts, a number of model parameters were used in a sensitivity analysis in order

to find out how robust the model results are. The yield, the share of manure in the total N applied to field as a fertilizer and the on-farm fuel consumption were varied with +10% and -10% after which the environmental impacts were calculated.

Since economic allocation was used to cut off impacts from barley straw, and hence to assign impacts to barley grains, moreover considering that predicting grain and straw prices in 2050 is almost impossible, the allocation factor for grains was also subjected to a sensitivity analysis. In contrast to the approach used for the other variables, in this case the ‘break-even point’ at which impacts in the 2050 scenarios would have the same impacts as in the 2010 scenarios, was calculated. This approach was considered to produce more relevant information than varying the allocation factor with +/- 10%, since the impacts would respond to such a variation in an almost linear way.

5.3 RESULTS AND DISCUSSION

The characterized results for the four 2010 scenarios are given in Table 5.2. From the table it can be seen that the differences between the scenarios are small. For most impact categories the larger environmental impacts are found for the sub-scenarios 1 and 2. This can be explained by the fact that barley cultivation on the sandy soils, where these scenarios are based on, results in lower yields. In addition the N norms are higher on these soils: 109 kg N/ha/y on sandy soils, and 97 kg N/ha/y on sandy loam soils.

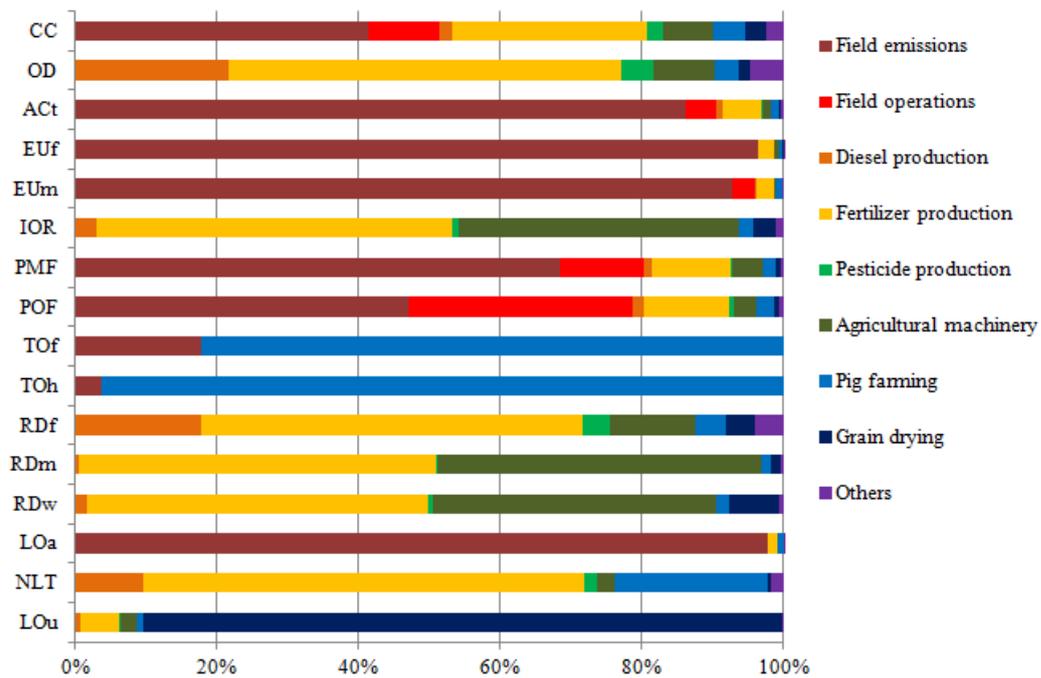
As a consequence, higher impacts related to fertilization are observed. In contrast, in ozone depletion, ionizing radiation, and resource depletion-related impact categories the impacts for the subscenarios 3 and 4 are higher. This is explained by the higher diesel consumption on the sandy loam soils on which these scenarios are based on, and in addition heavier harrowing machinery is used here. However, the fertilizer use is lower in these scenarios, which somewhat counterbalances the higher impacts from diesel use and machinery construction.

Table 5.2: Characterized impacts for barley cultivation in 2010

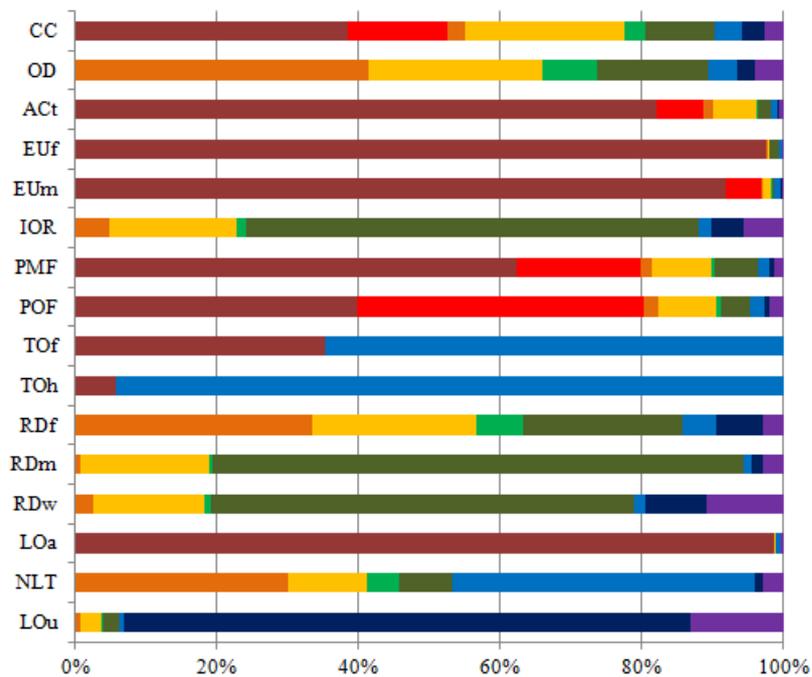
Environmental impact category	Abbreviation	Unit	Scenario			
			1	2	3	4
Climate change	CC	kg CO ₂ -eq	$3.31 \cdot 10^{-1}$	$3.31 \cdot 10^{-1}$	$2.97 \cdot 10^{-1}$	$2.98 \cdot 10^{-1}$
Ozone depletion	OD	kg CFC11-eq	$1.50 \cdot 10^{-8}$	$1.50 \cdot 10^{-8}$	$1.54 \cdot 10^{-8}$	$1.52 \cdot 10^{-8}$
Acidification, terrestrial	ACt	kg SO ₂ -eq	$7.14 \cdot 10^{-3}$	$7.14 \cdot 10^{-3}$	$5.84 \cdot 10^{-3}$	$6.02 \cdot 10^{-3}$
Eutrophication, freshwater	EUf	kg P-eq	$2.20 \cdot 10^{-4}$	$2.20 \cdot 10^{-4}$	$1.38 \cdot 10^{-4}$	$1.38 \cdot 10^{-4}$
Eutrophication, marine	EUm	kg N-eq	$6.78 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$	$5.14 \cdot 10^{-3}$	$4.32 \cdot 10^{-3}$
Ionizing radiation	IOR	kg U235-eq	$6.18 \cdot 10^{-3}$	$6.18 \cdot 10^{-3}$	$6.79 \cdot 10^{-3}$	$6.68 \cdot 10^{-3}$
Particulate matter formation	PMF	kg PM10-eq	$1.32 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$
Photochemical oxidant formation	POF	kg NMVOC	$1.73 \cdot 10^{-3}$	$1.73 \cdot 10^{-3}$	$1.68 \cdot 10^{-3}$	$1.68 \cdot 10^{-3}$
Toxicity, freshwater	TOf	PAF m ³ day	$1.50 \cdot 10^{-4}$	$1.47 \cdot 10^{-4}$	$1.48 \cdot 10^{-4}$	$1.71 \cdot 10^{-4}$
Toxicity, human	TOh	Cases	$1.78 \cdot 10^{-12}$	$1.77 \cdot 10^{-12}$	$9.90 \cdot 10^{-13}$	$9.86 \cdot 10^{-13}$
Resource depletion						
- fossil	RDf	kg oil-eq	$5.07 \cdot 10^{-2}$	$5.07 \cdot 10^{-2}$	$5.23 \cdot 10^{-2}$	$5.23 \cdot 10^{-2}$
- metal	RDm	kg Fe-eq	$2.50 \cdot 10^{-2}$	$2.50 \cdot 10^{-2}$	$2.88 \cdot 10^{-2}$	$2.84 \cdot 10^{-2}$
- water	RDw	m ³	$3.73 \cdot 10^{-1}$	$3.73 \cdot 10^{-1}$	$3.57 \cdot 10^{-1}$	$3.52 \cdot 10^{-1}$
Land use-related impacts						
- agricultural land occupation	LOa	m ² a	$1.91 \cdot 10^0$	$1.91 \cdot 10^0$	$1.67 \cdot 10^0$	$1.67 \cdot 10^0$
- natural land transformation	NLT	m ²	$9.25 \cdot 10^{-5}$	$9.25 \cdot 10^{-5}$	$8.49 \cdot 10^{-5}$	$8.43 \cdot 10^{-5}$
- urban land occupation	LOu	m ² a	$1.18 \cdot 10^{-2}$	$1.18 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$

The Figures 5.1a and b present a breakdown of the results for the scenarios 2010-1 and 2010-3. The first scenario is considered representative for the sandy soil scenarios, the second for sandy loam-based scenarios.

From Figures 5.1a and b it can be seen that in both scenarios the flows from the field are (by far) the main contributors to impacts in acidification, climate change, eutrophication, PM formation photochemical oxidant formation, and agricultural land occupation. Ozone depletion is dominated by diesel and fertilizer production, though the magnitude of both is different, dependent on scenarios (i.e. soil type). In the sandy soil scenario, fertilizer production is the largest contributor to ionizing radiation, and resource depletion-related impact categories, as well as natural land transformation. The majority of these impacts can be attributed to the production of calcium ammonium nitrate (CAN). In the sandy loam soil-based scenarios, less CAN is used but more fuel and heavier agricultural equipment. As a consequence, the share of fertilizer in the total impacts decreases so that diesel production becomes the largest contributor to ozone depletion and fossil depletion, whilst machinery production now becomes the main



(a)



(b)

Figure 5.1: Breakdown of the characterized results for two 2010 scenarios: (a) 2010-1 and (b) 2010-3. The abbreviations of the impact categories are given in Table 5.1.

contributor to metal and water depletion. Pig farming is now the largest contributor to natural land transformation.

Most toxicity impacts can be attributed to the feed used in pig farming, the manure of which is used as a fertilizer in barley cultivation. These high toxicity impacts can be attributed to a few pesticides: for freshwater ecotoxicity, linuron and diflufenzuron are the main contributors. The former pesticide is used in soy bean cultivation, the latter in the cultivation of sunflower. Clopyralid used in rapeseed cultivation is the main driver for human toxicity impacts. All of these compounds have high characterization factors, and in the case of linuron the emissions to air are high due to the volatility of this compound. Grain drying is the dominant contributor to urban land occupation impacts.

In paper 4 the impact assessment was limited to characterization. The motivation for this was twofold. The main purpose of any possible further step in LCIA after characterization is to allow comparison of impacts to a reference (normalization) and to perceived severity (weighing). Neither was the focus of paper 4, which aimed to compare impacts in 2010 and 2050. For this, characterization is the only necessary LCIA step required. A second reason is the nature of the normalization factors used in the ReCiPe method. These factors are based on population size and total environmental impacts in a certain reference year. For the 2050 scenarios, neither population nor environmental impacts are known. Even if they were, or could be forecasted, this would provide little information about the severity of the characterized impacts calculated for the 2050 scenarios as compared to the severity of the impacts in the 2010 scenarios.

However, since environmental impacts in current LCA practice are integrated over time and space, it can be argued that the reference values for a given year can in principle be used. In this case, the normalization step can be considered as a kind of internal standard to compare the impacts in both the 2010 and 2050 scenarios to. This provides little additional information compared to the characterized results, though.

When assuming that normalization results can be seen as a measure of the severity of impacts, an advantage of normalization is to determine in which impact categories the barley cultivation has the largest contributions to overall environmental impacts (and hence the study could be focused on these impact categories).

Normalizing the results of the 2010 scenarios using the ReCiPe 1.08 normalization factors gives the results presented in Figure 5.2. In this figure the results for water depletion have been omitted since there is no normalization factor available.

The toxicity results are shown separately, because these are indicative at best: since the human toxicity and freshwater ecotoxicity impacts were calculated using USEtox, these were expressed in units that are incompatible ($\text{PAF}\cdot\text{m}^3\cdot\text{day}$ for freshwater ecotoxicity, cases for human toxicity) with ReCiPe normalization factors ($\text{kg 1,4-DCB-eq/person}$). In order to allow for normalization of the toxicity results, the characterized impacts were converted to $\text{kg 1,4-DCB-equivalents}$ using the characterization factors for 1,4-dichlorobenzene emitted to freshwater and air present in USEtox. Even though such a manipulation gives characterized results with the units compatible with the normalization factors, such a conversion does not account for differences in fate and exposure modelling between the model used to calculate toxicity impacts in this study (USEtox) and the model used to derive the normalization factors (USES-LCA).

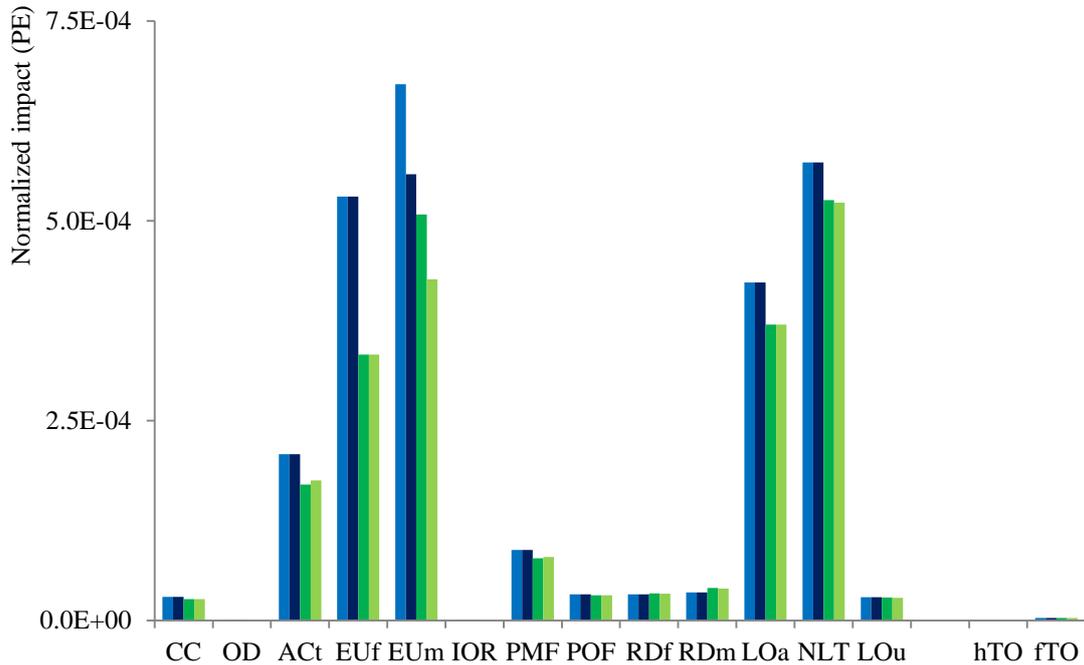


Figure 5.2: Normalized impacts for barley cultivation in the four 2010 scenarios (2010-1 in light blue, 2010-2 in dark blue, 2010-3 in dark green, 2010-4 in light green) for all impact categories except toxicity and water depletion. The abbreviations of the impact categories are given in Table 5.2.

Given these limitations it can be seen from Figure 5.2 that the impact categories with the highest normalized impacts are eutrophication, agricultural land occupation, and natural land transformation. As can be seen from Table 5.1, the impacts in the first two of these categories can largely be attributed to emissions from the field, whilst natural land transformation impacts are mainly composed of fertilizer production, pig farming and diesel production.

In Figure 5.3 the results for the 2050 scenarios are compared with those from the 2010 scenarios. In this figure the scenario with the largest impact in a given impact category are set to 1, and the impacts for the other scenarios are expressed as a fraction of the highest impact.

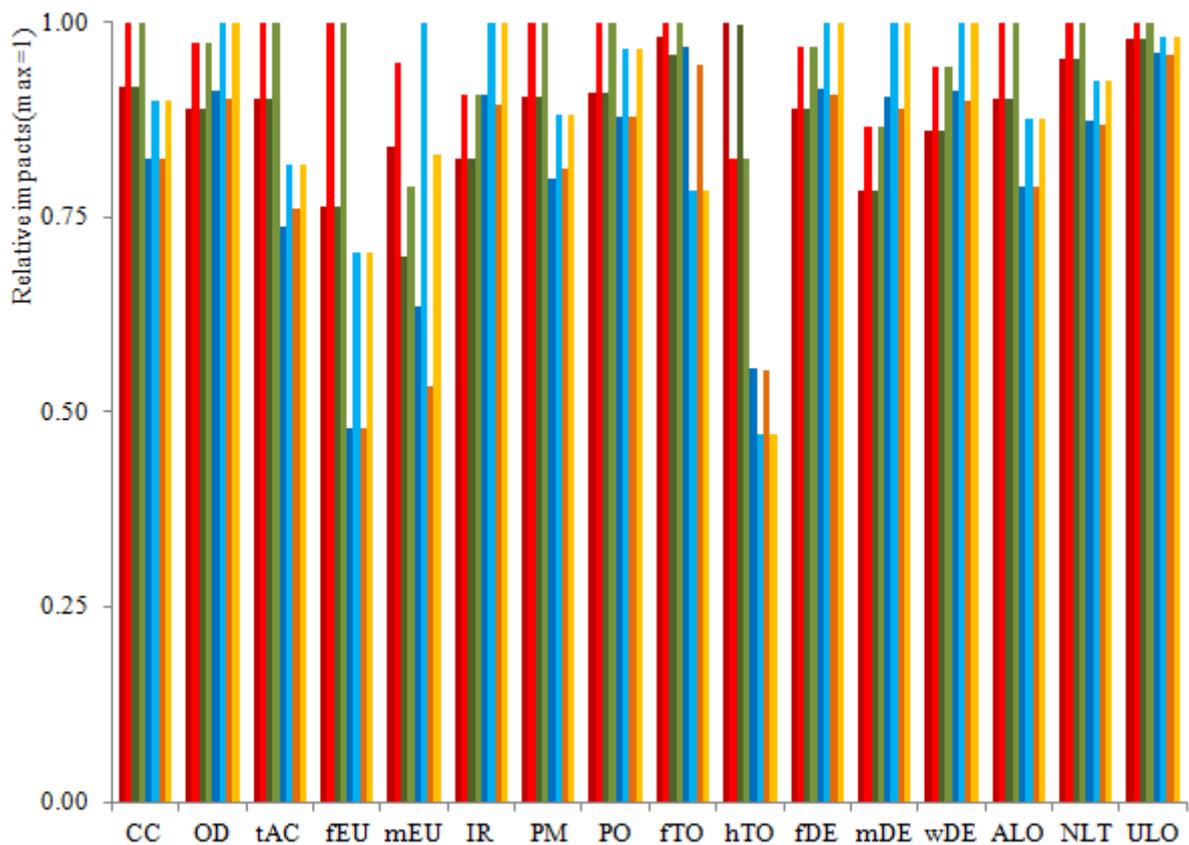


Figure 5.3: Comparison of the impacts for the 2010 and 2050 scenarios. The four scenarios are shown in red (scenario 1), green (scenario 2), blue (scenario 3), and yellow (scenario 4). For each scenario, the results for the 2010 climatic conditions are shown in dark shading, the results for the 2050 climatic conditions in the lighter colour. The abbreviations of the impact categories are given in Table 5.1.

From Figure 5.3 it can be seen that for sandy soil-based scenarios (scenarios 1 and 2) all impacts, with the exception of human toxicity, are higher under 2050 climatic conditions, compared to the 2010 conditions. In fact most impacts are approximately 10% higher, reflecting the yield decrease of 10%. This illustrates that the change in yield is an important parameter for the outcomes of the comparison. Human toxicity impacts decrease in the 2050 scenario, since the clopyralid emissions to air in rapeseed cultivation that largely determine the impacts in this category, are lowered under the 2050 climate. In contrast, freshwater eutrophication increases more than 10% in the 2050 scenarios. This is explained by the fact that this impact category in LCA practice is assumed to be mainly driven by P emissions. These emissions increase in the 2050 scenario since the P surplus in the field increases: the amount of P added by fertilization is unchanged whilst the removals of P from the field in the grain and straw are lower as a consequence of the lowered yield.

The sandy loam soil scenarios also shown in Figure 5.3 shows a picture that is largely the same as for the sandy soils, except for marine eutrophication and freshwater ecotoxicity. Regarding the first of these exceptions, the impacts are higher in these scenarios because the N emissions to water, which mainly drives marine eutrophication, were considerably increased on sandy loam soils in the 2050 scenarios compared to the 2010 scenarios. Moreover, the N emissions on sandy loam soils increased more than those from sandy soils. The freshwater ecotoxicity impacts are lower in the 2050 scenarios, mainly because a λ -cyhalotrin application in barley cultivation is removed.

The results of the sensitivity analysis for scenario 2010-1 showed that, of the tested parameters, the results were most sensitive to changes in yield. The toxicity impacts and natural land transformation were most sensitive towards changes in the allocation factor used for manure production in pig farming. This could be expected, given the large contribution to toxicity of the pesticides used in the cultivation of the different components of pig feed. Moreover, the major impacts of some of the components of the feed (soy bean meals and palm oils) are typically associated with land use change.

Analysis of the allocation factor for barley grains showed that for most impact categories the conclusion that the impacts in the 2050 scenario will be higher, remains valid until the allocation factor decreases from the 0.91 applied in the

scenarios to 0.82. Calculating this number back to grain and straw prices, it was found that the straw price in this case doubles compared to the grain price. Whether this will be the case in 2050 one can only try to guess. On the one hand there is the intention of the Danish government to have a fossil fuel free energy system in 2050 (Danish government, 2011). This may result in increasing prices for biomass. On the other hand have rising demands for food led to an increase of barley prices over the last decade (Statistics Denmark, 2013b). With the increasing global population, which in addition is becoming increasingly wealthy, the barley price increases can with reason be expected to continue.

Another aspect that needs to be considered when discussing the impacts of the 2050 scenarios compared to the 2010 scenarios, is the option of mitigation of impacts. In the modelling of the product system for which the results have been described in this chapter, mitigation has not been considered. That does, most likely, not mean that no efforts will be undertaken to mitigate environmental impacts if these turn out to increase in the future. Nutrient leaching may be limited by use of catch crops (Doltra, Lægdsmand & Olesen, 2012) or buffer zones (Jeppesen *et al.*, 2009), whilst pesticide consumption may decrease by the use of more targeted pesticide application (Djursing, 2013).

Despite this consideration, the importance of economic data which can by no means be predicted 40 years in advance in relation to the outcomes of the study seems an important disadvantage of the chosen way to deal with co-products. Even though economic allocation appears to be the most used method to deal with processes with multifunctional outputs in LCA (De Vries & De Boer, 2010), economic allocation has been criticized, for example by Pelletier and Tyedmers (2011). These authors argue that market information such as a product's price not only is volatile (i.e. prices change over time), but also incomplete: the market fails to include environmental externalities into a product price. In that sense, there is no clear relation between a co-products' prices and environmental impacts. Instead Pelletier and Tyedmers (2011) suggest using biophysical allocation, where for example energy or exergy content is used as the key to divide environmental impacts over several co-products.

However, when designing this study, allocation based on energy content (as well as mass) was rejected, due to the lack of physical causality between the co-

products that were to be allocated. After all, such a physical causality is usually considered a necessity when deciding on the allocation procedure.

The work presented in this chapter, as well as in paper 4, has compared the dependence of environmental impacts of barley cultivation under current and future climatic conditions. At the same time, no attempt has been made to expand the study to a full LCA of barley cultivation in 2050. In other words, only impacts caused by climate change have been assessed, while societal, political and technological changes have been excluded. Further research could focus in these areas and thereby try to further expand the applicability of LCA into assessment of (long-term) future scenarios. Some work in this field has already been done. For example, Weidema (2003) has described various techniques to draw scenarios of how the future may look like. When translating such future scenarios into flows to and from the ecosystem, Frischknecht, Büsler and Krewitt (2009) have demonstrated that both foreground and background LCI processes can be manipulated to represent future scenarios.

5.4 CONCLUSION

For the 2010 scenarios, the environmental impacts for the four sub-scenarios were very similar. Impact categories driven by flows from the field where barley is cultivated or agricultural processes carried out in this field, the impacts were typically higher for the scenarios for barley cultivation on sandy soils. In contrast, higher impacts are observed on sandy loam soil-based scenarios for impact categories, where machinery manufacturing or diesel combustion are important contributors.

The changes in the 2050 scenarios, when compared to the equivalent 2010 scenarios, were mainly driven by predicted yield reductions. All impact categories, with the exception of human toxicity and freshwater toxicity, show higher impacts in 2050. These conclusions were established using the same economic allocation factor in the 2010 and 2050 scenarios. The sensitivity analysis showed that this conclusion remains valid up to the point where the barley straw price doubles compared to the price of barley grains. Since these prices can not be predicted approximately 40 years in advance, the applicability of economic allocation in this context may be discussed.

6 CONCLUSIONS

This PhD project has dealt with various aspects of pesticide emission modelling for application in Life Cycle Inventory analysis (LCI).

The first aim of the project was to develop an LCI model that is capable of calculating pesticide emissions to the environment, to be applicable under European circumstances. In order to reach this aim, the PestLCI model was updated, expanded and shifted to a more transparent software platform. The model structure of PestLCI was maintained in the new model version, PestLCI 2.0. The boundaries between ecosphere and technosphere continue to be defined by a field box, consisting of the agricultural field, the soil beneath it up to a depth of 1 m and the air column above it, up to a height of 100 m. The model is constructed using primary and secondary fate processes, which calculate the emissions to the various environmental compartments. The modelling of several of these fate processes (wind drift, volatilization from leaves and soil, runoff) has been updated. The model was expanded by inclusion of a pesticide leaching pathway via macropore flow. Moreover additional climate and soil data sets were included in the model databases in order to cover a broad range of European climates and soils. The database of pesticide active ingredients was expanded with a number of substances that are frequently used in Europe.

The release of PestLCI 2.0 has provided the LCA community with a freely available tool to model pesticide emissions from an agricultural field to three environmental compartments: air, surface water and groundwater, allowing for spatial differentiation in terms of both soil and climate.

Validating the pesticide emission model by comparing it to other (risk assessment) models was the second aim of this project. Surface water emissions calculated by PestLCI 2.0 were compared to emissions calculated by SWASH. It was found that the emissions calculated by PestLCI were lower than those calculated by SWASH, which was attributed to the worst-case assumptions used in the modelling of the risk assessment model SWASH. In contrast, the results of the comparison between PestLCI 2.0 and PEARL for groundwater emissions showed that PestLCI 2.0 were higher, which was attributed to the exclusion of macropore flow in PEARL. The first version of PestLCI 2.0 was moreover concluded to probably overestimate the magnitude of pesticide emissions to groundwater via macropore flow. Based on this, the macropore flow modelling was improved.

The comparisons between PestLCI and the risk assessment models were limited by the fact that the input scenarios were not fully identical.

The third aim was to apply the PestLCI 2.0 model to estimate pesticide emissions in kiwifruit cultivation in New Zealand, as part of the development of a toxicity footprint of kiwifruit growing. In order to accurately model pesticide emissions for kiwifruit orchards in the Western Bay of Plenty (WBOP), PestLCI was further expanded in terms of the active ingredients, crops, soils, and climates. This version of PestLCI also was the first to apply the improved macropore flow modelling. The model was furthermore improved for modelling pesticide emissions from orchards. The characterized emission results showed that both human toxicological and freshwater ecotoxicological impacts were dominated by emissions of the growth regulator cyanamide. In addition, the need and necessity for (sub-) regional LCI data was discussed. For the WBOP, it was concluded that the differences in emissions and resulting impacts are probably smaller than the uncertainty associated with these comparisons.

A second application of the model was for assessment of barley cultivation in Denmark under current (2010) and future (2050) climatic circumstances. For the four scenarios for barley cultivation, small differences in impacts were found. Comparing impacts between 2010 scenarios and the corresponding scenarios for barley cultivation under future climatic circumstances showed that differences were mainly driven by yield decreases. Other critical factors in the comparison were the allocation factors used to split impacts between barley grains and straw. Considering the impossibility of predicting prices for products on a long term, the choice of economic allocation can be considered another critical factor.

Implications of the use of PestLCI 2.0 in LCA practice was discussed in the context of the technosphere-ecosphere boundary setting. Comparing the freshwater ecotoxicity impacts obtained using PestLCI 2.0 to model pesticide emissions, instead of the currently used Ecoinvent approach, showed that the impacts are on average a few orders of magnitude lower when PestLCI is used. Both approaches differ not only in their fate modelling approach, but also in the way the boundaries between technosphere and ecosphere are defined. Applying a third inventory approach, which was a hybrid of the PestLCI and Ecoinvent approaches, it was shown that the differences in ecosphere-technosphere boundary setting is the main explanation for the difference in toxicity results between the two approach-

es. Despite the considerable differences in toxicity impacts, it can't be concluded whether the PestLCI or the Ecoinvent approach applies the correct boundary setting, since different views exist on what exactly should be defined as the environment.

7 PERSPECTIVES

The application of PestLCI 2.0, in the work on pesticide emissions in kiwifruit growing as well as in the case study of barley cultivation under current and future climatic circumstances has led to a number of ideas for improvement of the model. Some suggestions focus on improving the modelling of pesticide fate, whilst others focus on making the model wider and easier applicable.

The comparison of different inventory approaches for pesticide emissions showed that toxicity results are strongly dependent on the chosen inventory approach. This is a barrier for comparing different LCA studies, for the communication of LCA results, and possibly for wider acceptance of LCAs of agricultural products. In the next years a solution will have to be found for the observed differences in impacts. One option would be the (further) development of various inventory approaches, which are accompanied by matching impact assessment methodologies, possibly in integrated models. In this case, LCA practitioners can choose a methodology that suits the aim of their study best, and that ideally is consistent with the method chosen to quantify other flows from the agricultural field to the environment. Though this approach does not improve the comparability of LCAs, it does justice to the different views about what a pesticide emission actually is. Another option may be a consensus process aimed at identifying which impacts have to be accounted for, how to model emissions leading to such impacts, and potentially providing a model to do so. Although the result of a consensus process may give LCA practitioners a clear signal about the approach to take for modelling pesticide emissions, there are a few important drawbacks. It may be difficult to reach a consensus about when a pesticide is emitted, i.e. about what LCA should seek to protect, in the first place. Moreover, consensus may hide the different opinions or approaches that exist among method developers. This may give LCA practitioners the false idea that there is only one correct way to model pesticide emissions, or rather, that there is just one correct definition of what the environment is.

In the course of this project, some research has focused on variations in emissions of a pesticide caused by differences in local circumstances such as climate or soil. Paper 1 illustrated variations in emissions of MCPA on different locations across Europe, whilst paper 3 studied how emissions vary within a region of approximately 2000 km² in New Zealand. Although the results suggest that the ap-

plicability of emissions data at a sub-regional level is currently limited, including spatial differentiation for pesticide emissions at a larger spatial scale in inventories would be an improvement compared to the current practice.

Very little work, if any at all, seems to have been done in LCA to assess the effects of climate change on agricultural production systems, and the resulting changes in environmental impacts. The study about barley cultivation described in this thesis is a small step into this direction, though limited to changes in climatic circumstances. More research may be dedicated to developing methods to assess environmental impacts of products and systems that are used under altered circumstances in the long-term future. Challenges are then in the development of realistic scenarios for the long-term future, in transformation of these scenarios into inventory data, as well as in finding strategies to find meaningful ways for evaluation of impacts of future emissions.

These last research subjects may mostly be research topics for the long-term future. On the short term, focusing on further improving pesticide emission modeling may be more realistic and useful.

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APPENDICES

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